



**REPUBLIC OF TURKEY
ADANA ALPARSLAN TÜRKES SCIENCE AND TECHNOLOGY
UNIVERSITY**

**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF MECHANICAL ENGINEERING**

**MOLECULAR DYNAMICS ANALYSES AND EXPERIMENTAL
INVESTIGATION IN THE EFFECTS OF THE NANOADDITIVES ON
THE THERMO-MECHANICAL PROPERTIES AND FRACTURE
TOUGHNESS OF BIODEGRADABLE POLYLACTIC
THERMOPLASTIC**

**BURÇAK ZEHİR
MASTER OF SCIENCE**



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ADANA 2022**

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I hereby declare that all information in this thesis has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all information that is not original to this work.

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Burçak ZEİR

ABSTRACT

MOLECULAR DYNAMICS ANALYSES AND EXPERIMENTAL INVESTIGATION IN THE EFFECTS OF THE NANOADDITIVES ON THE THERMO-MECHANICAL PROPERTIES AND FRACTURE TOUGHNESS OF BIODEGRADABLE POLYLACTIC THERMOPLASTIC

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Nowadays, Additive Manufacturing (AM) has become a modern manufacturing technique with the spread of other related technologies. Fused deposition modeling (FDM) is one of the well-known and widely used AM methods that emerges some advantages, such as low cost and high speed, and has been used in the production of polymer composite parts. However, FDM 3D printing has some limitations due to shortcomings in the thermo-mechanical properties of its building materials, known as polymeric filaments, although they have advantages such as easy processability, low cost, and good chemical resistance. Therefore, the FDM technique may be able to extend its application areas with the reinforcement of nanoparticles in building materials.

The aims of this study are to (i) expand the use of polymer-based nanocomposite parts with superior thermo-mechanical properties and fracture behaviors by using a rapid and cost-effective FDM technology and (ii) produce polymer-based nanocomposite parts by utilizing the injection molding process to investigate the effectiveness of molecular dynamics (MD) simulations in forecasting the mechanical performance of parts through the comparison of mechanical properties of produced parts with the results of MD simulations. In order to accomplish the first objective, polylactic acid (PLA), one of the foremost biodegradable

polymers, was chosen as the matrix material, while calcium carbonate (CaCO_3) nanoparticles were used as reinforcement materials. For this purpose, the PLA/ CaCO_3 nanocomposite filaments, containing different weight ratios (0, 0.5, and 1 wt%) of nanoparticles in the matrix, have been synthesized by melt-blending technique using a twin-screw extruder system. These filaments were used to produce samples by FDM technique with different printing parameters to study the effects of nanoparticles and printing parameters on the mechanical properties and fracture behavior of the PLA nanocomposites under mixed-mode fracture loadings. In this regard, this study investigates the effects and significance of these different parameters, which are called printing speed, weight fractions of nanoparticle addition, layer thickness, filling ratio, and internal architecture, on the fracture characteristics and mechanical behavior of FDM 3D printed PLA and PLA/ CaCO_3 nanocomposites. To this end, the analysis of the Taguchi L_{27} design has been conducted based on the experimental results to determine the optimized levels of factors by which the maximum level of material properties could be obtained. Thus, it has been determined which combination can be used in further FDM 3D printing of PLA-based materials, or which factor level will be appropriate. A response surface methodology (RSM) was employed to model and predict the mechanical and mixed-mode fracture properties of the PLA-based nanocomposites produced in different weight ratios and different FDM printing parameters. The produced samples were subjected to uniaxial tensile tests for mechanical characterization. Mixed-mode fracture behavior of the synthesized samples were studied by applying mixed-mode loadings on the pre-cracked samples using an in-lab developed fixture mounted on the uniaxial tensile test machine. Finite element simulations are employed to simulate the crack opening on such specimens and calculate the geometry shape functions of the fracture samples at different loading angles. Finally, after the experimental procedures, scanning electron microscopy (SEM) examinations have been conducted on the fractured surfaces of the test samples to reveal the fracture morphology of parts and validate the presence of nanoparticles. In addition, differential scanning calorimetry (DSC) analyses are conducted to determine the variations in the glass transition and heat capacity of the PLA polymer by the incorporation of CaCO_3 nanoparticles in the PLA matrix.

Secondly, uniaxial tensile test specimens of PLA and PLA/ CaCO_3 nanocomposites have been produced with the injection molding process to verify the MD simulations. Material Studio software is employed to investigate the physical behavior of injection molded PLA/ CaCO_3

nanocomposites in different weight ratios (1, 3, and 5 wt%) and to research the details of interactions between the molecules and nanoparticles on an atomic scale. For the reason that the molecular dynamics simulations verify the experimental results, graphene (GR) reinforced PLA nanocomposites were simulated to predict the mechanical properties of injection molded PLA/GR in different weight fractions. It has been observed that Materials Studio software provides accurate results in estimating the mechanical properties of materials.

Keywords: Nanocomposite materials, additive manufacturing, 3D printing, polylactic acid (PLA), molecular dynamics analyses, mixed mode fracture behavior, analysis of variance (ANOVA)



ÖZET

PARÇALANABİLEN POLİLAKTİK ASİT TERMOPLASTİKLERE NANO KATKI MADDELERİNİN İLAVESİNİN TERMO-MEKANİK ÖZELLİKLERİ VE KIRILMA TOKLUĞU ÜZERİNDEKİ ETKİLERİNİN MOLEKÜLER DİNAMİK ANALİZLERİ VE DENEYSEL OLARAK İNCELENMESİ

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Günümüzde, Eklemeli İmalat teknolojisi, diğer ilgili teknolojilerin yayılmasıyla modern bir üretim tekniği haline gelmiştir. Eriyik yığma modelleme (Fused Deposition Modeling-FDM), polimer kompozit parçaların üretiminde düşük maliyet ve yüksek hız gibi bazı avantajları ile öne çıkan, iyi bilinen ve yaygın olarak kullanılan eklemeli imalat yöntemlerinden biridir. Bununla birlikte, geleneksel yöntemlere kıyasla eriyik yığma modelleme tekniği, polimerik filamentler olarak bilinen yapı malzemelerinin kolay işlenebilirlik, düşük maliyet ve iyi kimyasal direnç gibi avantajlarına rağmen termo-mekanik özelliklerindeki eksiklikler nedeniyle bazı sınırlamalara sahiptir. Bu nedenle, eriyik yığma modelleme ile baskı tekniği, yapı malzemelerinde nanopartiküllerin güçlendirilmesi ile uygulama alanlarını genişletebilir.

Bu çalışmanın amaçları (i) hızlı ve uygun maliyetli bir FDM teknolojisi kullanarak üstün termo-mekanik özelliklere ve kırılma davranışlarına sahip polimer bazlı nanokompozit parçaların kullanımını yaygınlaştırmak ve (ii) parçaların mekanik performansının tahmin edilmesinde MD simülasyonlarının etkinliğini araştırmak amacıyla, üretilen parçaların mekanik özelliklerinin moleküler dinamik (MD) simülasyonlarının sonuçlarıyla karşılaştırılması için enjeksiyonlu kalıplama işlemi kullanılarak polimer bazlı nanokompozit parçalar üretmektir. Bunun için matris malzemesi olarak biyolojik olarak parçalanabilen polimerlerin başında gelen polilaktik asit (PLA) ve takviye malzemesi olarak kalsiyum

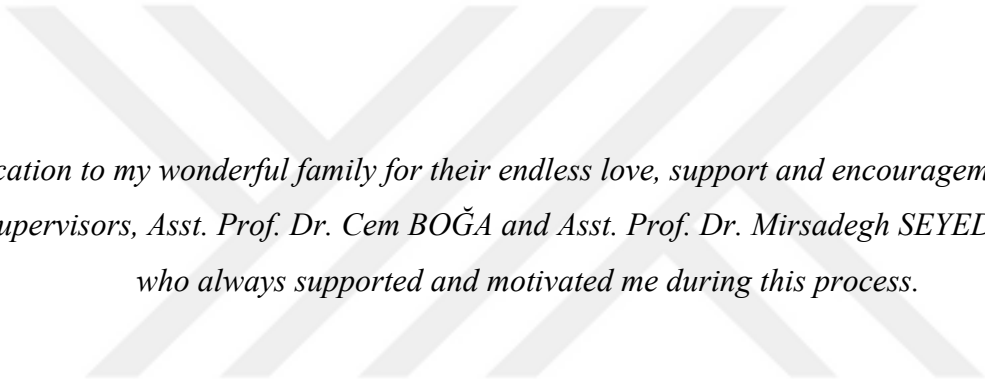
karbonat (CaCO_3) nanopartikülleri kullanılmıştır. Bu amaçla, PLA/ CaCO_3 nanokompozit filamentler, polimer matrise farklı ağırlık oranlarında nanopartikül takviyesi edilerek (%0, %0.5 ve %1) eriyik karıştırma tekniği ile çift vidalı ekstrüder sistemi kullanılarak sentezlenmiştir. Bu filamentler, nanopartiküllerin ve baskı parametrelerinin PLA nanokompozitlerinin mekanik özellikleri ve karışık mod kırılma yükleri altında kırılma davranışı üzerindeki etkilerini incelemek amacıyla, FDM tekniği ile farklı baskı parametrelerinde numuneler üretmek için kullanılmıştır. Bu bağlamda, bu çalışma, baskı hızı, nanoparçacık ilavesinin ağırlık fraksiyonları, katman kalınlığı, doldurma oranı ve iç mimari olarak adlandırılan bu farklı parametrelerin FDM 3D baskılı PLA'nın kırılma özellikleri ve mekanik davranışı üzerindeki etkilerini ve önemini araştırmaktadır. Bu amaçla, maksimum malzeme özelliklerinin elde edilebileceği optimize edilmiş faktör seviyelerini belirlemek için deneysel sonuçlara dayalı olarak Taguchi L_{27} tasarımının analizi yapılmıştır. Böylece gelecek çalışmalarda PLA tabanlı malzemelerin FDM 3D baskısında hangi kombinasyonun kullanılabileceği veya hangi faktör seviyesinin uygun olacağı belirlenmiştir. Farklı ağırlık oranlarında ve farklı FDM baskı parametrelerinde üretilen PLA bazlı nanokompozitlerin mekanik ve karışık mod kırılma özelliklerini modellemek ve tahmin etmek için bir yanıt yüzeyi metodolojisi (RSM) kullanılmıştır. Mekanik karakterizasyon için üretilen numuneler tek eksenli çekme testlerine tabi tutulmuştur. Numunelerin karışık mod kırılma davranışı, tek eksenli çekme test makinesine monte edilmiş laboratuarda geliştirilmiş bir fikstür kullanılarak ön çatlağa sahip numunelere karışık mod yüklemeleri uygulanarak incelenmiştir. Bu tür numunelerdeki çatlak açıklığını simüle etmek ve farklı yükleme açılarında kırık numunelerinin geometri şekil fonksiyonlarını hesaplamak için sonlu eleman simülasyonları kullanılmıştır. Son olarak, deneysel prosedürlerden sonra, parçaların kırılma morfolojisini ortaya çıkarmak ve nanoparçacıkların varlığını doğrulamak için test numunelerinin kırık yüzeyleri üzerinde taramalı elektron mikroskobu (SEM) incelemeleri yapılmıştır. Ek olarak, PLA matrisine CaCO_3 nanoparçacıklarının eklenmesiyle PLA polimerinin cam geçişindeki ve ısı kapasitesindeki değişiklikleri belirlemek için diferansiyel taramalı kalorimetri (DSC) analizleri yapılmıştır.

İkinci olarak, enjeksiyon kalıplama ile elde edilen farklı ağırlık oranlarına sahip (% 1, %3 ve %5) PLA/ CaCO_3 nanokompozitlerinin fiziksel davranışını araştırmak ve bir yüzey üzerinde moleküller ve nanopartiküller arasındaki etkileşimlerin ayrıntılarını atomik ölçekte sağlamak için Material Studio yazılımı kullanılarak moleküler dinamik (MD) simülasyonları

gerçekleştirilmiştir. Deneysel prosedürlerden elde edilen sonuçları doğrulamak için moleküler dinamik analizleri yapılmıştır ve moleküler dinamik simülasyonlar ile deneysel sonuçların birbiriyle uyumlu olması nedeniyle, enjeksiyonla kalıplanmış PLA/GR nanokompozitlerin mekanik özelliklerini tahmin etmek için farklı ağırlık fraksiyonlarında PLA/GR nanokompozit malzemeleri simüle edildi. Materials Studio yazılımının malzemelerin mekanik özelliklerini tahmin etmede doğru sonuçlar verdiği gözlemlenmiştir.

Anahtar Kelimeler: Nanokompozit malzeme, eklemeli imalat, 3 boyutlu baskı, polilaktik asit (PLA), moleküler dinamik analizleri, karışık modlu kırılma davranışı, varyans analizi





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NOMENCLATURE

AM	: Additive Manufacturing
CNC	: Computer Numerical Control
FDM	: Fused Deposition Modeling
PBF	: Powder Bed Fusion
SLS	: Selective Laser Sintering
SLM	: Selective Laser Melting
SLA	: Sterolithography
PLA	: Polylactic Acid
PETG	: Poly (Ethylene Terephthalate)-Glycol
ABS	: Acrylonitrile Butadiene Styrene
PET	: Polyester
PP	: Polypropylene
PS	: Polystyrene
PA	: Polyamide
PE	: Polyethylene
HIPS	: High Impact Polystyrene
PEEK	: Polyetheretherketone
PBT	: Polybutylene Terephthalate
3D	: Three-Dimensional
CAD	: Computer-Aided Design
CaCO ₃	: Calcium Carbonate
GR	: Graphene
SiO ₂	: Silicium Dioxide
CF	: Carbon Fiber
Ag	: Silver
PS	: Printing Speed
NA	: Nanaoparticle Addition
LT	: Layer Thickness

FR	: Filling Ratio
IA	: Internal Architecture
SEM	: Scanning Electron Microscopy
DSC	: Differential Scanning Calorimetry
MD	: Molecular Dynamics
RVE	: Representative Volume Elements
NVT	: Constant Volume Canonical
NPT	: Isothermal Isobaric
RDF	: Radial Distribution Function
E	: Modulus of Elasticity
G	: Shear Modulus
ν	: Poisson's Ratio
v	: Elongation in Fracture Mechanics
K_I	: Fracture Toughness in the Mode-I Loading
K_{II}	: Fracture Toughness in the Mode-II Loading
P_C	: Critical Load
J_I	: Strain Energy Release Rate in the Mode-I Loading
J_T	: Total Strain Energy Release Rate in the Mode-I/II Loading
J_{II}	: Strain Energy Release Rate in the Mode-II Loading
T_g	: Glass Transition Temperature
T_m	: Melting Temperature
T_c	: Cold Crystallization Temperature
X_C	: Percent Crystallinity

1. INTRODUCTION

A composite material is described as a substance that consists of two or more materials that have better material characteristics than its separated components. Each component in composite materials preserves its own mechanical, chemical, and physical characteristics. In other words, these parts do not entirely dissolve or blend into one another; they may be physically distinguished, yet they function in concert. In comparison to bulk materials, the key advantages of composite materials are their high strength and stiffness associated with low density (Açık, 2014) , (Campbell, 2010) , (Hull, 1981). Since this study comprises an investigation of composite materials composed of polymer matrix and particle reinforcement materials, the given information about the composite materials is limited to the manufacturing methods of polymer matrix composite materials. Two different approaches are used for the production of thermoplastic polymer materials, called extrusion and molding, and thermoplastic polymer parts have been produced in this study by using both methods: extrusion-based systems and the injection molding process.

Additive manufacturing (AM) technology has developed depending on inventions and improvements in a variety of associated technologies up to the present. In the last few decades, the potential uses of AM technology have been extended in many industries, especially in aerospace, automotive, and healthcare, owing to its advantages compared to traditional manufacturing technologies. Over the traditional manufacturing methods, AM significantly reduces the costs and production time, has the capacity to build complicated items with high precision, and provides flexibility even in lightweight structural designs. Other manufacturing processes, for instance, molding technology requires some pre-processes like the production of one or multiple molds, or computer numerical control (CNC) machining requires serial processes, which may include the building of fixtures before the desired product can be manufactured. Many of these multistage procedures may be eliminated or simplified with AM technology, and a wide range of different parts with various characteristics may be manufactured with the incorporation of several supporting technologies, such as drilling or polishing. Fused deposition modeling (FDM), one of the most widely used AM technologies, is based on the principle of extrusion of thermoplastic

polymers. Thermoplastic polymer filaments such as poly lactic acid (PLA), poly (ethylene terephthalate)-glycol (PETG), and acrylonitrile butadiene styrene (ABS) are deposited layer by layer to create complex geometries from three-dimensional (3D) CAD design models in a short time (Bayraktar, 2018) , (Gibson, 2015). As a consequence of its advantages, such as ease of production, creation of complex geometries, repeatability, no extra equipment required, and cost-effectiveness, the FDM method is promising in many fields, such as medicine with developing tissues or medical tools, automotive, food, and engineering (Wickramasinghe, Do, & Tran, 2020) , (Sanei & Popescu, 2020) , (Hsueh, et al., 2021).

Injection molding is the most typical method of producing thermoplastic polymer parts. This process is entirely different than FDM technology. The injection molding procedure is based on the principle of injecting the molten thermoplastic material into a pre-designed mold and rapidly cooling the injected material. According to the complexity of the part, lead time in the FDM process can be longer than in injection molding, but since the injection molding process requires a pre-design and prototype of the desired parts, the production cost in injection molding is significantly more expensive than in the FDM process (Açık, 2014) , (Creative Mechanisms, 2022). Most importantly, FDM fabricated parts have gaps and porosity in material structure caused by the nature of the FDM method. In the injection molding processes, there is no or less porosity or gaps in the material structure, which is highly similar to the simulated models of parts in MD simulations. This situation is the reason that the injection molded parts are suitable for comparison with MD simulated parts.

Most of the thermoplastic materials used in polymer processing technologies lead to environmental concerns since they have non-degradable properties. Some procedures may be followed in order to annihilate the non-degradable plastic waste. Nondegradable plastic waste can be regularly stored, incinerated, or recycled. However, among these methods, there is a limited area around to store the plastics regularly; incineration of plastics produces toxic gases into the environment because of its application method; and recycling requires a large amount of energy and cost (Açık, 2014). From this perspective, the production of environmentally friendly plastics, known as bioplastics, have gotten a lot of attention as a result of rising environmental concerns, legislation imposing pressure on plastic waste, and the rising cost of

petroleum-based products. Polylactic acid (PLA), a renewable aliphatic and versatile polyester polymer, is one of the most widely used biodegradable polymers in industry. Since pure polymers have some mechanical limitations in use, in order to enhance the thermo-mechanical, chemical, or electrical properties of pure polymers for industrial applications, different types of natural or inorganic additives are reinforced or blended into the molten filaments during the printing process (Rasal, Janokar, & Hirt, 2010) , (Liu & Zhang, 2011). Nanofiller materials such as calcium carbonate (CaCO_3), graphene (GR), silicium dioxide (SiO_2), carbonfibers (CF), silver (Ag) have been extensively used to polymer-based nanocomposite production in industry. Thermo-mechanical properties and fracture characteristics of nanocomposite parts are depend on the good dispersion of nanoparticles and printing parameters such as infill pattern, raster angle, and build orientation during FDM 3D printing process (Chan, Wu, Li, & Cheung, 2002) , (Vrsaljko , Blagojević, Leskovac, & Kovačević, 2008) , (Eiras & Pessan, 2009).

The aims of this study are to (i) expand the use of polymer-based nanocomposite parts with superior thermo-mechanical properties and fracture behaviors by using a rapid and cost-effective FDM technology and (ii) produce polymer-based nanocomposite parts by utilizing the injection molding process to investigate the effectiveness of MD simulations in forecasting the mechanical performance of parts through the comparison of mechanical properties of produced parts with the results of molecular dynamics (MD) simulations. In order to accomplish the first objective, polylactic acid (PLA), one of the foremost biodegradable polymers, was chosen as the matrix material, while calcium carbonate (CaCO_3) nanoparticles were used as reinforcement materials. For this purpose, the PLA/ CaCO_3 nanocomposite filaments, containing different weight ratios (0, 0.5, and 1 wt%) of nanoparticles in the matrix, have been synthesized by melt-blending technique using a twin-screw extruder system. These filaments were used to produce samples by FDM technique with different printing parameters to study the effects of nanoparticles and printing parameters on the mechanical properties and fracture behavior of the PLA nanocomposites under mixed-mode fracture loadings. In this regard, this study investigates the effects and significance of these different parameters, which are called printing speed, weight fractions of nanoparticle addition, layer thickness, filling ratio, and internal architecture, on the fracture characteristics and mechanical behavior of FDM 3D printed PLA and PLA/ CaCO_3 nanocomposites. To this

end, the analysis of the Taguchi L_{27} design has been conducted based on the experimental results to determine the optimized levels of factors by which the maximum level of material properties could be obtained. Thus, it has been determined which combination can be used in further FDM 3D printing of PLA-based materials, or which factor level will be appropriate. A response surface methodology (RSM) was employed to model and predict the mechanical and mixed-mode fracture properties of the PLA-based nanocomposites produced in different weight ratios and different FDM printing parameters. The produced samples were subjected to uniaxial tensile tests for mechanical characterization. Mixed-mode fracture behavior of the synthesized samples were studied by applying mixed-mode loadings on the pre-cracked samples using an in-lab developed fixture mounted on the uniaxial tensile test machine. Finite element simulations are employed to simulate the crack opening on such specimens and calculate the geometry shape functions of the fracture samples at different loading angles. Finally, after the experimental procedures, scanning electron microscopy (SEM) examinations have been conducted on the fractured surfaces of the test samples to reveal the fracture morphology of parts and validate the presence of nanoparticles. In addition, differential scanning calorimetry (DSC) analyses are conducted to determine the variations in the glass transition and heat capacity of the PLA polymer by the incorporation of CaCO_3 nanoparticles in the PLA matrix.

Secondly, uniaxial tensile test specimens of PLA and PLA/ CaCO_3 nanocomposites have been produced with the injection molding process to verify the MD simulations. Material Studio software is employed to investigate the physical behavior of injection molded PLA/ CaCO_3 nanocomposites in different weight ratios (1, 3, and 5wt%) and to research the details of interactions between the molecules and nanoparticles on an atomic scale. For the reason that the molecular dynamics simulations verify the experimental results, graphene (GR) reinforced PLA nanocomposites were simulated to predict the mechanical properties of injection molded PLA/GR in different weight fractions. It has been observed that Materials Studio software provides accurate results in estimating the mechanical properties of materials.

The present master's thesis study has been organized in six chapters as follows:

The first chapter of the thesis briefly introduces the thermoplastic polymer matrix composites and their methods of manufacturing; additive manufacturing technology in general with a focus on their process chains, application areas, and drawbacks; and secondly, molding processes in general with a focus on injection molding processes. The chapter then presents polylactic acid (PLA) and nanoparticle reinforcement materials for the application of PLA-based nanocomposite materials. The first chapter of the thesis ends with the introduction of nanoparticle reinforcements on an atomic scale.

Chapter 2 represents a comprehensive review of the literature relevant to the thesis and identifies the unexplored areas that require further investigation.

Chapter 3 represents the materials and methods used in case study. In order to investigate the effects of printing parameters and nanoparticle reinforcements on the parts produced with the FDM method, first of all, pure, 0.5 wt% CaCO_3 , and 1 wt% CaCO_3 reinforced filaments produced by melt blending method. Then, PLA and PLA based nanocomposites have produced with the FDM technique. In order to compare the mechanical properties of PLA and PLA-based nanocomposites on an atomic scale with using MD analyses, parts also have been produced with an injection molding method. For mechanical and fracture characterization of FDM 3D printed parts, the uniaxial and mixed-mode fracture tests have been conducted. Taguchi L_{27} and Analysis of Variance (ANOVA) optimization method have employed to create design for FDM printing parameters and to determine the best sequence of parameters for better characteristics according to experimental results. SEM and DSC analyses have been conducted to morphological and thermal analysis of parts. Molecular dynamic (MD) simulations using Material Studio software is employed to investigate the physical behavior of the injection molded PLA/ CaCO_3 and PLA/GR nanocomposites and provide details of interactions between the molecules and nanoadditives in an atomic scale. These production processes, experimental and simulation analysis procedures have been introduced extensively in Chapter 3.

Chapter 4 represents and discusses the results of the experimental procedures with the given tables and graphs as well as results of SEM and DSC analyses. In order to better understand the significance of parameters, the results of Taguchi analysis and Analysis of Variance (ANOVA) were represented and 3D response surface graphs have been plotted according to interactions of significant parameters. MD simulation results was discussed for injection molded parts.

In Chapter 5, the prominent results of this study are given.

Chapter 6 comprises the recommendations for further studies.

1.1. Thermoplastic polymer matrix composite materials

Composite materials, which can be found in artificial or natural forms in the world, have two constituents, called the matrix and reinforcement materials. Polymers, metals, or ceramics can be used as the matrix materials, which bind the components together and transfer and disperse stresses; as a result, the mechanical, thermal, or fracture characteristics of the materials are determined by the matrix materials. The reinforcing materials can exist in the form of fibers, granules, or particles and they are often tougher than the matrix materials, hence, they provide strong interactions between the matrix and reinforcements, resulting in stiffer and better crystallinity in the properties of composite materials. To this end, the amount of reinforcement material must be considered.

Polymer composite materials are the most prevalent form of composite materials, and they are composed of a polymeric matrix, such as epoxy or polyester, that is reinforced by a variety of fillers. Polymers have several benefits over other alternative matrices, such as the fact that processing polymers does not require high pressure or high temperatures, and it has lower production costs. Furthermore, they may achieve mechanical requirements such as tensile strength, elongation at break, or flexural strength. In thermal properties, they may result in high heat and moisture expansion coefficients, and in different directions, they may result in lower elastic characteristics. These may be regarded as disadvantages for various polymeric materials, depending on the application (Kaw, 2006) , (Chawla, 2013) , (Schwartz, 1996) , (Sawyer & Grubb, 1987). In the continuation of this master's thesis, the main information can be obtained by narrowing down from the production methods of thermoplastic polymer matrix composite materials to the detailed properties of the polymer and reinforcement materials used in this study.

Polymer matrix composite materials are widely preferred in many industries due to their lower production costs as well as many advantages. Thermoplastic polymer composite materials are fabricated using two different approaches, which are called extrusion-based systems and molding processes. In this study, pure and PLA/CaCO₃ thermoplastic composite parts have been fabricated with FDM 3D printing technology and injection molding processes.

1.2. Additive manufacturing technology

Additive manufacturing (AM) is a generalized expression for the manufacturing technology commonly called rapid prototyping or 3D printing. This generalized term has been coined to make it easier to classify the new AM technologies in the future (Gebhardt, 2011). The use of AM technology has expanded over time with the inventions and advances in a variety of associated technologies, like other manufacturing techniques. Figure 1.1 represents a brief information about the development of AM technology in years. As can be seen from Figure 1.1, the use of AM technology started with the invention and production of the stereolithography (SLA) 3D printer machine. Thereafter, the other techniques of AM have been developed and used in industries for consecutive years.

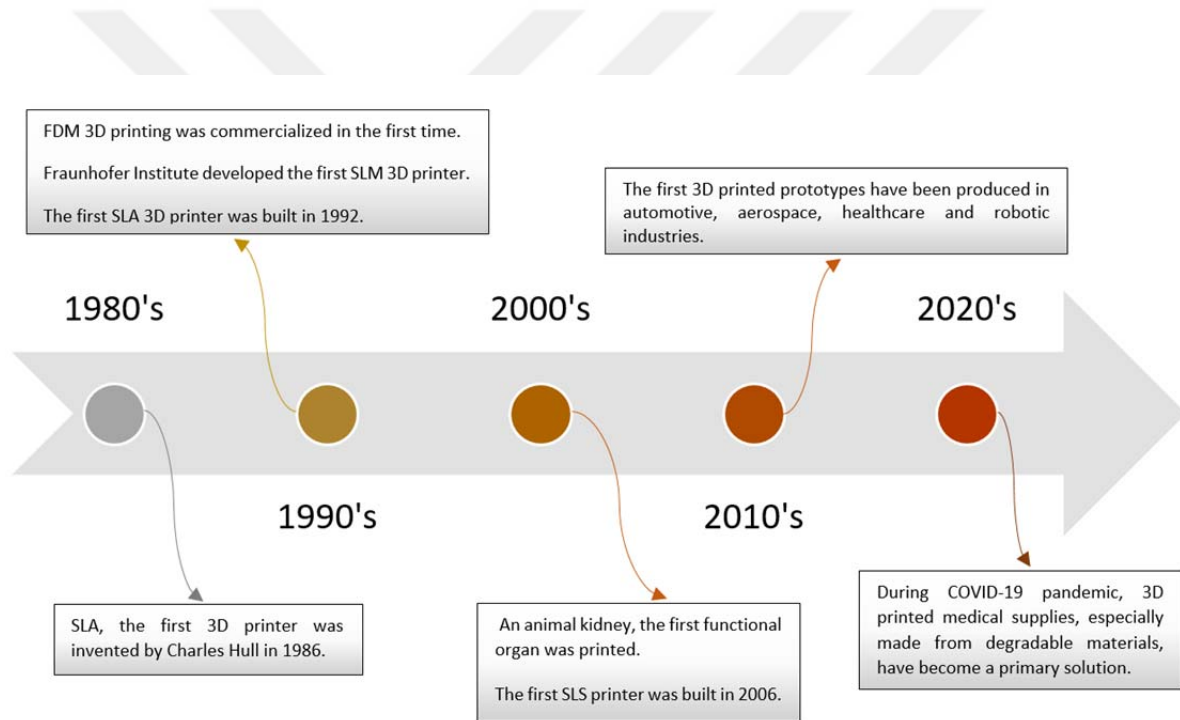


Figure 1.1. A brief history of the additive manufacturing technology.

AM technology is based on the principle of a layer-by-layer based fabrication process to create three-dimensional physical objects using three-dimensional (3D) data obtained from Computer-Aided Design (CAD). The newly created physical object may be derived from a prototype or basic model. In the most general sense, the manufacturing process starts with three-dimensional data of the solid part to be created, which can be obtained from CAD or scanning technologies. Then, the data set is imported into special software to be sliced into layers of the desired thickness. After all printing parameters have been determined in the

slicing software, additive manufacturing of the desired physical part is started in a quick and easy process (Gebhardt, 2011). Depending on the used AM technique, some post-processing methods may be needed to finalize the form of the part. Figure 1.2 represents the basic schematic of the FDM 3D printing process, starting with a three-dimensional CAD drawing of the rectangle-shaped tensile testing part to be sliced in special programs, the printing process after slicing, and after all, applications of parts. In that case, parts have been polished before testing for technical reasons related to testing procedures.

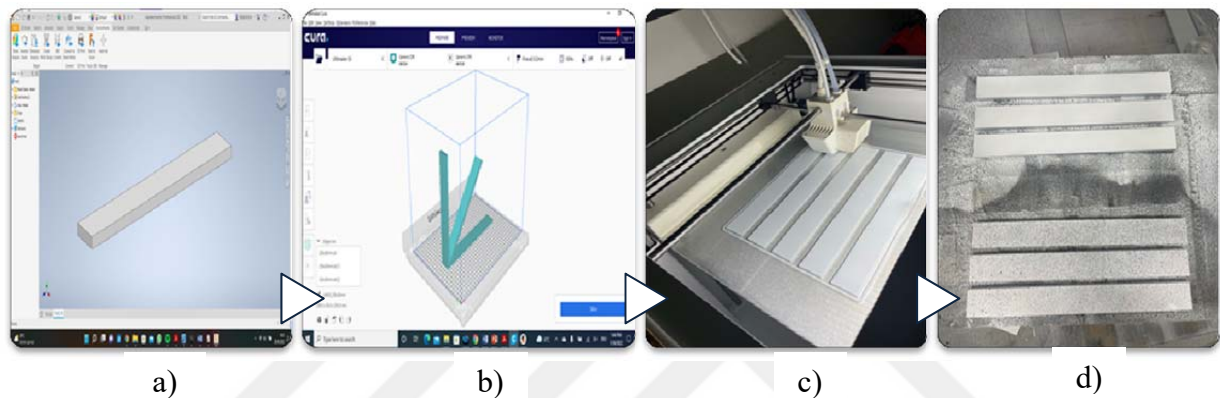


Figure 1.2. Representation of a basic process of FDM 3D printing technology a) CAD image of some parts for tensile testing, b) parts in slicing, c) printing process, d) polishing/preparing the part for testing.

1.2.1 Applications of additive manufacturing

Today, AM technologies have been widely used in the world and this usage is increasing every day because of their advantageous properties compared with traditional manufacturing methods. While providing flexibility to create lightweight and complex structures with high accuracy, AM also reduces production time. In addition, processes do not require additional tools like molds since the production method is based on layer-by-layer fabrication in any desired geometry, that's because the data has been sliced into layers first. Other manufacturing procedures demand a thorough examination of the part geometry to establish things like the order in which distinct features can be produced, the equipment and processes that must be employed, and any additional fixtures that may be necessary to finish the part. In this way, with AM, the production cost is automatically reduced, and this makes AM technologies a

prominent solution in the aerospace, automotive, healthcare, and food industries (Bayraktar, 2018) , (Gibson, 2015) , (Gebhardt, 2011) , (Başara, 2017).

All types of AM technology have been based on the same principles. The main differences are the materials that may be utilized, how the layers are formed, and how the layers are connected to one another. Such discrepancies will influence factors such as the finished part's precision, as well as its material and mechanical properties. These differences also determine the process factors like the lead time, whether the post-processing is necessary or how much post-processing is necessary, the size of the AM machine employed, and the total cost of production and machine. Contrary to popular belief, AM methods are not just limited to the creation of models, when combined with other technologies to construct process chains, AM methods have the potential to decimate product development time and costs (Gibson, 2015).

1.2.2 Process chain of additive manufacturing

In AM methods, the entire process comprises several steps that begin with the CAD model to get the final part. However, there might be slight changes in the process chain depending on the purpose of use of the produced part, the raw material type of the desired part, the complexity of the part, whether post-processing processes will be required to complete the desired part, or the specifications/limitations of AM machines. But always, the primary requirement to start the AM process is a comprehensive and accurate 3D data set file that works correctly.

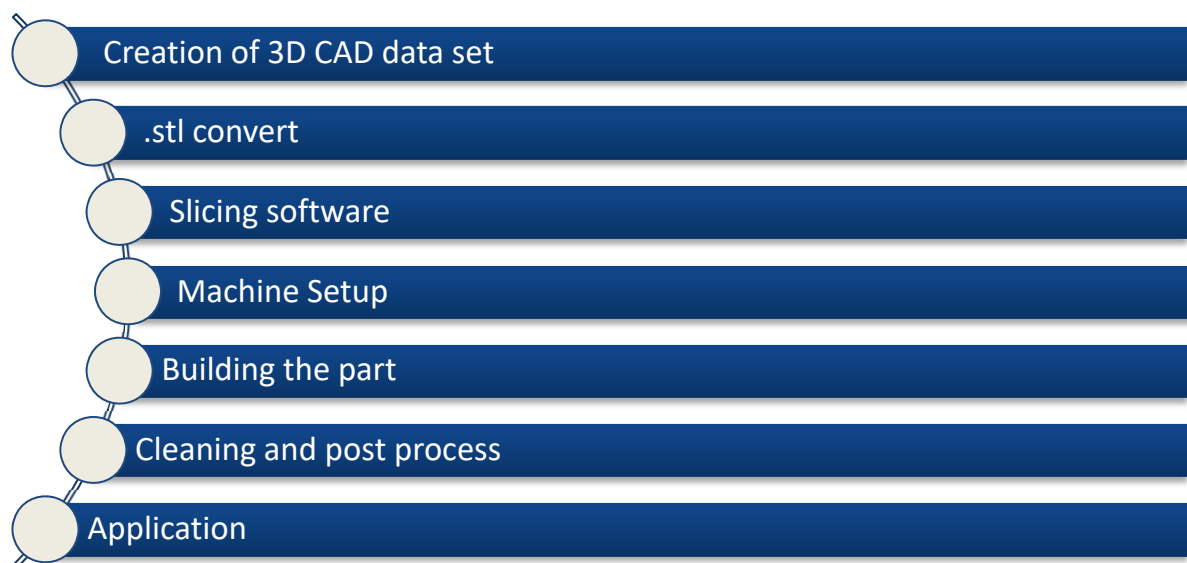


Figure 1.3. General AM process procedure in seven stages.

As mentioned above and illustrated in Figure 1.2 and Figure 1.3, the 3D data is an obligation to start the production process. As a matter of fact, the 3D data does not have to be obtained just from CAD designs, there are some different 3D data sources are available with the improving technology, the data can be obtained from scanning or imaging processes such as computerized tomography (CT-scanning). In order to get started in the AM process, the 3D data set has to be converted to .stl file format. In the simplest terms, the .stl format is a basic way of defining a 3D model in terms of just its geometry, with no further information about parts such as the material type, color, or units. Once the conversion of the .stl file is complete, the printing parameters such as print orientation or layer thickness can be determined by using slicing software. After all the parameters have been set up and the machine preparation is done, the AM process can be started. Figure 1.4. shows and explains all of the process chain steps for selective laser sintering (SLS) technology.

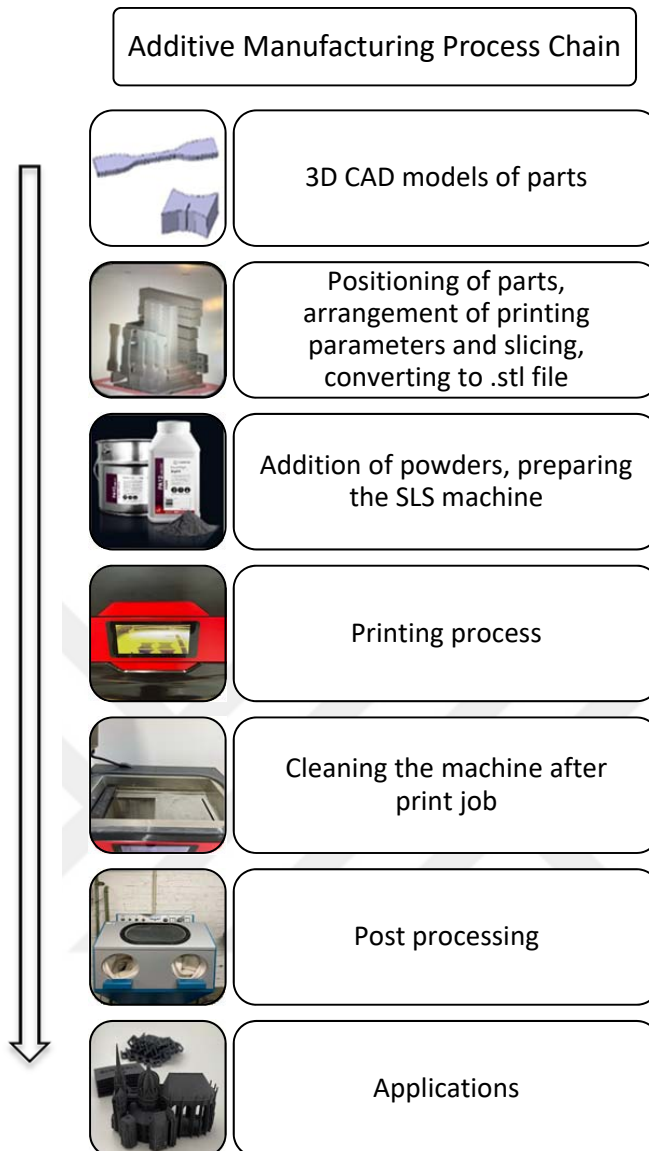


Figure 1.4. Schematic representation the process chain of one of the widely used AM process, selective laser sintering (SLS).

1.3. Methods of additive manufacturing

The most commonly used additive manufacturing methods, including the fused deposition method, used in this study have been explained in this section.

1.3.1. Extrusion-based processes

Extrusion-based method is the most widely used AM technology in the world. The basic principle of any extrusion-based system comprises several steps which start with loading the raw material onto the AM machine. In the second place, the raw material, commonly called as

filament in extrusion-based systems, has to be gone through into the liquefaction process. Thereafter, the molten filament is deposited layer by layer by applying pressure into the printing bed through the nozzle until the part is done. Post-processing methods may be required to removal if the support parts have generated while printing.

1.3.1.1. Fused deposition modeling (FDM)

Fused deposition modeling (FDM) is one of the commonly used extrusion-based AM technology methods developed in the 1980s. FDM technology is based on the principle of depositing thermoplastic polymers layer by layer and fusing them together based on a selective pattern implemented by a positioning system to prototype functional complex geometries from three-dimensional CAD design models in a short time. As can be seen from Figure 1.5, a FDM machine with essential components comprises a heated build chamber that includes a build platform that is movable in the z-direction and a print head which extrudes the molten filament onto a heated print bed and solidifies into the final part at room temperature. FDM technology does not use a laser-based scanning system, it is based on the extrusion process of molten thermoplastic polymers. In other words, the deposition of materials is carried out by the extrusion head, which is movable in x-y contours and placed in the build chamber. Due to its advantages such as ease of production, creation of complex geometries, repeatability, no extra equipment required, and cost-effectiveness, the FDM method is promising in many fields such as aerospace, healthcare with developing tissues or medical tools, automotive, and food engineering (Wickramasinghe, Do, & Tran, 2020) , (Sanei & Popescu, 2020) , (Hsueh, et al., 2021).

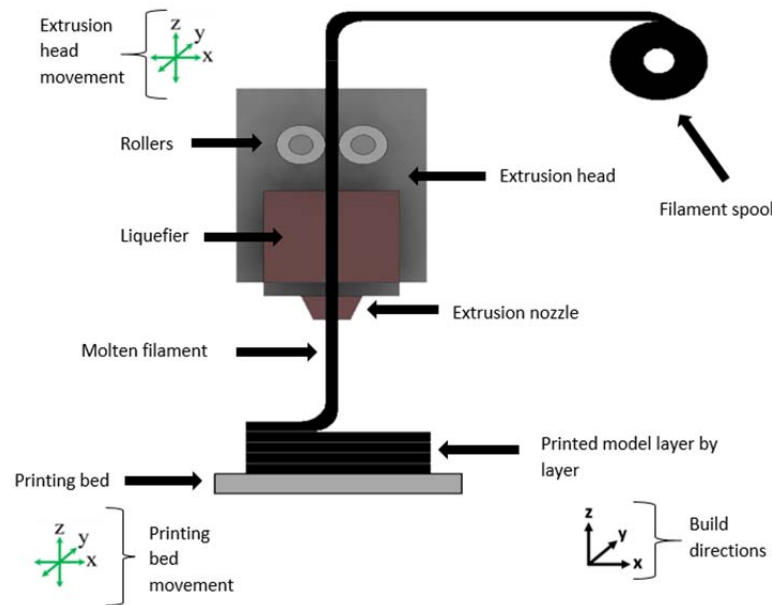


Figure 1.5. A schematic overview of FDM process.

One of the most important points in the FDM technology is the adjustment of printing speed and, correspondingly, lead time to avoid the negative effects of the limitations of the FDM technique. The leading time of a part is directly affected by feed rate and printing speed, and the performance of feed rate is affected by the ability of the nozzle to provide the material and the rate at which the liquefier can melt the material and send it through the nozzle. Adjusting the liquefier to enhance the material flow rate would probably result in an increase in total mass, and it would probably create some difficulties in more rapid movement of the nozzle. A lead-screw configuration is commonly used in charting systems for accurate movement. Belt drives can be used in low-cost systems, but the bending in the belts makes them less precise, and the torque reduction to the drive motor is likewise lower. Printing parameters in FDM printing highly affect the characteristics of parts. To this end, the effects of different printing parameters such as printing speed, filling ratio, and internal architecture have been investigated in this study, and the significance of parameters has been determined with ANOVA analyses.

1.3.2. Powder bed fusion processes (PBF)

Powder bed fusion techniques were first designed to make plastic prototypes in 1993 at the Massachusetts Institute of Technology (MIT) and it uses a point-wise laser scanning approach. The same set of process chain may be found in all PBF methods; one or more thermal sources for inducing powder particle fusion, a method for controlling powder fusion to a predefined region of each layer, and mechanisms for adding and smoothing powder layers are among these. Lasers are the most popular thermal source for PBF, and laser sintering equipment is used in PBF techniques that use lasers.

PBF technique has been employed in tissue engineering, aerospace, and electronics due to its multiple benefits. The key advantages of this technique are the fine resolution of the printed parts, the flexibility of the material utilized, room temperature processability, and superior surface quality, all of which make it particularly appropriate for advanced applications. Nevertheless, using a binder might result in a porous end product as well as contamination. Furthermore, it is a time-consuming and expensive operation. As a result, probably only sophisticated industries adopt this strategy (Wang, Jiang, Zhou, Gou, & Hui, 2017) , (Ngo, Kashani, Imbalzano, Nguyen, & Hui, 2018).

1.3.2.1 Selective laser sintering (SLS)

Selective laser sintering (SLS) is a powder bed fusion technique that uses high-powered laser beams to sinter thermoplastic polymer, ceramic, and metal powders layer by layer to create three-dimensional polymer components. Owing to its advantages such as printability of a wide range of materials from stiff to flexible, high-quality surface finishes of parts, strong layer bondings with higher tensile strength and modulus values, and no support structures even in complex parts are required during printing, SLS manufactured parts have become popular in industrial applications such as robotics, automotive, and electronics (Chen, et al., 2018). Figure 1.6 shows the simple schematic profile of SLS machine. Basically, the SLS process follows the principle of laser beams melting powder particles and layer solidification and in a simple way, a SLS machine a laser scanning system on top of the chamber that arrays each layer in an x-y direction, and a preheated build chamber with a piston that can move at any z-level to fill the chamber with powder (Gebhardt, 2011).

The SLS fabrication procedure begins with powder pre-heating, in which the printer heats the powder for 2-3 hours to a temperature which does not exceed the melting point of the raw material, which after powders are spread by the recoater on the build platform, and once the printing temperature has been reached, the laser begins fusing powders, and the melted powder fuses and cools. This process is repeated layer by layer to create a proper component. After the fabrication is completed, the build chamber must be progressively cooled to room temperature to avoid warping and mechanical failures of parts, and then the parts must be removed from the build chamber. After that, post-process treatments are used to clean up the excess powder on the parts.

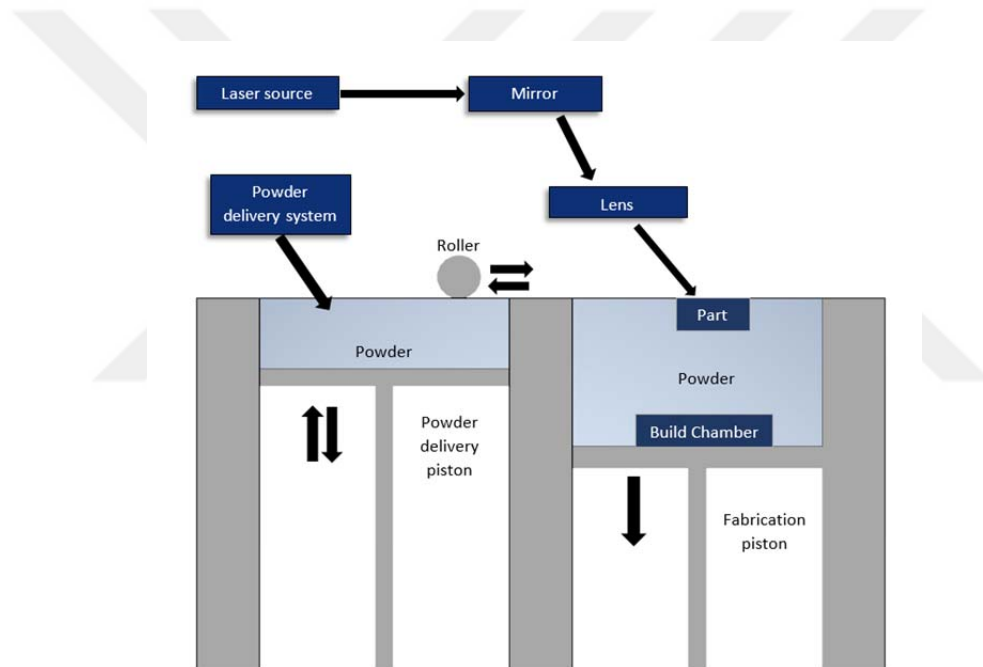


Figure 1.6. A schematic profile of a powder bed fusion process/SLS machine.

1.3.2.2 Selective laser melting (SLM)

Selective laser melting (SLM) is one of the PBF processes that used for metal powders such as stainless steel, titanium and aluminum. Unlike SLS, the metal powders are completely melted by a laser beam. Therefore, the final product of SLM has outstanding mechanical properties. The most important concerns in PBF processes are good dispersion and bonding behavior of molten powders, which are highly affecting the thermo-mechanical behavior and other characteristics of final product.

1.3.3. Stereolithography (SLA)

Stereolithography, one of the most prominent solid free-form approaches that are still used today, is the oldest AM method, and it was invented in 1986. SLA technology polymerizes UV-active monomers into a two-dimensional structural layer using a ultraviolet (UV) laser or an electron beam. As can be seen from Figure 1.7, once one layer has been set, the platform is shifted below, and the next layer is patterned on top of the previous one. This process is continued until to create a three-dimensional model. Post-process treatments such as polishing, finishing, and painting may be necessary to improve the surface quality after printing. Photo curing in a UV oven can also be employed to complete polymerization and achieve better mechanical properties of the final product (Bayraktar, 2018). The intensity of the laser and laser power, scan speed, and exposure time are the essential process parameters that influence the quality of the final prototype in the SLA techniques. In the SLA process, photo initiators and UV absorbers are particularly valuable since they directly impact the degree of polymerization.

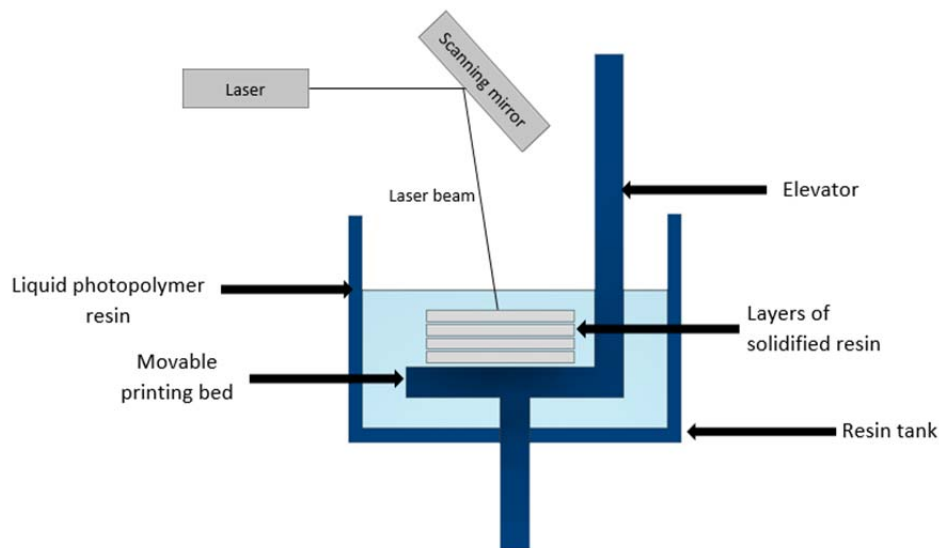


Figure 1.7. A schematic profile of SLA machine.

SLA can be used to fabricate complex polymer nanocomposites due to its main benefit that SLA produces high-quality parts with precise resolution down to 10 microns. SLA also has the benefit due to based on a nozzle-free technology, which avoids all blockage concerns

during printing, yet, the SLA process is a time-consuming and costly operation (Wang, Jiang, Zhou, Gou, & Hui, 2017). Furthermore, as compared to other 3D printing methods, the maximum printed product size is quite small, and the material types appropriate for SLA are limited. Furthermore, the curing process involves a large number of control factors, making SLA difficult to use in fundamental applications. SLA may be used to fabricate sophisticated polymer nanocomposites based on the mentioned benefits and drawbacks (Melchels, Feijen, & Grijpma, 2010) , (Prakash, Nancharaih, & Rao, 2018) , (Manapat, Chen, Ye, & Advincula, 2017).

1.3.4. Laminated object manufacturing (LOM)

In contrast to other AM technologies, laminated object manufacturing (LOM) entails both subtractive and additive manufacturing procedures of polymer composites, metals or papers. The process is based on cutting the raw material layer by layer and then gluing the printed layers together and the final parts can be used in different industries such as paper manufacturing or sensor applications. Depending on the material, layers are first cut with mechanical cutters or a laser beam, then bonded together with pressure and heat or conversely. For metallic and ceramic materials, for example, the form-then-bond method is preferable since the forming process may be more difficult following thermal bonding of layers. Excess material can be simply removed from the body when cutting and bonding is accomplished. Post-processing treatments may be required according to purpose of the final part or the material properties. In use of the creation of complex geometries, LOM has some disadvantages such as low dimensional accuracy in z-axis, this consumes time and more raw material while printing. Unlike SLA, LOM processed parts have poor resolution and surface finish. Table 1.1 summarizes the materials, drawbacks and application areas of AM methods mentioned in this chapter.

Table 1.1. Summary of materials, drawbacks and application areas of additive manufacturing methods mentioned in this chapter.

Methods of AM	Materials	Advantages	Disadvantages	Application areas
Extrusion-based systems (FDM)	Filaments of thermoplastic pure or reinforced polymers	- Cost effective - High reliability - High speed - Reusable raw material - Variety of material selection - No complexity in use	- Warping - Porosity - Clogging in nozzle - Processing only thermoplastic polymers - Layer adhesion - Weak mechanical properties	- Toys - Healthcare - Aerospace - Architecture
Powder bed fusion processes (SLS, SLM)	Powders of alloys, metals or certain polymers	- Good resolution in parts - Reusable powders - Different types of materials can be used - No need to supporting structures	- Longer printing time - Post-processing is required - High power usage - Weaker structural properties	- Military - Commercial aircraft - Automotive
Stereolithography (SLA)	- Light-reactive thermoset materials (resin) - Polymer-ceramic materials	- Shorter printing time - Smooth surface finishes of parts - Printable for miniature as well as complex geometry of parts - Variety of material selection	- High-cost - Non-environmental friendly - After print job, curing process is required - Not usable for larger parts - Lower mechanical properties	- Prototypes in engineering - Rapid tooling - Patterns for molding and casting - Optics
Laminated object manufacturing (LOM)	- Adhesive-coated paper - Metals and Ceramics - Polymer materials	- No support material requires - Cost effective - Usable for production of large parts	- Poor surface finish of parts - Weaker internal bonding of layers	- Electronics - Paper manufacturing

1.4. Molding processes

1.4.1 Injection molding

Injection molding is the most typical method of producing thermoplastic polymer parts. The injection molding procedure is based on the principle of injecting the molten thermoplastic material, usually in the form of granules or pellets, into a pre-designed mold and rapidly cooling the injected material. A hopper feeds the thermoplastic granules to be molded into an electrically heated barrel where it is melted. This molten material is injected into the mold under high pressure and cooled until it solidifies and shrinks volumetrically, and then the final part is retrieved by opening the mold. Melting temperature, injection and back pressures, and sample size highly influence the quality of injection molded materials. In order to complete the cyclical phases of the process, injection molding equipment includes injection and clamp units (Rosen, 1993) , (Ebewe, 2000) , (Yeşil, 2010) , (Svečko, et al., 2013). A simple schmatic of injection molding machine is represented in Figure 1.8. According to the complexity of the part, lead time in the FDM process can be longer than in injection molding, but since the injection molding process requires a pre-design and prototype of the desired parts, the production cost in injection molding is significantly more expensive than the FDM process (Açık, 2014).

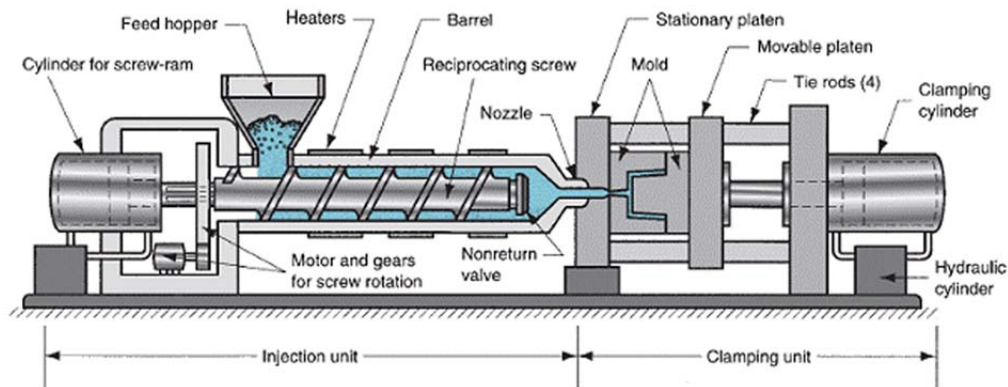


Figure 1.8. A simple schmatic of injection molding machine. (Jinan Hao Jia Mould Technologies Co., Ltd., 2022)

1.4.2 Compression molding

In the compression molding process, a specific amount of material is placed into the lower half of a heated mold or cavity, as the top half of the mold is then put on top of the bottom half. The force plug is lowered into the cavity, and the powdered or granular polymer is subjected to pressures ranging from 20 to 1000 tons. The substance melts and fills the mold cavity under heat and pressure. The mold is opened once a reasonable amount of time has passed, and the component is expelled while still hot, and outside the mold, the sample is allowed to cool. In certain circumstances, bubbles in the molded sample are caused by gases created by heating and moisture trapped in the material. Figure 1.9 represents a simple schematic of the compression molding machine.

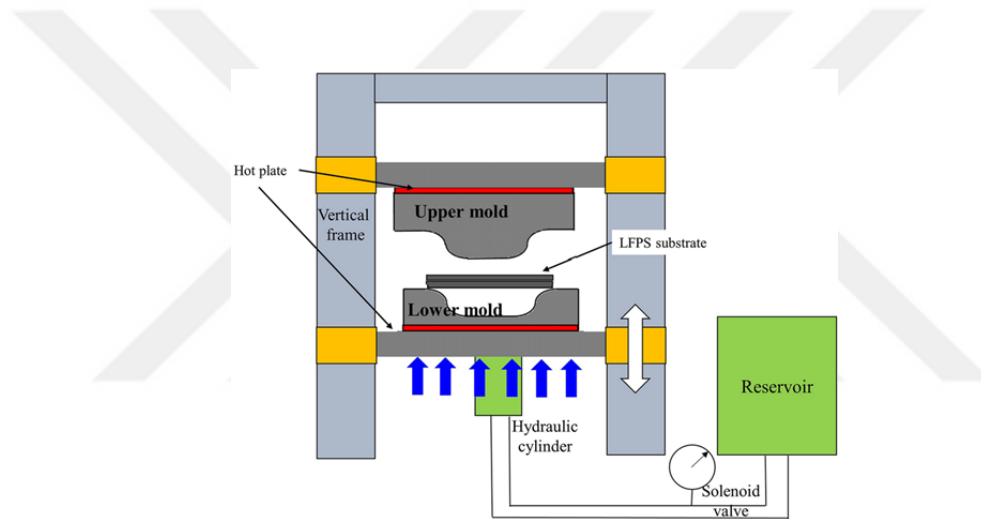


Figure 1.9. A simple schematic of compression molding machine. (Kim, Lee, & Lee, 2020)

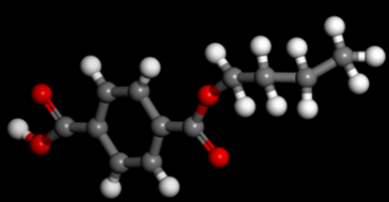
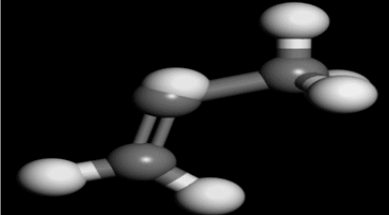
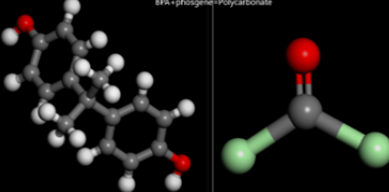
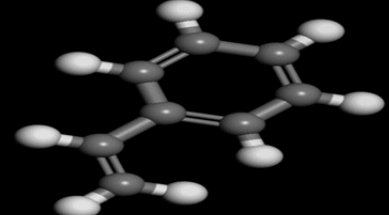
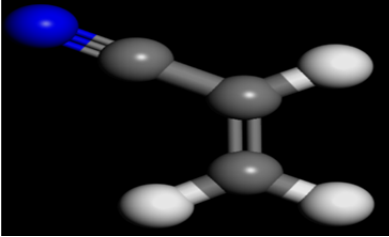
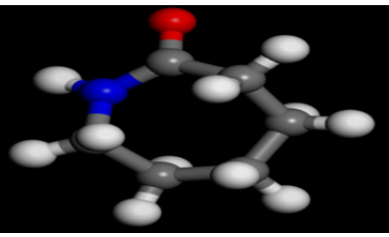
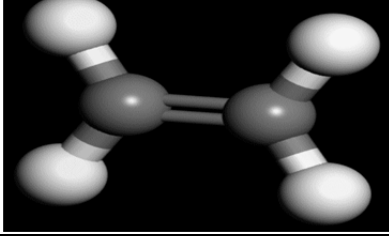
1.5. Thermoplastic polymer materials

The present study uses the fused deposition modeling (FDM) technique and injection molding for the production of parts. In FDM method, thermoplastic polymer materials such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), high impact polystyrene (HIPS), polyetheretherketone (PEEK) or polyethylene terephthalate glycol (PETG) are widely used in many areas of the industry with their non-toxic, lightweight and recyclable properties (Krajangsawasdi, et al., 2021) , (Panneerselvam, Raghuraman, & Krishnan, 2021) , (Hanon, Marczis, & Zsidai, 2019). PETG, one of the most popular engineering polymers, stands out from other polymers with its mechanical properties, such as high-impact resistance, strength, flexibility, toughness and machinability. Besides its mechanical properties, it is very suitable

for 3D printing in food industry with its advantages such as being odorless, brightness and color ability (Hodzic & Pandzic, 2019) , (Ranganathan & Pradeep, 2020) , (Swetha, Morampudi, Prabha, & Kumar, 2020). In FDM, thermoplastic filaments are usually wrapped in a diameter of 1.75 mm or 3 mm and are fed to the melting chamber with the help of a motor. Table 1.2 shows the main characteristics, application areas and molecular structures of the most commonly used thermoplastic materials in the industry.



Table 1.2. Technical names, molecular structures, characteristics and and typical applications of some popular thermoplastic materials.

Thermoplastic Polymer	Molecular/Monomer Structure	Characteristics	Typical Applications
Polyester (PET)(PBT)		✚ High strength ✚ High rigidity ✚ High toughness ✚ Good chemical and moisture resistance ✚ Good fatigue strength	Industries such as: ✚ Electronic ✚ Medical ✚ Food ✚ Automotive
Polypropylene (PP)		✚ Low density ✚ High resistance to heat ✚ Excellent chemical resistance, electrical properties and fatigue strength	✚ Medical industry ✚ General usage such as luggages or boxes for food
Polycarbonate (PC)		✚ Low density ✚ Easy machinability ✚ High impact resistance ✚ Ductility ✚ Colorless ✚ Chemical resistance at normal level	Industries such as: ✚ Electronical ✚ Medical ✚ Optical ✚ Semicon
Polystyrene (PS)		✚ Brittle ✚ Colorless ✚ High rigidity ✚ Good thermal and electrical properties ✚ Good UV resistance ✚ Low cost	✚ Electronic industry ✚ General usage such as toys, household appliances
Acrylonitrile butadiene-styrene (ABS)		✚ Excellent mechanical strength and toughness ✚ Good heat resistance ✚ Good electrical properties ✚ Flammable ✚ Easy bonding ✚ Good machinability ✚ UV resistance ✚ Low cost	✚ Automotive industry ✚ Housings ✚ Electronics industry
Polyamide (PA) (Nylon6)		✚ High wear resistance and thermal stability ✚ Good strength and hardness ✚ High damping characteristics ✚ Good chemical resistance ✚ High durability ✚ Low cost	✚ Electrical industry ✚ Medical industry ✚ General usage such as fishing line, guitar strings
Polyethylene (PE)		✚ Low density ✚ Low strength ✚ Low friction ✚ High impact resistance ✚ Wear resistance ✚ High chemical and corrosion resistance ✚ Low moisture absorption ✚ High electrical insulation	✚ Electrical industry ✚ General usage such as toys, flexible bottles

1.5.1. Polylactic acid (PLA)

Today, due to increasing concerns in the world, efforts to storing or recycling waste materials create some problems. While the high labor and energy costs required for recycling have become a problem in the industry, the storage of waste thermoplastic materials has become impossible because of the space they occupy and CO₂ emissions. Among these materials, polylactic acid (PLA), as a biodegradable, aliphatic and versatile polyester type of material, derived from renewable sources such as corn starch, sugarcane or tapioca, is widely used in medical applications such as sutures, scaffolds, drug carriers, orthopedic interventions and medical tools/equipments. PLA has become the second most synthesized bioplastic in the world since it has a cost efficient production method (Qazi, et al., 2020) , (Nagarajan, Mohanty, & Misra, 2016). It is also widely used in the automotive, aerospace, construction, and food industries. Particularly in the medical and biomedical fields, the production of PLA-based parts is seen as a necessary technology, especially for many patients, the fabrication of implants and prostheses using three-dimensional printer technology has been a source of hope. Biocompatibility of PLA is a key benefit for its widespread use in biomedical applications, as it causes relatively minimal harm to human health.

As mentioned before, PLA has biodegradable, colorless, odorless, non-toxic properties and due to these properties, it is widely used in healthcare and food industries. However, the application of PLA has been restricted due to shortcoming in thermo-mechanical properties of this material that makes it subjected to various processing defects and in-service-damages and shows brittle behavior at room temperatures, to this end, nano fillers such as graphene or calcium carbonate can be added to improve the mechanical, thermal and morphological performance of PLA . Also, the physical, thermal, mechanical and rheological properties of PLA are all highly influenced by its transition temperatures. High L-lactide level in PLA components allows them to form crystalline polymers, whereas high D-lactide content in PLA components makes them more amorphous. The temperature restrictions for commercial usage are determined by the glass transition (T_g) for amorphous PLAs and the T_g and melting point (T_m) for semi-crystalline PLAs (Açık, 2014). These transition temperatures are influenced by fundamental structure, thermal history, and molecular weight, in addition to optical composition (Ahluwalia & Mishra, 2007). The thermo-mechanical properties of the printed PLA samples depend on many factors such as the internal architecture, filling ratio, and

molecular structure of the material, hence, nanoparticle addition to pure polymers generates some improvements in these properties (Kwapisz, Bajor, & Krakowiak, 2019) , (Xu, Kang, Niu , Kang , & Ma, 2019). In polymer nanocomposites, the binding energy between the polymer and the nano fillers and the uniformity of the dispersion of these particles in the matrix play important roles (Yang , Xu, Niu , Kang, & Ma, 2018). Detailed properties of PLA are given in Table 1.3.

Table 1.3. Properties of PLA in details.

Technical name	Polylactic acid (PLA)
Chemical formula	$(C_3H_4O_2)_n$
Mechanical Properties	
Tensile strength (MPa)	61-66
Elongation at break (%)	10-100
Flexural strength (MPa)	48-110
Thermal Properties	
Melting temperature (°C)	157-170
Injection molding temperature (°C)	178-240
Heat deflection temperature (°C)	40-45,135
Glass transition temperature (°C)	55-56
Physical Properties	
Specific gravity (g/cm ³)	1.25
Melt flow rate (g/10min)	4.3-2.4

1.5.1.1. Lactic acid monomer and syntesis of polylacid acid

Figure 1.10 shows the optical monomers of polylactic acid. A lactic acid monomer is a chiral molecule since it has four distinct groups linked to the core carbon atom. The optically active forms of chiral molecules are called "L" and "D," with D = R representing right-handedness and L = S representing left-handedness. Chemically generated lactic acid produces a mixture of around 50% L and 50% D isomers, whereas lactic acid produced via fermentation normally contains 99.5% L and the rest 0.5% D isomers. The cyclic lactide dimer can be produced in three different forms: D, D-lactide, L, L-lactide, and L, D or D, L-lactide (meso-lactide). The

optically active forms of cyclic lactide are D and L, but the meso-form is not optically active (Vink, Rabago, Glessner, & Gruber, 2003).

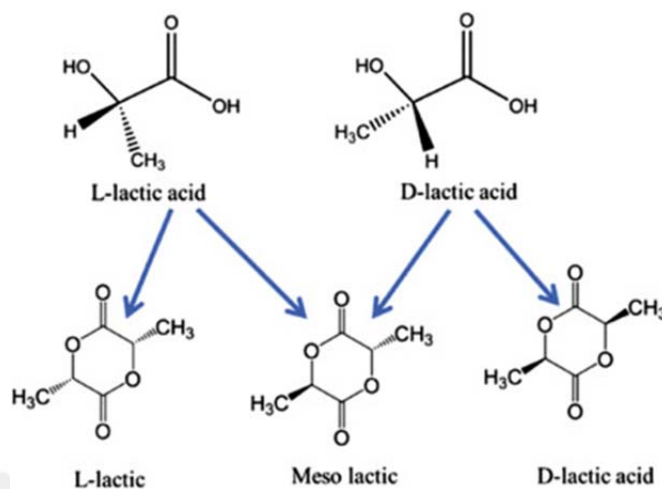


Figure 1.10. Optical monomers of polylactic acid. (Jiang, et al., 2016)

The two approaches to polymerizing lactide acid monomer are shown in Figure 1.11. Two distinct processes are used to create a cyclic dimer intermediate called lactide, which is then followed by catalytic ring-opening polymerization of the cyclic lactide. The processes can either be solvent-free or solvent-based. Since the direct condensation method uses an equilibrium process, getting rid of water and impurities might be difficult. The ultimate result frequently has a low molecular weight. Lactide ring-opening polymerization is employed in commercial manufacture since the direct condensation method is challenging (Rasal, Janokar, & Hirt, 2010) , (Drumright, Gruber, & Henton, 2000).

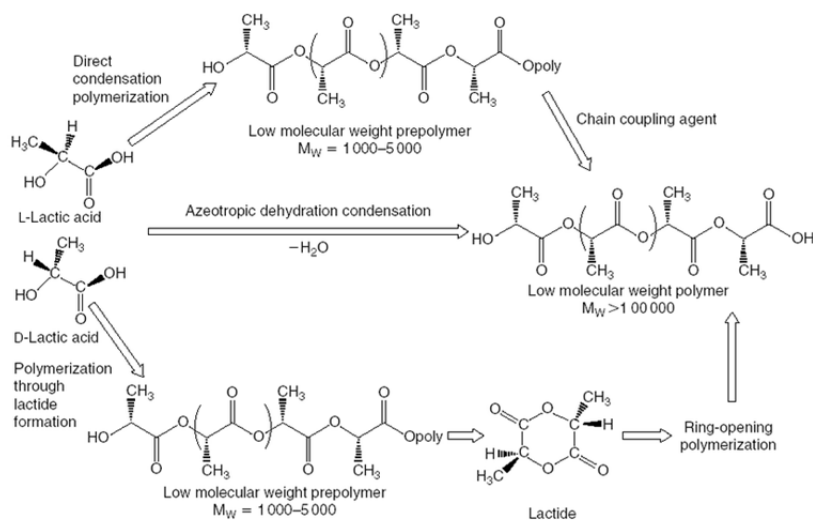


Figure 1.11. Polymerization methods of lactic acid and syhntesis of PLA. (Avérous, 2008)

1.6. Polymer additives/Nanoparticles

According to reported large number of reported researches based on the PLA and PLA-based nanocomposites in the literature in following chapter, the application of PLA has been restricted due to shortcoming in the thermo-mechanical properties of this material that makes it subjected to various processing defects and in-service-damages, to this end, nanoparticles such as graphene (GR), silicium oxide (SiO_2) or calcium carbonate (CaCO_3) can be incorporated to enhance the mechanical, thermal and morphological performance of PLA. Recently, fabrication of nanoparticle reinforced polymer-based composite materials easy and quick with the AM methods has been expanded. Fused Deposition Modeling (FDM) which is the most preferred AM methods can be used to produce the high-precision polymer based nanocomposite materials with the excellent thermo-mechanical, electrical, chemical or fracture performance of filaments with nanoparticle reinforcements.

1.6.1. Calcium carbonate (CaCO_3)

An inexpensive inorganic nanoparticle called as calcium carbonate (CaCO_3) has been used in this study to save costs and enhance thermo-mechanical and fracture properties of pure PLA thermoplastic. The chemical compound calcium carbonate has the structure CaCO_3 . It is a common substance found in rocks as the minerals calcite and aragonite, most notably in limestone, a sedimentary rock that is primarily composed of calcite. Under typical conditions, the thermodynamically stable form of CaCO_3 exists as hexagonal $\beta\text{-CaCO}_3$ (the mineral calcite) (Wikipedia, 2022). Figure 1.12 represents the formula and molecular dynamics simulated structure of the CaCO_3 molecule, and calcite, a member of the carbonate minerals, is the most stable polymorph of CaCO_3 .

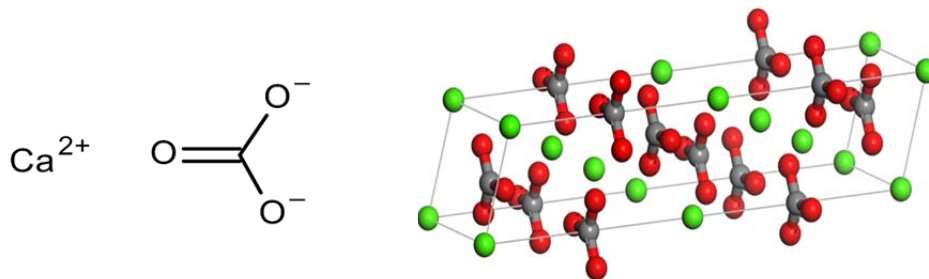


Figure 1.12. Molecular structure of CaCO_3 molecule and representation of calcite unit cell built with MD simulations.

1.6.2. Graphene (GR)

The reinforcement of graphene into a polymer matrix provides superior properties with promising applications in many industries, such as aerospace, electronics, energy, structural and mechanical, as well as healthcare applications. Graphite is the most stable allotrope of graphene under standard conditions and is composed of many layers of graphene. Due to its properties such as lower density, superior mechanical characteristics, higher thermal and electrical conductivity, graphite can be a suitable choice to production of nanocomposites.

Graphite is an allotrope of polymorphic carbon atom, which can be found in nature in three different forms, called as diamond, graphite and fullerenes. Each carbon atom in graphite is connected to three other carbon atoms by covalent bonds, forming a continuous covalent structure. In graphite, each carbon atom sp^2 (trigonal) hybridized, while in diamond, each carbon atom sp^3 (tetrahedral) hybridized. In graphite, these carbon atoms are arranged hexagonally and create a layer-like structure and it consists of carbon layers (Wikipedia, 2022). Graphene reinforcement in different weight fractions into PLA matrix has been investigated with MD simulations according to consistent results of injection molded PLA/CaCO₃ nanocomposites. Figure 1.13 represents the MD simulation of a graphite unit cell to create graphite nanocluster.

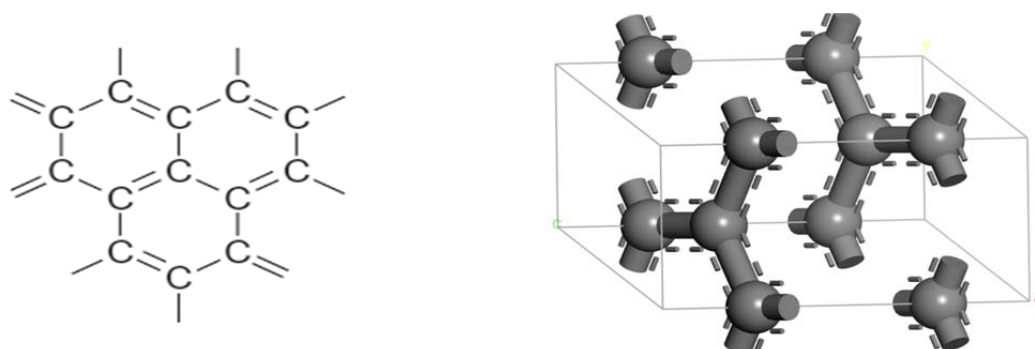


Figure 1.13. Molecular structure of graphene molecule and representation of graphite unit cell built with MD simulations.

2. LITERATURE REVIEW

Thermoplastics such as PLA, ABS, HIPS or PETG can be used in many areas of the industry with their non-toxic, lightweight and recyclable properties (Somireddy, Singh, & Czekanski, 2019) (Krajangsawasdi, et al., 2021) (Panneerselvam, Raghuraman, & Krishnan, 2021) (Hanon, Marczis, & Zsidai, 2019). Among these materials, polylactic acid (PLA), as a renewable aliphatic and versatile polyester type of material, is widely used in medical applications such as sutures, scaffolds, drug carriers, orthopedic interventions and medical tools/equipments. PLA has become the second most synthesized bioplastic in the world since it has a cost efficient production method (Qazi, et al., 2020) (Nagarajan, Mohanty, & Misra, 2016). However, the application of PLA has been restricted due to shortcoming in thermo-mechanical properties of this material that makes it subjected to various processing defects and in-service-damages, to this end, nano fillers such as graphene or calcium carbonate can be added to improve the mechanical, thermal and morphological performance of PLA.

The thermo-mechanical properties of the printed PLA samples depend on many factors such as the internal architecture, filling ratio and molecular structure of the material, some studies in the literature shows the nanoparticle addition to pure polymers generates some improvements in this properties (Kwapisz, Bajor, & Krakowiak, 2019) (Xu, Kang, Niu , Kang , & Ma, 2019). The binding energy between the polymer and the nano fillers and the uniformity of the dispersion of these particles in the matrix play important roles in polymer matrix composites. (Yang , Xu, Niu , Kang, & Ma, 2018). Inorganic CaCO_3 nanoparticles are frequently used to improve the thermo-mechanical properties of thermoplastic polymers (Hsueh, et al., 2021). Limited information exists on CaCO_3 reinforced nanocomposites, which are widely used in biotechnology due to their properties such as water resistance, hardness and lightness in structure (Varga, et al., 2019) (Donate , et al., 2020). Varga et al. produced PLA/ CaCO_3 nanocomposites with different weight ratios using the FDM 3D printing method to investigate the usability of these materials in cast, orthosis and splint production. According to the results from the mechanical tests, they have stated that the addition of CaCO_3 to neat PLA increases the rigidity and brittleness of the material.

Donate et al. proposed the production of PLA parts reinforced with CaCO_3 and β -tricalcium phosphate by 3D printing, as PLA has become difficult to use in tissue engineering because of some of its structural properties. They have demonstrated that the addition of additives to pure PLA has an advantage, as the microporosity of the material increases, the degradation rate increases. Chan et al. showed that the addition of CaCO_3 nano fillers does not change the melting temperature (T_m) and the crystallinity of polypropylene (PP). Decrease in the size of spherulites and interaction between CaCO_3 nanoparticles increased the impact strength by 300% and Young's modulus by 100% at nano filler concentration of 9.2vol%. Eiras and Pessan studied the influence of CaCO_3 nanoparticles on the mechanical properties of PP. They reported that the Young's modulus and yield stress of the nanocomposite increased with increasing the nano filler content in the matrix. Additionally, the impact strength increased and the ductile-to-brittle transition temperature decreased significantly by incorporation of the CaCO_3 nanoparticles in PP.

On the other hand, addition of graphene nanoparticles in the polymer matrix has been found to enhance the stiffness and strength of the polymers (Young, et al., 2018). Graphene filled polymer nanocomposites exhibited superior mechanical, thermal, and electrical properties than the neat polymer (Ryu & Shanmugaraj, 2014) (Prashanta & Roger, 2017) (Caminero, et al., 2019) (Guo, Ren, Bi, Xu, & Cai, 2019). Physical and chemical properties of the graphene-based polymer nanocomposites depend on the distribution of graphene layers in the polymer matrix and the interfacial bonding between the graphene layers and the matrix (Pati, Pattojoshi, & Roy, 2016). Graphene or graphene oxide reinforced PLA materials have recently been widely used in the biomedical field and tissue engineering. The graphene additive can improve the growth and proliferation of stem cells (Bayer, 2017). Belaid et al. produced a 3D printed reinforced PLA scaffold with different concentrations of graphene oxide (0.1 wt%, 0.2wt%, 0.3wt%) designed for use in biological applications. Examining the biocompatibility and structural properties of these materials, as well as their mechanical, chemical and morphological properties, the authors emphasized that the mechanical properties of pure PLA improved as the percentage of graphene oxide increased. In addition, the surface roughness has increased and the percentage of crystallization has decreased. Prashanta et al. proved the feasibility of the FDM 3D printing method to produce a conductive and biodegradable thermoplastic matrix. The authors conducted various tests to examine the mechanical, electromagnetic induction shielding and electrical properties of pristine and 10

wt% graphene reinforced PLA produced with the FDM 3D process. They reported that addition of graphene to PLA improved the thermo-mechanical and dielectric properties of the nanocomposite. Dul et al. synthesized pristine and xGnP filled ABS filament using compression molding process and examined the effects of such nano-additives on the thermo-mechanical properties of samples produced FDM technique. The best mechanical properties were reported for the 3D printed samples with ABS filaments containing 4wt% of xGnP nanoplatelets in the matrix. It was also reported that the xGnP reduced the thermal expansion coefficient of 3D printed parts and increased their stability under prolonged loadings. In the investigation of the effect of filling percentage and layer thickness on the mechanical properties of FDM 3D printed PLA/GR parts, Camargo et al. stated that as the linear layer thickness increases, the mechanical properties develop and as the filling percentage increases, the tensile and bending strength of the material increases, while the impact energy decreases. Mansour et al. produced pure and graphene nanoparticle reinforced PLA filaments and evaluated the effects of such nanoparticles on the behavior of synthesized 3D printed parts under compression and vibration loadings. They showed that while the graphene addition caused an increase in the compression modulus and damping capacity of the samples, the material also reached a stable condition with fewer vibration characteristics. Bustillos et al. emphasized that graphene additive to pure PLA improves the friction and wear resistance of composites, and showed that the graphene additive increases the wear resistance of pure PLA by 14%. One of the most commonly used processing techniques for production of polymer nanocomposites is the solution-based processing technique that disperses graphene sheets into a polymer matrix. Previous studies include the polymerization of polystyrene, polymethylmethacrylate, poly (styrenesulfonic acid) and polymers that contain graphene nanoparticles in the original solution of the polymer before in-situ polymerization (Moujahid, Besse, & Leroux, 2003) (Wei & Bai, 2015). However, the solution-based technique takes a long processing time and requires the application of large quantities of solvents that make this process either impractical for industrial applications or unfriendly for environment. In contrast, melt-blending technique has been introduced as the only way to mass produce graphene nanocomposites. Pinto et al. produced PLA films with graphene additives between 0.2% to 1% by weight using the solvent casting method. While they saw the maximum properties in composites containing 4% graphene, it was emphasized that the graphene additive increased the glass transition temperature of pure PLA, increased the tensile strength by 15% and the Young's modulus by 85%. Istrate et al. reported significant enhancement in

mechanical properties of polyethylene terephthalate (PET)/graphene nanocomposite, synthesized by melt-blending process, at nanofiller concentration of 0.07 wt%. They also found that increase in the graphene content over 0.1 wt% deteriorated the mechanical properties of the PET polymer.

Furthermore, computational techniques using the concept of representative volume elements (RVE) provide powerful tools for modeling the properties of composites (Li, Wang, & Wang, 2019). Among these techniques, molecular dynamic (MD) simulations are effective computational methods to investigate the physical behavior of composites and provide details of interactions between the molecules and nanoadditives in an atomic scale (Li, Wang, & Wang, 2019), (Sharma, Chandra, Kumar, & Kumar, 2015). Through the development of forcefield computations, large molecular systems have been studied to predict the macroscopic properties of polymers. In a recent study, Seyedzavvar et al. investigated the thermo-mechanical properties of polybutylene terephthalate (PBT)/CaCO₃ nanocomposite parts using molecular dynamics simulations. In order to verify the accuracy of MD simulations in the forecasting of thermo-mechanical properties of parts, they produced PBT/CaCO₃ parts with an injection molding process and applied uniaxial tensile tests, thermal conductivity, DSC, and x-ray diffraction microscopy examinations to the parts. It was observed that the nanoparticle addition has resulted in better thermomechanical properties on the parts due to the good dispersion of nanoparticles in the polymer matrix. They revealed that the addition of 5 wt% CaCO₃ resulted in an enhancement of the thermal conductivity of the nanocomposites by up to 38%. Also, they showed that the length of the polymer chain in MD simulations does not affect the binding energy between molecules and the mechanical properties of nanocomposites. Sharma et al. simulated the mechanical properties of polycarbonate/MWCNT composite using force modulus in material studio software. Wei et al. used molecular dynamics simulation technique combined with experimental methods to establish the relationship between the microstructure and mechanical properties of PLA polymer filled with different fractions of o-carboxymethyl chitosan (CMC) particles in the matrix. The results proved the consistency between the simulation and the experimental results, showing that the CMC additives reduced the fractional free volume and molecular chain mobility and increased the density of the samples. Dikshit et al. used molecular dynamic approach to investigate the mechanical properties of graphene reinforced epoxy nanocomposite. It was seen that graphene reinforced epoxy composite was 8 times stiffer than

pure epoxy matrix. Pashmforoush et al. predicted the physical properties of polystyrene (PS)/CaCO₃ nanocomposites with a maximum error of 14.7% as compared with experimental data. Sharma et al. used molecular dynamics approach to study the effects of functionalized CNTs on the physical properties of Cu₆₄Zr₃₆ metal glass.

Fused deposition of thermoplastic polymers in the form of filaments, is a 3D printing technique to freeform continuous filaments thermoplastic material based on CAD models of desired configurations (Hamzah, Shafiee, Abdalla, & Patel, 2018). Boğa et al. produced continuous PLA filaments through an extrusion method and utilized filaments in the FDM 3D printing process with different internal architectures in 70% filling ratio. The authors revealed that the parts printed at triangular internal architecture has resulted in highest mechanical properties, while the parts printed at hexagonal internal architecture showed the lowest. Sang et al. synthesized composite filaments of polylactic acid and polycaprolactone polymers and basalt fiber (PLA-PCL/KBF) at different ratios of PLC in the matrix. They employed such filaments to produce samples for mechanical, thermo-dynamic and rheology analyses using FDM 3D printing technique. The authors ascribed the superior energy absorption capacity of the circular honeycomb structures of PLA-PCL30/KBF filament under in-plane compressive forces to the ductility of the matrix and strong interfacial adhesion between the matrix and the basalt fibers. Pentek et al. have produced PLA and ABS based carbonfiber upper limb prosthesis composites (PLA/ESD and ABS/ESD) to reveal its improved mechanical and electrical properties. Batakliiev et al. investigated the effect of the simultaneous and separate addition of graphene nanoplatelets (GNPs) and multiwall carbon nanotubes (MWCNTs) nanofillers to pure PLA on the mechanical properties. They produced pure PLA, PLA/GNP, PLA/MWCNT and PLA/GNP/MWCNT with FDM 3D printing, performed mechanical tests and examined their morphological properties. The authors emphasized that 1.5 wt% GNP and 4.5 wt% MWCNT/PLA materials had the best mechanical properties. In addition, nanoparticles are homogeneously dispersed in the PLA matrix. Hohimer et al. synthesized multiwall carbon nanotubes (MWCNT) reinforced thermoplastic polyurethane filaments with melt-blending technique and employed such filaments to produce tensile and flexural test samples using FDM technique. Ivanov et al. proved that graphene nanoplatelets and MWCNT reinforced 3D printed PLAs have significant improvements in their thermal and electrical properties in addition to mechanical properties. Zeybek et al. produced PLA/POSS reinforced with 1 wt% and 3 wt% POSS by 3D printing and compression molding method in order to create an alternative to biomedical materials and examined the mechanical, thermal

and morphological properties of the materials. As a result of the experiments, the authors emphasized that the mechanical and fracture properties of 3D printed parts are always more advanced than compression molded parts. According to DSC and TGA analysis, it was revealed that there is no significant difference between the thermal properties of the 3D printed and compression molded parts.

Wang et al. described different 3D printing techniques based on the idea that 3D printing offers many advantages such as high precision, cost-effectiveness, and customized geometry in composite material production. The authors provided an overview of the properties and performance of 3D printed parts and introduced common 3D printing techniques of polymer composite materials. Weng et al. synthesized ABS nanocomposite filaments at different mixing ratios of organic modified montmorillonite (OMMT) nanoparticles by melt-blending technique using single screw extruder and applied the FDM method to produce mechanical test samples of such filaments. The authors conducted tensile, flexural, and thermo-dynamic mechanical tests to investigate the effects of nanoparticles on the thermo-mechanical properties of nanocomposite ABS. They reported that the addition of 5% OMMT improved the tensile strength of 3D printed ABS samples by 43% while the tensile strength of injection molding ABS samples was improved by 28.9%. They found that the addition of OMMT considerably increased the tensile modulus, flexural strength, flexural modulus, and storage modulus of the ABS/OMMT nanocomposite 3D printed samples. Ning et al. synthesized samples by FDM technique using ABS filaments containing different fractions of carbon fiber strands in the matrix. They conducted experiments to investigate the effects of length and fraction of CF fillers in the matrix on the tensile and flexural properties of the synthesized composite samples. The authors reported the maximum tensile strength and Young's modulus were observed at 5 and 7.5wt% concentrations of CR strands in the ABS matrix, respectively. Also, the CFRP composite with 5wt% carbon fiber content had greater flexural properties. The authors studied the effects of the air gap, raster orientation, and nanoparticle concentration in the PE matrix on the mechanical properties of the samples. They reported that with increasing the concentration of MWCNTs in the PE matrix, the ultimate tensile strength decreased by as much as 47% at nanoparticle concentration of 2wt%, while the modulus of elasticity increased by 54% as compared with those of pure PE.

In order to investigate the mixed-mode fracture behavior of the materials, different fixtures have been introduced in a number of studies to apply mixed-mode loading on samples of

specific configurations and crack lengths (Wang, Wang, Zhang, & Li, 2020). In a recent study, Boğa investigated mixed mode behavior of Arcan fracture ABS/CF parts produced with FDM 3D printing process in different internal architectures. It was revealed that addition of CF increased the brittleness of ABS parts, while the addition of 15wt% of CF increases the K_{IC} of hexagonal parts by about 64%. Seyedzavvar et al. showed that the addition of CaCO_3 nanoparticles increases the mechanical and fracture properties of FDM 3D printed ABS parts and linear internal architecture resulted in the highest fracture toughness while the parts printed at triangular internal architecture showed the highest mechanical properties. Li et al. produced 3D printed ABS test specimens in different structures and printing directions to investigate the fracture behavior using the extended finite element and experimental methods. They optimized the topological patterns to enhance the fracture toughness and strength of the samples. Boğa et al. studied the effects of the internal architecture on the fracture properties of FDM 3D printed PLA parts under Mode-I, Mode-I/II and Mode-II loadings. To this aim, they fabricated PLA Arcan fracture samples using FDM 3D printing technique using four different internal architecture, called linear, triangular, hexagonal and 3D infill, in 70% filling ratio and they conducted FEM analyses to calculate the geometrical factors of parts. They revealed that the parts printed at triangular internal architecture showed high resistance to fracture in the Mode-I and mixed mode loadings, while the parts printed at hexagonal internal architecture showed highest fracture toughness in the Mode-II loading. In addition, triangular internal architecture has resulted in highest strain energy release rates in all loadings. Ahmed et al. fabricated PLA tensile test and fracture samples that contain crack-like notches with FDM 3D printing process. They revealed that as temperature increased, fracture resistance and interlayer fracture resistance of material has increased. The fracture toughness of the PLA parts produced by 3D printing has changed as the deposition angle changes, and the fracture toughness of the parts produced at 0° and 90° is higher than the parts produced at 30° and 60° . Aliheidari et al. produced double cantilever beam (DCB) ABS parts with pre-crack using the FDM 3D printing method to investigate the effect of printing temperature on fracture resistance. The authors applied a Mode I fracture test to the samples and calculated the fracture energy corresponding to the beginning of the crack propagation using the J integral method. At the end of the study, they showed that as the printing. Abadi et al. performed mixed-mode fracture tests on a modified version of Arcan samples to obtain the critical failure load of dissimilar adherends of aluminum/polymer joints. Similar methods have also been used to investigate the fracture behavior of samples fabricated by FDM technique.

Moreover, to improve the mechanical performance and fracture toughness of ABS, Lanzilotti et al. have optimized the printing parameters by applying mixed mode fracture tests, tensile tests and finite element simulations. According to the findings, the authors emphasized that by optimizing the raster angle, the fracture toughness of the material increased by 30% and the maximal strength by 20%. Avcu et al. investigated the mechanical properties and mixed-mode behavior of glass-fiber reinforced polymers produced with sheet molding compound (SMC) compression molding process. The study has revealed that in the longitudinal direction of SMC plates, parts showed better mechanical properties by about 46% than in the transverse direction. Moreover, the longitudinal fracture samples showed better toughness and strain energy release rates than transverse fracture samples.

Besides studies about the mechanical and fracture behavior of 3D printed PLA and PLA nanocomposites, there are also studies investigating the surface properties, melting and crystallization behavior and thermal properties of these materials (Coppola, Cappetti, Di Maio, Scarfato, & Incarnato, 2017) (Coppola, Cappetti, Di Maio, Scarfato, & Incarnato, 2018) (Horst & de Andrade Junior, 2020) (Horst D. J., de Andrade Junior, Duvoisin, & Vieira, 2020) (Abeykoon, Sri-Amphorn, & Fernando, 2020) (Hyelim & Lee, 2020) (Chacón, Caminero, García-Plaza, & Núñez, 2017).

Abeykoon et al. argued that properties such as optimum process parameters, dimensions of materials etc. are not on a global scale in studies related to 3D printing and that printing parameters are interdependent. For this purpose, the authors produced PLA, ABS, CFR/PLA, CFR/ABS and CNT/ABS materials with different printing parameters and investigated the optimum printing properties by applying mechanical, thermal and morphological tests. According to DSC analysis, they emphasized that different printing temperatures have a small effect on the crystallization behavior of the materials and from the TGA analysis, the degradation temperatures (T_d) of the materials are consistent with the commercial data. Investigating the electrical behavior of honeycomb pure PLA, PLA/GR and PLA/CB nanocomposites, Kim et al. also tried to find the optimum printing parameters. Bhandari et al. and Park et al. explained the relationship between the variables of annealing temperature and printing parameters and the thermoelastic behavior of thermoplastic materials. Bhandari et al. found that carbon fiber additive reduced mechanical performance in intermediate layers of PETG and PLA composites by thermal and morphological analysis. They showed that the mechanical performance of the materials improved when the annealing temperature was

higher than the glass transition temperature of the polymers and lower than the cold crystallization temperature.

In the FDM 3D printing process, printing parameters are so crucial for mechanical performance and dimensional stability of the part (Srinidhi, Soundararajan, Satishkumar, & Suresh, 2021). Chacon et al. produced PLA parts with FDM 3D printing and investigated the effect of printing parameters on the mechanical and morphological properties of the material and analyzed the optimal values of these parameters. Some researches say that mechanical strength is directly proportional to the filling ratio. It is undeniable that the 100% filling ratio will increase the printing cost by increasing the raw material and production time. Srinivasan et al. emphasized that the 100% filling ratio increases the tensile strength about 15 MPa.

Based on an extensive research given above, the thermo-mechanical properties of the printed PLA samples depend on many factors, including the internal architecture and filling ratio of the material. As illustrated in the review above, the incorporation of the nanoparticles in the pristine polymer has resulted promising improvements in the thermo-mechanical properties of the polymers. In this regard, the binding energy between the polymer and the nanofillers and the uniformity of the dispersion of these particles in the matrix play important roles. Therefore, in this research the effects of calcium carbonate (CaCO_3) on the thermo-mechanical properties and fracture toughness of the PLA samples have been investigated. For this purpose, the PLA/ CaCO_3 nanocomposite filaments, containing different weight ratios (0, 0.5, and 1 wt%) of nanoparticles in the matrix, have been synthesized by melt-blending technique using twin-screw extruder system. These filaments were used to produce samples by FDM technique with different printing parameters to study the effects of nanoparticles and printing parameters on the mechanical properties and fracture behavior of the PLA nanocomposites under mode-I, mode-II and mixed-mode fracture loadings. In this regard, this study investigates the effects and significance of these different parameters, which are called printing speed (PS), weight fractions of nanoparticle addition (NA), layer thickness (LT), filling ratio (FR) , and internal architecture (IA), on the fracture characteristics and mechanical behavior of FDM 3D printed PLA and PLA/ CaCO_3 nanocomposites. To this end, the analysis of the Taguchi design has been conducted based on the experimental results to determine the optimized levels of factors by which the maximum level of material properties could be obtained. Thus, it has been determined which combination can be used in further FDM 3D printing of PLA-based materials, or which factor level will be appropriate. A

response surface methodology (RSM) was employed to model and predict the mechanical and mixed-mode fracture properties of the PLA-based nanocomposites produced in different weight ratios and different FDM printing parameters. The produced samples were subjected to uniaxial tensile tests for mechanical characterization. Mixed-mode fracture behavior of the synthesized samples were studied by applying mixed-mode loadings on the pre-cracked samples using an in-lab developed fixture mounted on the uniaxial tensile test machine. Finite element simulations are employed to simulate the crack opening on such specimens and calculate the geometry shape functions of the fracture samples at different loading angles. Finally, after the experimental procedures, scanning electron microscopy (SEM) examinations have been conducted on the fractured surfaces of the test samples to reveal the fracture morphology of parts and validate the presence of nanoparticles. In addition, differential scanning calorimetry (DSC) analyses are conducted to determine the variations in the glass transition and heat capacity of the PLA polymer by the incorporation of CaCO_3 nanoparticles in the PLA matrix.

Injection molding has been used to produce uniaxial tensile test parts as well as the FDM method for the reason that the injection molded parts are suitable to compare with MD simulations. Since the nature of the FDM process, parts naturally have many gaps or porosity. But MD simulates the parts with no gaps, and injection molded parts are more suitable for the comparison since the parts have no or fewer gaps and porosity. In brief, injection molding process have conducted to produce parts for the comparison of mechanical properties with MD simulated parts. In order investigate the mechanical properties of injection molded parts, uniaxial tests have been conducted. Molecular Dynamic (MD) simulations using Material Studio software is employed to investigate the physical behavior of injection molded PLA/ CaCO_3 nanocomposites in different weight ratios (1, 3 and 5wt%) and provide details of interactions between the molecules and nanoparticles on an atomic scale. Molecular dynamics analyses were carried out to verify the results obtained from the experimental procedures and for the reason that the molecular dynamics simulations and experimental results are consistent with each other, PLA/GR nanocomposite materials in different weight fractions were simulated to predict the mechanical properties of injection molded PLA/GR nanocomposites. It has been observed that Materials Studio software provides realistic results in estimating the mechanical properties of materials.

3. MATERIALS AND METHODS

3.1. Materials

Polylactic acid ((C(CH₃)(OH)HCOOH)_n) granules, that have the melt flow index range as 5 g/10 min at 190 °C under 2.16 kg that described in ISO 1133 standards, with the density of 1.24 g/cm³ and the glass transition temperature of 65 °C were purchased from RiİZ Makine (Turkey). Moreover, calcium carbonate nanoparticles that have rhombohedral crystalline structure, are provided by XFNANO, INC. (China). According to the technical datasheet, the particle size of CaCO₃ particles ranges from 0.04 µm to 0.08 µm and specific surface area of 40 m²/g, without making any other adjustments, the nanoparticles were used to produce composite materials. Tables 3.1 and 3.2 summarize the main properties of PLA granules and CaCO₃ nanoparticles used in this study, purchased from RiİZ Makine and XFNANO, INC.

Table 3.1. The main properties of Polylactic acid (PLA) granules.

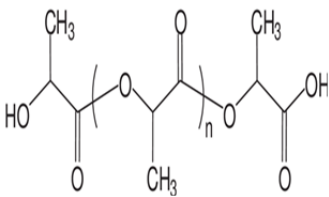
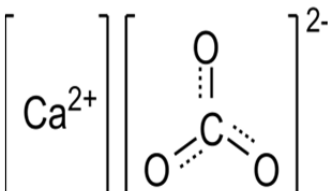
	Property	Value
	Material Type	Polylactic acid (PLA)
	Melting Point (°C)	175
	Tensile Strength (Mpa)	≥50
	Elongation at break (%)	<5
	Printout density (g/cm ³)	1.24

Table 3.2. The main properties of CaCO₃ nanoparticles.

	Property	Value
	Material Type	Calcium Carbonate (CaCO ₃)
	Appearance	Powder
	Particle size (µm)	50-100
	Bulk density (g/mL)	0.45
	Moisture (%)	0.5
	Whiteness (%)	>90
	pH	9.5-10

3.2. Production process of PLA and PLA-based nanocomposites

Figure 3.1 summarizes the production processes and processing parameters used in this study. Production of PLA and PLA-based nanocomposites comprises two different methods, called the extrusion method and the injection molding process, where PLA has chosen as a matrix material and CaCO_3 has used for nanoparticle reinforcement into the matrix. The first method, called the extrusion process, started with the production of polymer filaments and then the filaments were utilized in the FDM 3D printing method for the fabrication of uniaxial tensile test and Arcan fracture test samples. The samples have been produced with different weight ratios of CaCO_3 nanoparticles (0, 0.5, and 1 wt%) and different FDM 3D printing parameters, which are called printing speed, layer thickness, filling ratio, and internal architecture, respectively. The second method, an injection molding process, is utilized for the production of PLA and PLA/ CaCO_3 nanocomposite uniaxial tensile test samples in different weight ratios of CaCO_3 nanoparticles (0, 1, 3, and 5wt%).

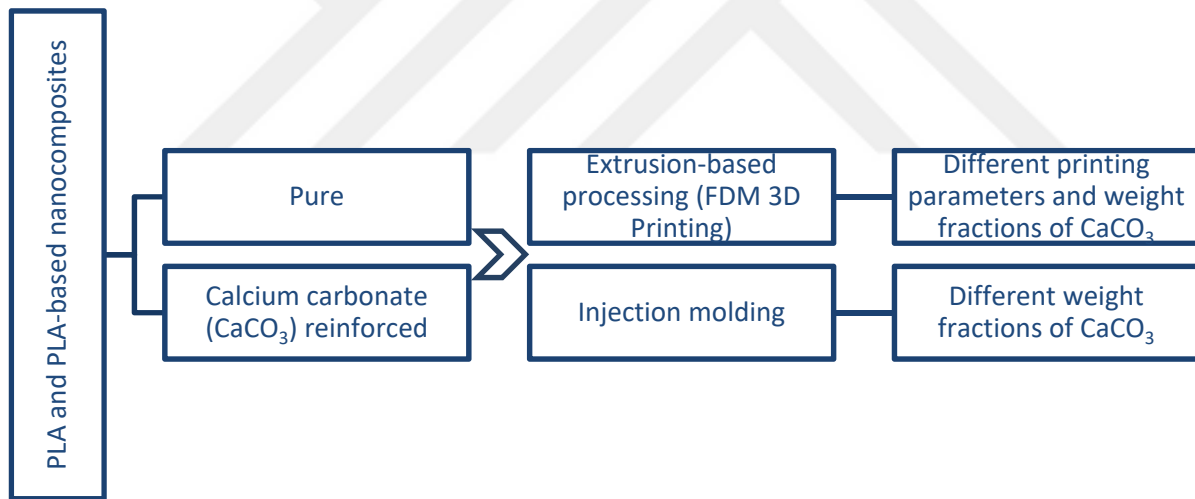


Figure 3.1. Process chart of this study.

3.2.1. Extrusion process of PLA and PLA-based nanocomposites

3.2.1.1. Production of pure and calcium carbonate reinforced polylactic acid filaments

Extrusion is a polymer manufacturing method in which powdered or granular thermoplastic materials are transformed into a continuous homogeneous melt and then forced through a die to generate objects with uniform cross-sectional areas. In a basic way, an extrusion process

starts with the granules being placed into a hopper, which feeds the polymer to the die. The electric heaters mounted in the hopper provide melting of the feed material. The moving component of the extruder is the screw that is housed inside the hopper, which is designed to collect, mix, compress, and convey the polymer as it transforms from solid particles to a viscous melt from the hopper to the die. A motor driving a gear reducer powers the screw's rotation within the hopper (Dorgan, Lehermier, Palade, & Cicero, 2001).

Figures 3.2 and 3.3 show the schematic representation of the creation of PLA/CaCO₃ nanocomposite filaments with various weight percentages of nanoparticles and the filament extrusion system used in this study. In order to evaporate the moisture, the PLA granules and CaCO₃ nanoparticles were heated in a Thermomac vacuum oven at 60 °C for 10 hours. A twin-screw extruder was used to combine the granules and nanoparticles with weight fractions of 0.5 and 1 wt%, and the resulting masterbatch granules were then pelletized. Specifications of the extruder are equipped as a 22 mm screw, a 44 mm L/D ratio, and a 40 rpm screw speed. The temperatures of the four heaters from the feeder to the die were set at 185, 190, 190, and 170 °C, respectively. In order to produce PLA/CaCO₃ nanocomposite filaments with a diameter of 1.75 mm, the pelletized masterbatch was later combined with pure PLA granules in the ratios that satisfied the final compositions of 0.5 and 1 wt% of CaCO₃ nanoparticles in the matrix. These filaments were then extruded using a single screw extruder designed and built with water cooling, an automatic winder, and a 1.85 die. The single-screw extruder's characteristics matched those of the double-screw extruder's specifications exactly.

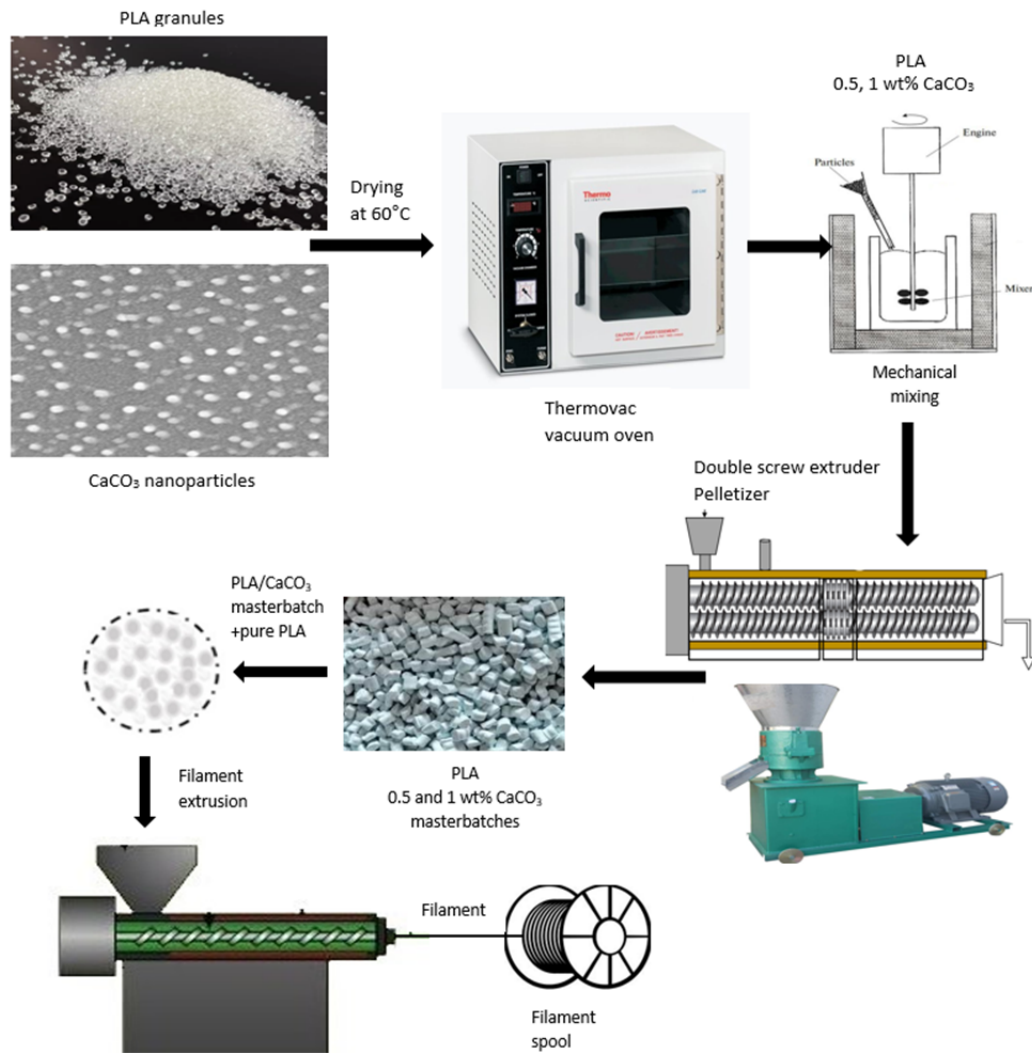


Figure 3.2. Schematic representation of PLA/CaCO₃ nanocomposite filament fabrication with extrusion process.

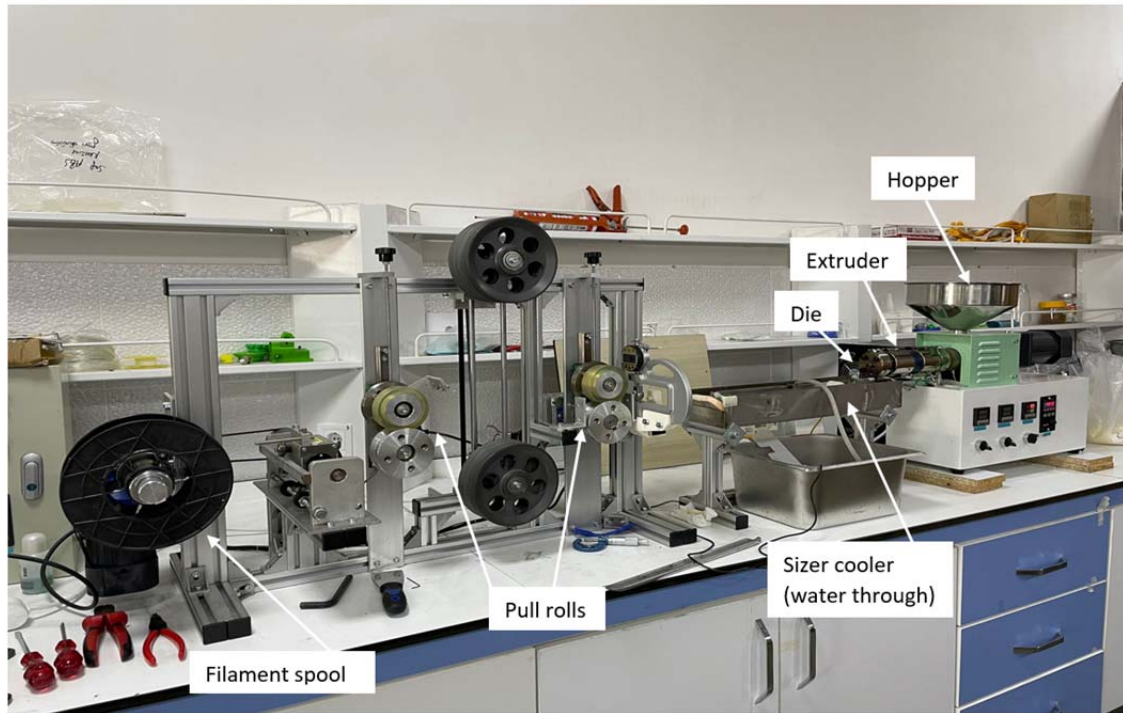


Figure 3.3. Representation and major parts of the extruder.

3.2.1.2. Fused deposition modeling of specimens

The FDM technique of tensile and Arcan fracture test samples was conducted on a Flashforge Creator 3 dual extruder 3D printer, which is represented in Figure 3.4, equipped with a 0.4 mm diameter extrusion nozzle and a printing bed dimension of 300 x 250 mm. The process parameters of the FDM technique are represented in Table 3.3. In order to better understand the internal architecture and printing orientation of specimens, printed patterns in a 10% filling ratio are shown in Figure 3.5. According to the figure, the distribution of fused layers is about equiaxed in the deposition plane for all of the printing patterns, confirming the notion that they are orthogonally isotropic. For this reason, the tensile test samples and the fracture test samples were printed in the same orientation as Figure 3.6.

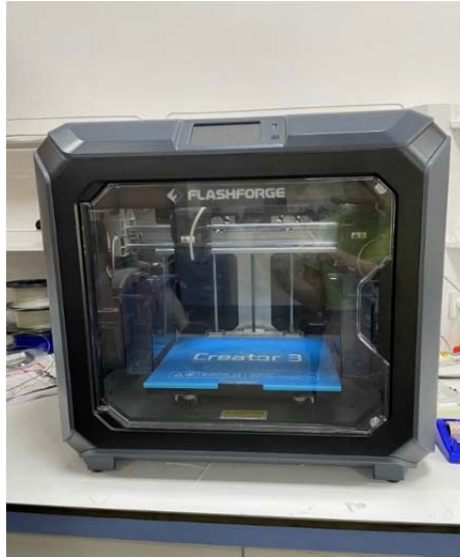


Figure 3.4. Flashforge Creator 3 FDM printer.

Table 3.3. Process parameters of FDM method to production of specimens used in this study.

Printing Parameters	Values
Nozzle temperature (°C)	230
Table temperature (°C)	90
Printing speed (mm/s)	20; 40; 60
Layer thickness (mm)	0.09; 0.12; 0.15
Filling ratio (%)	50; 75; 100
Weight ratio of CaCO ₃ nanoparticles (wt%)	0; 0.5; 1
Filament feed rate (mm/s)	1.25
Internal architecture	Linear, Triangular, Hexagonal
Filament diameter (mm)	1.75
Nozzle diameter (mm)	0.4

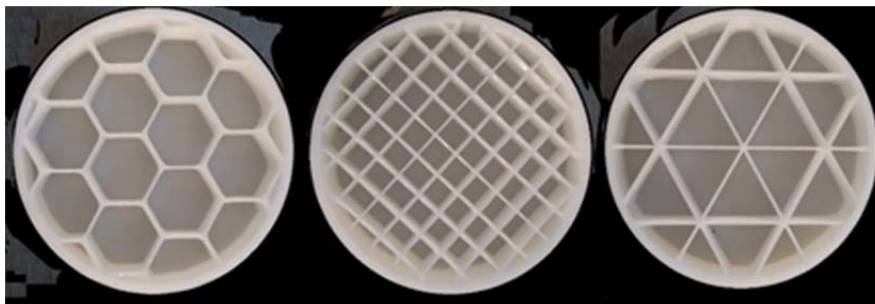


Figure 3.5. Representation of internal architectures printed at 10% filling ratio.

To investigate the effects of different layer thicknesses and printing orientations, the dumbbell-shaped tensile specimens have been designed and tested based on the guidelines of ASTM D638-14 (ASTM, 2014). A special fixture was developed in order to carry out mixed-mode fracture tests on single edge-notched Arcan fracture test specimens built in different layer thicknesses. The characteristic dimensions B and W were 20 mm and 32 mm, respectively. The notch of the Arcan fracture specimen, having a total length of 10 mm, was designed to form during the FDM process. The uniaxial and fracture test specimens were designed using Autodesk Inventor 2019, and the .stl files were then imported to the FlashPrint slicing program, and the parts were placed in the building chamber, then the created G-code was imported to the FlashForge Creator 3 3D printer to start the printing process. The schematic representation of the in-house developed Arcan fixture and the samples of uniaxial tensile and mixed-mode fracture tests are shown in Figure 3.7.

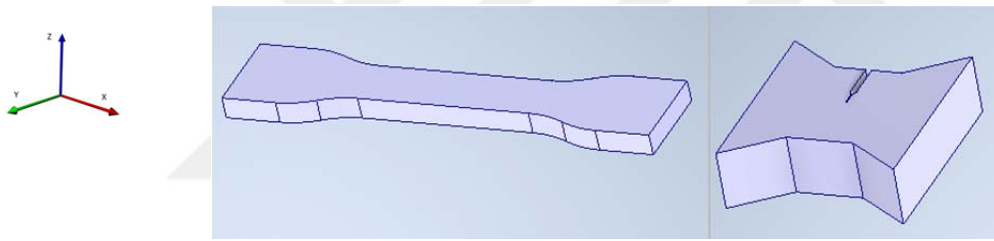


Figure 3.6. 3D CAD views of specimens isometrically.

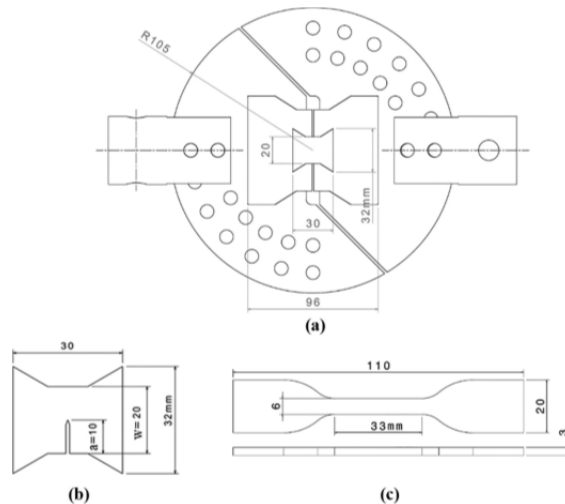


Figure 3.7. a) Schematic representation of in-house developed Arcan fixture, b) test specimen with small size (specimen thickness $t = 10$ mm) and c) dimensions of tensile specimen. (Boğa C. , 2021)

3.2.2. Injection molding of pure and calcium carbonate reinforced polylactic acid specimens

Uniaxial tensile test samples to be used in MD simulation comparisons have been produced with the injection molding process. The production of the PLA/CaCO₃ masterbatch process is the same as the production explained in section 3.2.1. The masterbatches that were produced in the filament production process were re-extruded while adding extra PLA granules and nanoparticles to obtain nanocomposites containing 1, 3 and 5wt% CaCO₃ nanoparticles in the matrix. In order to produce uniaxial tensile test specimens, the extruded pellets were injection molded using a horizontal injection molding machine, with nozzle and mold temperatures of 190 and 60 °C, respectively.

3.3. Characterization of PLA and PLA-based nanocomposites

In order to investigate the effects of the nanoparticles in different weight ratios and printing parameters on the characteristic properties of PLA parts, several mechanical, thermal, fracture, morphological, and rheological analyses were conducted on the test samples. Scanning electron microscopy (SEM) examinations have been conducted on the fractured surfaces of the test samples to reveal the fracture morphology of parts and validate the presence of nanoparticles. In addition, differential scanning calorimetry (DSC) analyses have been utilized to determine the variations in the glass transition and crystallization properties of the PLA polymer by the incorporation of nanoparticles into the matrix. Furthermore, molecular dynamic (MD) simulations using Materials Studio software have been employed to investigate the physical behavior of the PLA/CaCO₃ and PLA/GR nanocomposites and provide details of interactions between the molecules and nano additives on an atomic scale.

3.3.1. Uniaxial tensile tests for the mechanical characterization

In materials science, the determination of the force that must be applied to cause a specific deformation in a material or the deformation that will occur when the material is subjected to a particular force consists of important steps. The circumstances in which the material can be shaped or used depending on the relationship between strain and the force that creates strain. The tensile test is the simplest way to examine the relationship between force and strain. It is based on the principle of subjecting a specimen designed to specific standards to uniaxial

tensile forces until it breaks. Mechanical properties such as elastic and plastic behavior of the material under static loads can be determined with tensile tests. The strength of the material is one of the important parameters in industrial designs, and the strength values of samples according to certain standards are determined in tensile tests. These obtained values determine the mechanical properties of the materials (Eren, 2017).

The maximum tensile strength and elongation at break values of the part can be determined by tensile tests. In addition, the characteristic properties of the material, such as modulus of elasticity (E), Poisson's ratio (ν), and yield strength, can be determined. With the tensile test, the maximum stress value that the material can cause or withstand plastic deformation can be determined. These values are one of the issues (in the form of safety factors) that should be considered in engineering design. In addition, the ductility of the material can be determined by the tensile test. Ductility is a measure of how much the material can deform before breaking, and it is rarely included directly in the design, but rather in material properties to ensure quality and toughness. Low ductility in the tensile test indicates low resistance to fracture.

In the present study, uniaxial tensile tests have been conducted to investigate the effects of printing parameters and nanoparticles on the mechanical properties of pure and reinforced PLA parts. To this end, the dumbbell-shaped tensile test specimens were designed and built by following ASTM D638-14 standards. All tests were carried out at room temperature using a Shimadzu AGS-X tensile testing machine with a 100 kN load cell for displacement and force measurement, running at a constant cross head speed of 1 mm/min, respectively. Figure 3.8 represents the tensile test machine used in this study. The elongation in the axial direction and contraction in the transverse direction were recorded using a digital camera extensometer. A schematic drawing of a dumbbell-shaped specimen in ASTM D638-14 standards is given in Figure 3.9 (ASTM, 2014). Given the aforementioned standard, the dumbbell-shaped specimens were produced with the dimensions indicated in Table 3.4.



Figure 3.8. Tensile test setup.

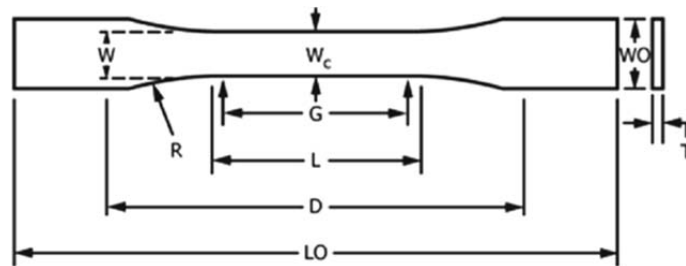


Figure 3.9. Schematic drawing of dumbbell shaped specimen in ASTM D638-14 standards.
(ASTM, 2014)

Table 3.4. Dimensions of fabricated tensile test specimens.

Overall Length (mm)	LO	110
Gage width	W_c	6
Gage length (mm)	G	33
Radius of fillet (mm)	R	15
Width of narrow section (mm)	W	6
Width overall (mm)	WO	20
Thickness (mm)	T	3

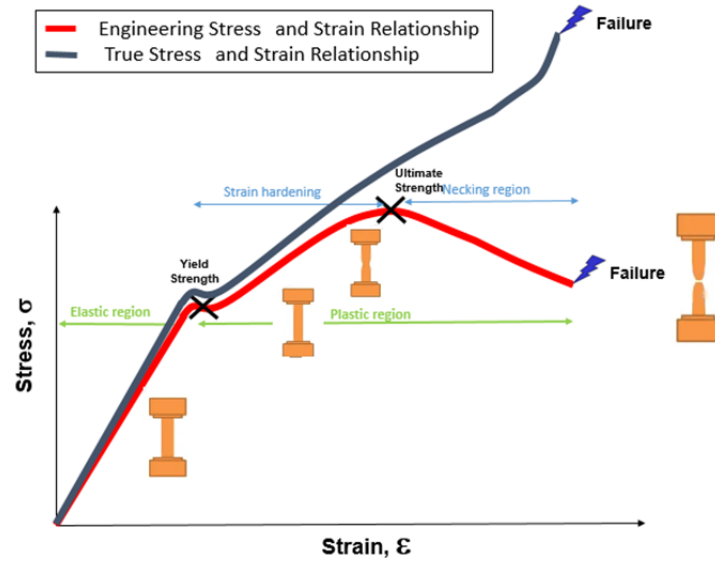


Figure 3.10. Engineering stress/strain and true stress/strain diagrams. (Çapar, 2022)

In order to determine the material properties, the stress-strain curve is plotted by recording the stress discrepancy with strain while elongating the specimen until the material fractures. It is frequently claimed that, during the whole deformation process, the cross-sectional area of the material remains the same. This is incorrect since elastic and plastic deformation causes the region to shrink while deforming. The actual stress-strain curve is different from the engineering stress-strain curve in that it is based on the instantaneous cross-section area and length. The engineering stress-strain curve is based on the original cross-section and gauge length. The tensile force is measured as a function of the increment in the gauge length. Figure 3.10 shows the engineering and true stress-strain diagrams. Engineering stress, or nominal stress given in Eq. (1), is defined by the applied load divided by the original cross-sectional area of the material.

$$\sigma = \frac{F}{A_0} \quad (1)$$

where σ is the stress, F is the tensile force and A_0 is the original cross-sectional area of the material. Furthermore, engineering strain given in Eq. (2), is defined by;

$$\varepsilon = \frac{\Delta L}{L_0} \quad (2)$$

where ε is the strain, L_0 is the initial length of gage section and ΔL represents the change of the length in gage section ($\Delta L = L - L_0$).

The width and thickness values of the specimens were measured using a digital caliper before performing the uniaxial tensile test, the stress calculation is based on the actual cross-sectional area of each specimen. One end of the test specimen was clamped in the fixed-grip of the lower jaw, while the other end was clamped in the upper jaw, undergoing controlled displacement. After the tensile testing procedure of the machine was determined according to the material type of the specimen, the specimen began to stretch upwards at the determined tensile speed rate. From the obtained data after the tests have been performed, the Young's modulus and yield strength values of each sample were determined as the slope of the elastic region and the intersection of a 0.2% strain offset of this slope with the stress-strain curve, respectively. The Poisson's ratios of the samples were also calculated according to Eq. (3) using the data obtained by the digital extensometer. Each experiment was performed five times, and stress-strain plots for the parts were obtained using the average force-elongation values generated by the testing machine to assess the modulus of elasticity, yield stress, and Poisson's ratio. Figure 3.11 shows the experiments on the uniaxial tensile test machine. Figure 3.11 (a) represents the tensile test sample mounted between the two jaws of the machine; and (b) represents the tensile test sample after the experiment. All of the results, graphs and comparisons were reported in the "results and discussion" chapter.

$$\nu = -\frac{\varepsilon_t}{\varepsilon_l} \quad (3)$$

where ν is the Poisson's ratio, ε_t is the transverse strain (mm/mm) and ε_l is the longitudinal strain (mm/mm).

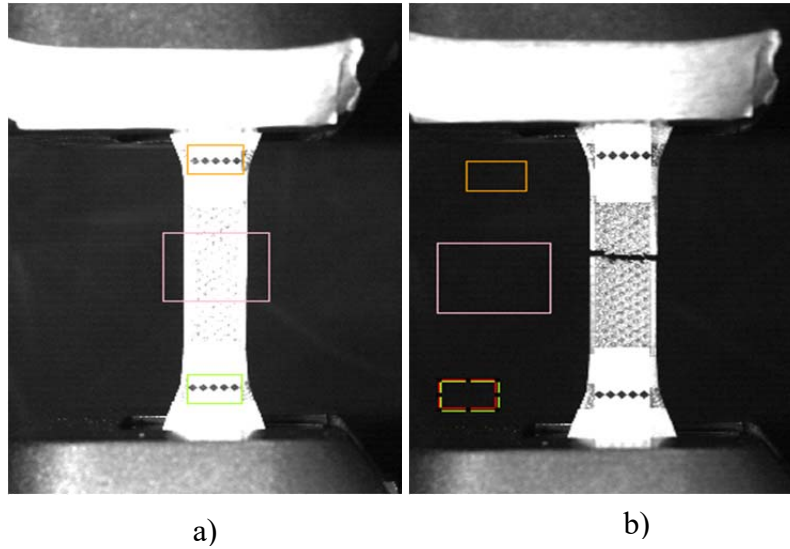


Figure 3.11. Performing experiments on uniaxial tensile test machine; a) tensile test sample mounted between the two jaws of the machine, b) tensile test sample after the experiment.

3.3.2. Mode-I, Mode-II and mixed mode fracture tests for the fracture characterization

Experimental data obtained by mixed-mode testing of PLA/CaCO₃ nanocomposites and evaluation of the properties of the related polymer and reinforcement are used to support the criterion. Fracture damage may occur as a result of the slow or sudden impact of the loads applied to the material. In order for materials to be used as structural elements, it is necessary to know the fracture behavior of materials under varying conditions such as different crack parameters and different loadings (Kaya, Balcioğlu, & Gün, 2021). Fracture mechanics was first introduced by aeronautical engineer A. A. Griffith, who studied the fracture behavior of brittle materials during World War I. The main subject of fracture mechanics is to determine the conditions under which a crack in a structural element will start to spread and cause fracture damage (David, 1986).

The crack propagation in materials according to the loading type is classified into three different categories. These are expressed as Mode-I (opening mode), Mode-II (sliding shear mode), and Mode-III (tearing mode). Mode I, which is caused by normal stresses, is the major crack propagation mode that causes the most damage. In this crack mode, the displacements of the crack surfaces are perpendicular to the crack plane. In the Mode-II, the displacement of the crack surfaces occurs in the plane of the crack and is perpendicular to the leading edge of

the crack. In the Mode III, caused by out-of-plane shear stresses, the crack surface displacements occur in the plane of the crack and parallel to the leading edge of the crack (David, 1986). The objective of linear elastic fracture mechanics (LEFM) is to predict the critical loads that will cause crack growth in a material, and the crack propagation can be calculated in two ways in LEFM. These are expressed as the energy stored in the part as a result of loading has exceeded a critical value (strain energy release rate approach) and the stress at the crack tip has reached a critical value (stress intensity factor approach) (Yayla, 2019).

3.3.2.1. Griffith criterion for brittle materials/Linear elastic fracture mechanics (Strain energy release approach)

Energy is one of the parameters that expressing fracture in the linear elastic fracture mechanics. Griffith's Criterion represents an infinite cracked plate with fixed two ends under a stress σ . Figure 3. 12 (a) represents the Griffith's criterion of the plate has a unit thickness of a , and a central transverse crack of length $2a$.

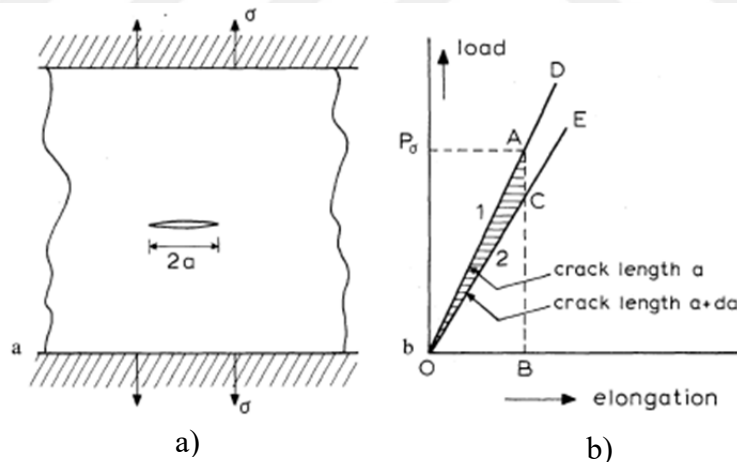


Figure 3.12. Griffith's criterion of a) fixed infinite cracked plate and b) load-displacement diagram. (David, 1986)

The area OAB in the load-displacement graph gives the elastic energy contained in the plate. Since the ends of the fixed plate are exposed to stress, when the crack extends to the length of the “ da ”, both the stiffness of the plate will decrease and some energy will be released from the plate. This means that the elastic energy stored in the plate will decrease, and as can be seen in the graph, the elastic energy will be limited to the OCB area when the crack length is

" $a+da$ ". In other words, as the crack length increases, the amount of elastic energy stored in the plate decreases, and when the crack length is " $a+da$ ", an amount of elastic energy release occurs in the plate equal to the OAC area. If the crack length increases as da when the plate is subjected to a higher stress, the energy released from the plate will be greater. Griffith's failure criterion summarizes the situation. If the energy released as the crack grows provides the energy required for the crack to grow, crack propagation occurs. If the crack propagation does not occur, the plate must be subjected to a higher stress. The energy field that will increase as the crack grows is shown by the ODE lines (David, 1986). The crack growth condition of fixed plate is:

$$\frac{dU}{da} = \frac{dU_d}{da} \quad (4)$$

where the U is the elastic energy and U_d is the energy required for crack growth. dU/da is calculated according to stress field calculations for per unit thickness as:

$$\frac{dU}{da} = \frac{2\pi\sigma^2 a}{E} \quad (5)$$

then,

$$G = \frac{\pi\sigma^2 a}{E} \quad (6)$$

where G is the energy release rate per crack tip or the crack propagation rate, the energy consumed in crack propagation dU_d/da is called crack resistance R and it is a constant value because it assumed that the energy required to create crack is the same for each increment in da . A representation of a cracked plate is shown in Figure 3.13.

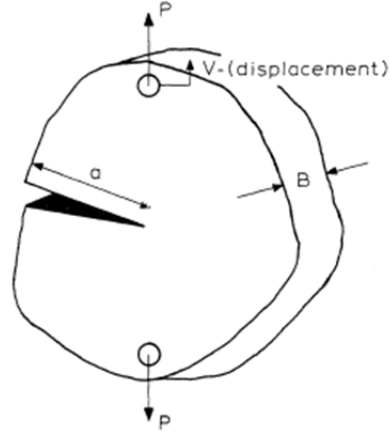


Figure 3.13. Cracked plate. (Anderson, 2017)

The given information above explains the crack propagation of a plate for fixed ends. External loads do not work since the ends of the plate are fixed, but in the opposite situation, if the ends of the plate are free during crack elongation, the work is done by external loads. In this case, the elastic energy content of the plate increases (Yayla, 2019). The total energy balance of the cracked plate under the force P is:

$$U_e = U_s + U_k + U_d \quad (7)$$

where U_e is the work done by external forces, U_s is the elastic energy generated in the system as a result of the external forces to the system, U_k is the kinetic energy of the system, in static or quasi static state, this value can be 0. Energy balance in case of crack propagation in unit width of the plate is:

$$\frac{d}{da}(U_e - U_s) = \frac{dU_d}{da} \quad (8)$$

$$G = R \quad (9)$$

Eq. (8) specifies the amount of energy expended for a unit width plate. When the plate of width B is subjected to the force P, the point where the force is applied is displaced by the length v. In other words, when the crack extends to “da”, the application point of the force changes as much as “dv”. In this case, the work done by external forces is $du=Pdv$, then the Eq. (4) is arranged for a width B plate:

$$G = \frac{d}{da} (U_e - U_s) = \frac{1}{B} \left(P \frac{dv}{da} - \frac{dU_s}{da} \right) \quad (10)$$

Unless there is crack propagation in a system under the force F, the v elongation is directly proportional to the applied force. This situation is called compliance of the plate and expressed as follows:

$$\text{elongation } (v) = \text{compliance}(C) \times \text{force } (P) \quad (11)$$

In this case, the strain energy of the elastic plate is:

$$U_s = \frac{CP^2}{2} \quad (12)$$

Thus, from Eqs. (10) and (11);

$$G = \frac{P^2}{2B} \frac{dC}{da} \quad (13)$$

In plane stress conditions,

$$\frac{dU_d}{da} = G = \frac{\pi a \sigma^2}{E} \quad (14)$$

In plane strain conditions,

$$\frac{dU_d}{da} = G = (1 - \nu^2) \frac{\pi a \sigma^2}{E} \quad (15)$$

The critical energy release rate (G_C) can be calculated with the compliance values obtained depending on the crack length. Compliance value points create a curve and this curve expresses the change in the compliance of the plate depending on the crack length, the slope of this curve gives the G_C and it also gives the slope of the force-strain curve. According to Eq. (8), for the crack propagation to start, the G value must be equal to or greater than the R . In other words, for the crack propagation, the G value must reach the critical strain energy release rate in other words, fracture toughness (G_{IC}).

$$G_{ic} = \frac{\pi \sigma_c^2 \alpha}{E} \quad (16)$$

If $G \geq G_{ic}$, crack propagation occurs.

The Griffith criterion was developed for brittle materials, and in the following years, Irwin revealed a modified energy approach for ductile materials based on the Griffith criterion. According to Irwin's approach, in ductile materials such as metals, plastic deformation occurs

at the crack tip, and this plastic region is formed by crack propagation. That is, the energy required for the formation of the plastic region is also the energy required for crack propagation. The R value can be said to be the plastic energy value for ductile materials because the surface energy is negligible. In brief, the strain energy release rate (G) is expressed as the decrease in total potential energy per increase in fracture surface area of a material (Kaya, Balcıoğlu, & Gün, 2021). When this value reaches a certain critical value, breakage occurs in the material. That is, if there is an increase in strain energy release rate, it means that the decrease in potential energy is increasing and there is an increase in the fracture surface area. The increase in the fractured surface area means that the material breaks relatively quickly. If the G value is decreasing, it means that the amount of reduction in potential energy is decreasing, which means that there is little or no increase in the fracture surface area, the fracture resistance of the material can be said to be high. The reason for the increase in the G_{IC} value as the crack length increases is that there is an increase in the fracture surface area and an increase in the decrease in potential energy.

3.3.2.2. Stress intensity factor approach

The stress intensity factor (K_I) is the state of stress at a crack tip, which is used to create the failure criteria due to fracture, and when K_I is known, the entire stress field at the crack tip is known. Stresses and strains at the crack tip can be determined using the stress intensity factor and when these stresses and strains reach a critical value, crack propagation occurs. In other words, when the stress intensity factor reaches a critical value, crack propagation occurs and this value is called fracture toughness or critical stress intensity factor (K_{IC}). Once the K constant is determined, the stresses at the crack tip can be calculated (Yayla, 2019). Stress fields at the crack tip for Mode I;

$$\sigma_{xx} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] \quad (17)$$

$$\sigma_{yy} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] \quad (18)$$

$$\tau_{xy} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \sin \frac{\theta}{2} \cos \frac{3\theta}{2} \quad (19)$$

$$\sigma_{zz} = \begin{cases} 0 & \text{for plane stress} \\ \nu(\sigma_{xx} + \sigma_{yy}) & \text{for plane strain} \end{cases} \quad (20)$$

$$\sigma_{xz} = \sigma_{yz} = 0 \quad (21)$$

For Mode-II;

$$\sigma_{xx} = -\frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \left[2 + \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \right] \quad (22)$$

$$\sigma_{yy} = \frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \quad (23)$$

$$\tau_{xy} = \frac{K_{II}}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] \quad (24)$$

$$\sigma_{zz} = \begin{cases} 0 & \text{for plane stress} \\ \nu(\sigma_{xx} + \sigma_{yy}) & \text{for plane strain} \end{cases} \quad (25)$$

$$\sigma_{xz} = \sigma_{yz} = 0 \quad (26)$$

The failure criteria according to stress intensity factor approach and the calculation of K_I and K_{IC} in plane strain condition is;

$$K_I = K_{Ic} = \sigma \sqrt{\pi \alpha} f \left(\frac{\alpha}{W} \right) \quad (27)$$

$$\begin{aligned} \text{If } K_I < K_{Ic}, & \quad \text{crack propagation not occurs} \\ \text{If } K_I \geq K_{Ic}, & \quad \text{crack propagation occurs} \end{aligned}$$

Where σ is the critical fracture stress, α is the crack length, w is the width of the specimen, and $f(a/w)$ is the geometrical factor, this factor can be calculated from FEA analysis. In order to calculate the fracture toughness with Eq. (27), it is necessary to investigate whether the material properties are suitable for the LEFM behavior and plane strain conditions. First, the load-displacement graph of the material should be examined to check whether it meets the LEFM behavior. Second, the plane-strain conditions at the crack tip must be satisfied according to ASTM standards (Katanchi, Choupani, Khalil-Allafi, Tavangar, & Baghani, 2018). If the material properties satisfy this significant conditions, the stress intensity factor also becomes the critical stress intensity factor. When these conditions are not met, the fracture toughness will be a different value from K_I and calculated from the crack tip opening displacement and J integral. These ASTM requirements are;

$$0.45 < \frac{a}{W} < 0.55 \quad (28)$$

$$B, a, W \geq 2.5 \left(\frac{K_{Ic}}{\sigma} \right) \quad (29)$$

The purpose of fracture tests is to calculate the stress intensity factor or fracture toughness which means a materials resistance to fracture. Fracture toughness is calculated with the

critical load value (P_C) obtained from the force-elongation graphs of mixed-mode fracture tests and the geometric properties of the material. If the resistance of a material against breaking is high, it means that it needs higher tension values to break. The brittle materials that break easily have relatively lower fracture toughness. On the other hand, since ductile materials have higher fracture resistance, they have higher fracture toughness (Rahmani, Choupani, & Kurtaran, 2019). The area under the stress-strain graph gives the energy required to fracture the material. In this case, brittle materials have low fracture energy compared to ductile materials (Yayla, 2019). When the loading angle is 0° , the material is forced to opening, at 45° it is forced both to opening and sliding, when it is 90° , it is forced to sliding. The reason that K_{IC} value (fracture toughness in the Mode I) decreases as the loading angle increases from 0° to 90° is that when the angle is 0 it is forced opening and is forced to sliding as the angle increases. Therefore, the fracture toughness of the material in the Mode I state will be maximum when the angle is 0° . Likewise, the reason that the K_{IIC} value (fracture toughness in the Mode II) increases as the angle increases to 90° , the material is forced to slide completely when the angle is 90° and the fracture resistance is maximum. Eqs. (30) and (31) represents the relationship between G and K in plane stress and plane strain conditions.

$$K^2 = EG \text{ (plane stress)} \quad (30)$$

$$K^2 = \frac{EG}{1 - \nu^2} \text{ (plane strain)} \quad (31)$$

3.3.2.3. Mixed-mode fracture

Systems can be subjected not only to tensile loading, but also to mixed-mode loads simultaneously, and these loads create a stress condition at the crack tip. Since cracking does not proceed on the same line in mixed mode loading, the Griffith Energy Balance Approach is not used (Yayla, 2019). In mixed mode loads, crack initiation and crack propagation are related to the stress intensity factor. The crack tip and stress area are three-dimensional and the stress varies throughout the thickness as shown in Figure 3.14.

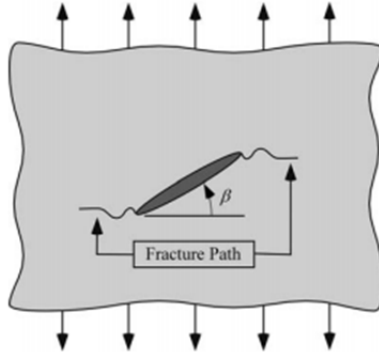


Figure 3.14. Mixed-mode loading. (Anderson, 2017)

Stress fields at the crack tip for Mode I and Mode II can be calculated from Eqs.(17) to (24).;

$$\sigma_{xx} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] - \frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \left[2 + \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \right] \quad (32)$$

$$\sigma_{yy} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] + \frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \quad (33)$$

$$\tau_{xy} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \sin \frac{\theta}{2} \cos \frac{3\theta}{2} - \frac{K_{II}}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] \quad (34)$$

The strain energy release rate for mixed mode I/II loading;

$$G_T = G_I + G_{II} = \frac{K_I^2}{E'} + \frac{K_{II}^2}{E'} \quad (35)$$

where $E'=E$ for plane stress, and $E'=E/(1-\nu^2)$ for plane strain conditions.

$$K_{IC} = K_I^2 + K_{II}^2 + \frac{E'(1+\nu)K_{III}^2}{E} (G - Criteria) \quad (36)$$

The stress intensity factors will be:

$$K_I = \sigma \sin^2 \beta \sqrt{\pi a} \quad (37)$$

$$K_{II} = \sigma \cos \beta \sin \beta \sqrt{\pi a} \quad (38)$$

3.3.2.4. Elastic-plastic fracture mechanics for ductile materials

In ductile materials, large areas subject to plastic deformation are formed around the crack, this region is called the crack tip plastic zone. The reason for the formation of crack tip plastic regions is that the stresses applied to the material exceed the yield strength of the material. Since this area is exposed to excessive deformation, the crack tip is blunt and its sharpness is reduced. The stress value in this region is not infinite and the crack tip opens up to the length δ and it is called Crack Tip Opening Displacement (CTOD). Different types of ductile materials show different reactions at the crack tip. In polymer materials, gaps are formed at the crack tip, and fibers are formed between these gaps, this region is called the craze zone (Yayla, 2019). There are two methods used to determine fracture toughness in elastic-plastic fracture mechanics. These are the CTOD and J-integral method. The J integral is one of the methods developed to calculate fracture toughness in materials with plastic deformation and deals with the strain energy density of the region at the crack tip.

$$J = \int_p w dy - T \left(\frac{du}{dx} \right) ds \quad (39)$$

where the p is an arbitrary counterclockwise path, w is the strain energy density, T is the tensile vector along p in the direction of the normal n , u is the displacement vector and ds is the length increment along the contour p . An arbitrary contour around the tip of a crack is represented in Figure 3.15.

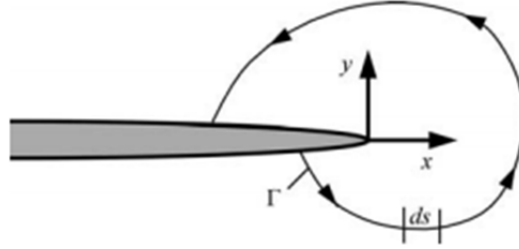


Figure 3.15. An arbitrary contour around the tip of a crack. (Anderson, 2017)

J is an energy absorption value and Rice has proven that the strain energy release rate (G) used in LEFM is equal to the integral of J in nonlinear elastic materials (Anderson, 2017). The potential energy difference between the first and last length of the crack is:

$$J = \frac{1}{B} \frac{dU}{da} \quad (40)$$

where B is the width of the material and U is the strain energy or the work done. In order to obtain better results from compact tension or three point bending tests, the following criteria should be applied;

$$B \geq 25J_{IC}/\sigma_Y \quad (41)$$

Based on the experiment results, J is calculated as follows:

$$J = \frac{U}{B(w - a)} \quad (42)$$

where U is the total energy below the force-displacement diagram, w and B are the width and thickness of the specimen, a is the crack length. Figure 3.16 shows an overview of fracture samples mounted fixture under different loadings.

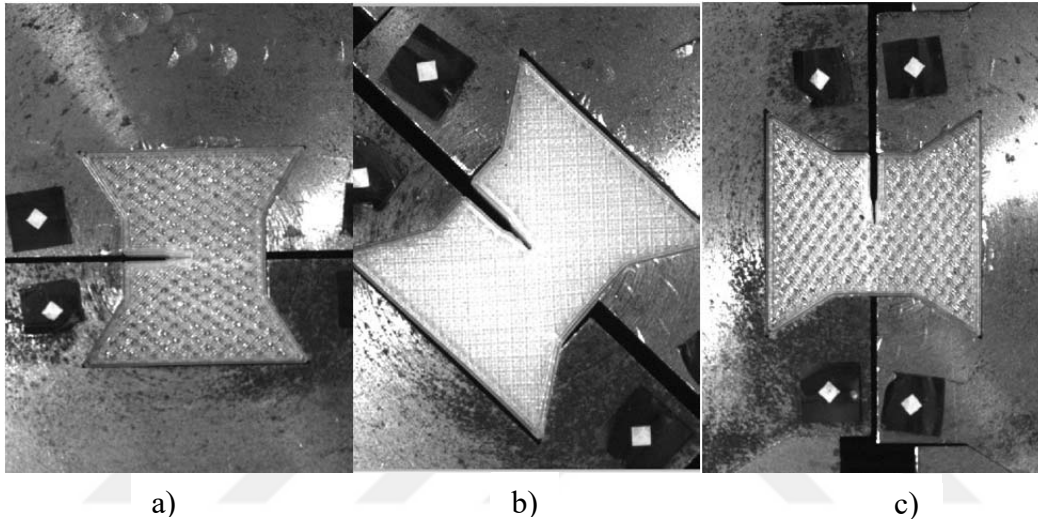


Figure 3.16. Overview of fixture and Arcan fracture of PLA nanocomposite specimens under different loading angles; a) mode-I (0°), b) I/II mixed-mode (45°), and c) mode-II (90°).

3.3.3. Finite element model (FEM) simulations

In order to calculate the geometry correction factors of the Arcan fracture samples under various mixed-mode loading angles, Finite Element Model (FEM) simulations were performed. The stress intensity factor of the geometry specified in the ABAQUS environment was calculated using the maximum tangential stress criteria. Figure 3.18 displays the results of the simulation of the maximum principal strain distribution around the crack tip for a typical Mode I loading of 3000 N together with the mixed-mode fracture loading fixture fitted with samples. In order to characterize the mechanical characteristics of the FDM 3D printed samples, the mechanical properties of stainless steel were first computed for the two formers. All samples had an initial crack length to width ratio of $a/w = 0.5$, and the entire specimen

was modeled using CPS8R elements, which are 8-node biquadrilateral plane-stress quadrilaterals with a single mode collapsible element at the cracked tip.

The J-integral in fracture mechanics of I/II mixed-mode loading coincides with the total energy release rate as $J=G_T=G_I+G_{II}$, where G_I and G_{II} are the energy release rates associated with the stress intensity factors in the mode-I and mode-II, respectively. Abaqus software, as a versatile finite element modeling package, was used to calculate the J-integrals of the Arcan fracture samples under different loading angles. To obtain the square root singularity at the crack tip, a ring of collapsed quadrilateral elements was defined around the crack tip as shown in Figure 3.17 (a). Accordingly, all the three nodes, a, b, and c, have the same geometric location on the crack tip. When one side of the element is collapsed, the two mid-side nodes connected to the crack tip were displaced to a quarter point of the second-order isoparametric element, creating a singularity of $1/\sqrt{r}$. The partition pattern of the entire specimen and refined elements at the crack tip and a set of rings of collapsed quadrilateral elements around the crack tip are shown in Figure 3.18.

As shown previously in Figure 3.16, the geometry of the test set-up consisted of two metal parts as the main fixture and a small Arcan sample at the center. The model in the Abaqus was also partitioned with the same geometries, with the mechanical properties of stainless steel defined for the fixture and that of the 3D printed samples assigned to the Arcan specimen. The elastic properties for stainless steel were entered as 210 GPa as Young's modulus and 0.3 as Poisson's ratio. Overall, 16973 nodes and 5374 elements were defined for the fixture and the Arcan sample.

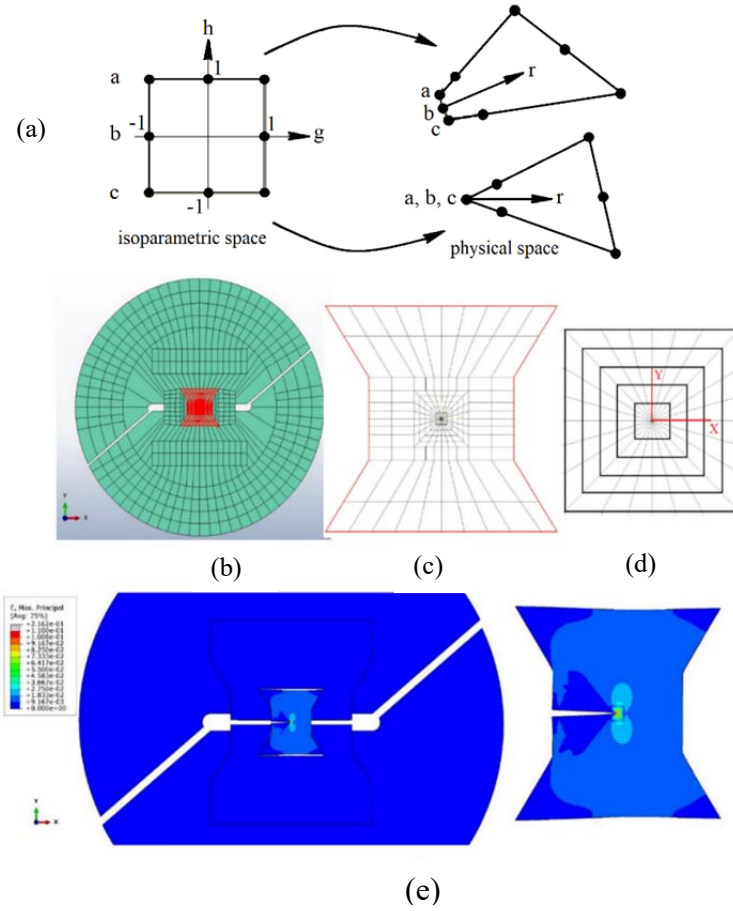


Figure 3.17. Partition pattern of the finite element model; a) collapsed two-dimensional element, b) entire model, c) Arcan specimen, and d) refined partition around the crack-tip e)mixed-mode stress areas after analyses. (Seyedzavvar & Boğa, 2022)

3.3.4. Design of experiments and response surface methodology

Polymer deterioration may be brought on by extreme manufacturing conditions and moisture. As a result, the processing parameters may have a big impact on the mechanical or fracture characteristics of the final parts. The weight fractions of nanoparticles and printing parameters of the FDM method determine the characteristics of materials. In this regard, this study investigates the effects of these different parameters in different values, which are called printing speed (PS), weight fractions (wt%) of nanoparticle addition (NA), layer thickness (LT), filling ratio (FR), and internal architecture (IA), on the mixed-mode fracture characteristics and mechanical behavior of FDM 3D printed pure and CaCO_3/PLA parts, and at which levels of these factors result in the best in terms of realizing the quality of the parts are determined by using the Taguchi L_{27} method. Optimizing these values will enhance the

thermo-mechanical and mixed-mode fracture characteristics of FDM 3D printed PLA and PLA-based nanocomposites and provide the best strength and toughness. The Taguchi method reveals various combinations of experiments using the determining factors (input parameters) for the mechanical and fracture characteristics of PLA and PLA-based nanocomposites and the determined levels of these factors. After the experimental procedures are carried out by following these determined combinations, the combination that gives the best output values (in this study, modulus of elasticity, yield strength, fracture toughness, critical loads, and strain energy release rates) is determined by entering the calculated result values as the output values through the MINITAB program.

Table 3.5. Taguchi L_{27} design of experiments with factors designed from MINITAB.

Taguchi experimental run	PS (mm/s)	NA(%)	LT (mm)	FR (%)	IA
1	20	0	0.09	50	1
2	20	0	0.09	50	2
3	20	0	0.09	50	3
4	20	0.5	0.12	75	1
5	20	0.5	0.12	75	2
6	20	0.5	0.12	75	3
7	20	1	0.15	100	1
8	20	1	0.15	100	2
9	20	1	0.15	100	3
10	40	0	0.12	100	1
11	40	0	0.12	100	2
12	40	0	0.12	100	3
13	40	0.5	0.15	50	1
14	40	0.5	0.15	50	2
15	40	0.5	0.15	50	3
16	40	1	0.09	75	1
17	40	1	0.09	75	2
18	40	1	0.09	75	3
19	60	0	0.15	75	1
20	60	0	0.15	75	2
21	60	0	0.15	75	3
22	60	0.5	0.09	100	1
23	60	0.5	0.09	100	2
24	60	0.5	0.09	100	3
25	60	1	0.12	50	1
26	60	1	0.12	50	2
27	60	1	0.12	50	3

The experimental design technique is based on regression analysis, and the purpose of regression analysis is to determine the existence of a clear mathematical relationship between the independent input variables and the dependent output variable. The point to be noted here is that this is the case where the independent and dependent variables are countable. The Taguchi method and experimental design methods can be used very effectively and efficiently when the goal is not to express the relationship between cause and effect mathematically but to investigate the existence of this relationship. Inputs are called independent variables (X), while outputs are called dependent variables (Y). The dependent variable is the variable of primary interest, and the independent variables are the variables that affect the dependent variable in the experiments. An experiment can involve more than one independent variable at the same time. With experimental design techniques, determining the most effective factors on the output variable studied, determining the effective factors that bring the studied output variable closer to the desired value and these factor values, determining the effective factors that decrease the variability of any output variable and the values of these factors, situations such as determining the values of controllable variables that minimize the effect of the variables can become possible. Statistical methods are used for the analysis of data after the experimental results have been produced. In order to prevent the analysis from being biased and based on judgments about the process, Statistical methods cannot prove the effects of factors or factors, but they can also give an idea about the reliability of the results. After the analysis, some practical inferences can be made based on the obtained result.

The standard statistical analysis, signal-to-noise ratio (S/N), can be used instead of the average results, the reason is that the experimental results include multiple results. The change in the quality of the product under investigation in an experimental design due to a factor is defined as the "signal" of the desired effect. However, when an experiment was performed, the design was not implemented and there could be many external factors that could affect the result. These external factors are defined as noise factors and their effect on output is called "noise". The signal-to-noise ratio (S/N) measures the sensitivity of a controlled quality characteristic to external factors (noise) that are not under control but affect the result. In general, a definition can be made as S/N is the ratio of the mean to the standard deviation. In general, the purpose of any experiment is to achieve the highest S/N ratio for the result value. A high signal-to-noise ratio indicates that the signal is more susceptible to the random effects of noise factors. If the product design or process design is stable at a high S/N ratio, it always yields optimum quality and minimum variation.

In this study, the design of experiments was conducted using the Taguchi orthogonal matrix L_{27} technique, which is suitable for factors and levels. The experiments were repeated five times for each set of experimental runs represented in Table 3.5, and an average of measurements were reported as the response variables of PLA/CaCO₃ nanocomposites produced by the FDM process. The analysis of variance (ANOVA) was performed to evaluate the significance of input parameters mentioned above, on the mixed-mode fracture characteristics and mechanical properties of PLA/CaCO₃ nanocomposites. To this aim, the statistical software Design Expert 13 was employed and the highest polynomial order was obtained based on the statistical parameters of p-value and adjusted R^2 . The analysis of the Taguchi design has been conducted based on the experimental results (output variables), with the criterion that the larger is the better option for the analyses. Therefore, the optimized levels of factors by which the maximum level of material properties could be obtained are determined. Thus, it has been determined that this combination can be used in other FDM 3D printing and PLA production applications, or which factor level will be appropriate. As a result, methodical information was obtained on optimizing the mechanical and fracture characteristic values after the production of PLA and nanocomposites with FDM 3D printing. All of the results for every desired output variables are given and discussed in Chapter 4.

3.3.5. Scanning electron microscopy (SEM) for morphological characterization

A more advanced and extremely important research tool is the scanning electron microscope (SEM). An electron beam is used to scan the surface of the object being studied, and the reflected (or back-scattered) electron beam is then collected and projected at the same scanning rate on a cathode ray tube. The exterior features of the specimen are represented by the image on the screen, which is photographable. The surface must be electrically conductive; for nonconductive materials, a very thin metallic surface layer must be added. It is possible that the surface has been polished and etched and to generate incredibly deep fields of vision as well as magnifications ranging from 10 to more than 50,000 times (Callister Jr & Rethwisch, 2020).

In materials science, the mechanical and fracture characterization of FDM 3D printed parts highly depend on the volume fraction of nanoparticles and their dispersion in the polymer matrix. To this end, the fracture characteristics and the dispersion of nanoparticles of the material must be known. SEM is a useful tool to reveal the failure mechanism of fractured parts. In this study, SEM analysis was employed to investigate the failure mechanism and

elastomer dispersion of fracture surfaces of the FDM 3D printed PLA and PLA-based nanocomposites. In SEM analysis, it is relatively easy to explain the polymer morphology for the reason that the information obtained in the form of magnified images. The scanning electron microscopy employed in this study is shown in Figure 3.18 (a). In order to get SEM images of the surface, the fracture surfaces of Arcan samples were first sputter-coated with gold. Then, SEM micrographs of the coated surfaces were taken with a Quanta 650 field-emission microscope with an acceleration voltage of 20 kV and an emission current of 100 nA. In this study, mixed mode fractured surfaces of the specimens were imaged at x100, x500 x1000, x15000 and x30000 magnifications were taken for each specimen. In order to introduce the magnified images, one of the obtained images at the x500 magnification from SEM analyses from this study is given as an example in Figure 3.18 (b). At the x500 magnification, molten filaments, their arrangement with the gaps between them and the cavities on filaments caused by the nanoparticles can be seen easily.

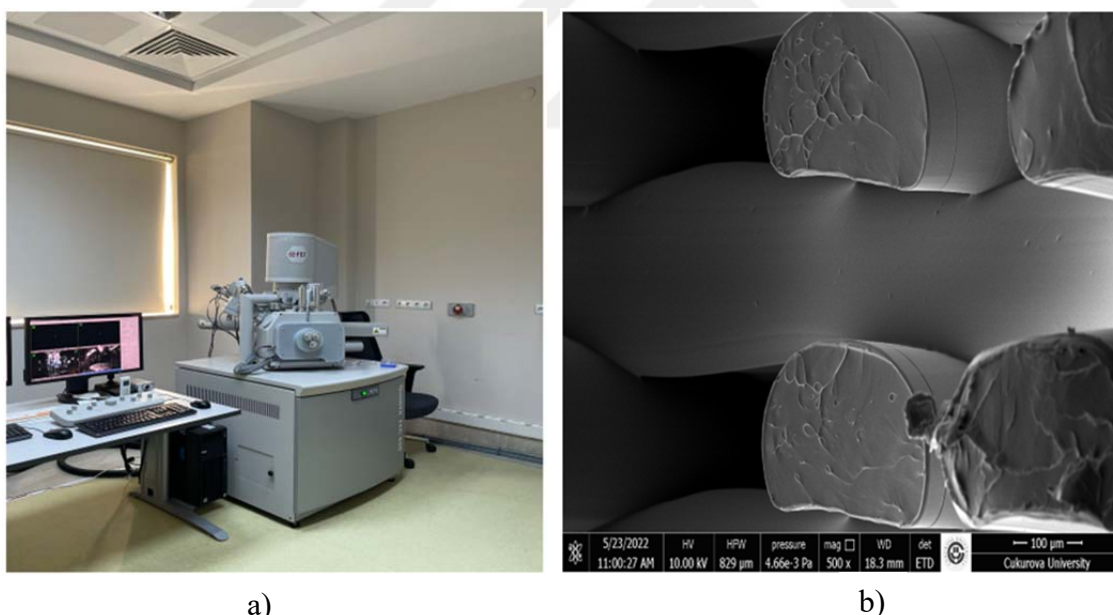


Figure 3.18. Scanning electron microscopy (SEM) and an example of the SEM results obtained in this study.

3.3.6. Differential scanning calorimetry (DSC) for thermal characterization

The amount of heat required to raise the temperature of a sample and a reference pan is assessed as a function of time in DSC analyses. The sample and reference temperatures are kept at about the same temperature. The underlying premise behind this technique is that

when a sample undergoes a physical change, such as a phase transition, the amount of heat necessary to achieve this change is greater or lesser than the heat required to maintain the reference temperature. Transitions of the material might be either endothermic or exothermic. For example, melting a solid material is an endothermic process that necessitates greater heat input to the sample. In contrast, crystallization is an exothermic process that requires less energy to raise the temperature of the sample. It is feasible to measure the amount of energy required for specific phase transitions by examining the difference in heat flow between the reference pan and the sample.

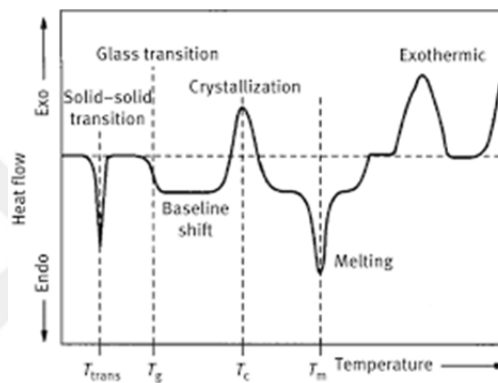


Figure 3.19. Typical DSC curve. (Abd-Elghany & Klapötke, 2018)

A typical DSC curve is shown in Figure 3.19. Differential scanning calorimetry (DSC) is one of the most prevalent methods for determining the thermal features (i.e. glass transition, crystallization and melting temperatures) as well as the degree of crystallization (X_c) for semicrystalline polymers. In order to determine the degree of crystallinity of a polymer, the amount of heat that is required to melt a given polymer (known as enthalpy of melt, ΔH_m) is divided by the heat required to melt a sample with 100% crystallinity (ΔH_m^{100}) (Lanyi, Wenzke, Kaschta, & Schubert, 2020). The glass transition is a reversible change from a hard, generally brittle state to a liquid or rubber-like state in amorphous materials or in amorphous areas within semi-crystalline materials (ISO 11357-2, 1996). The glass transition temperature is the degree at which this transformation takes place. The crystal of the material liquefy and dissolve at this temperature. If the heat of fusion for the fully crystalline polymer is known, the heat necessary for the cold crystallization and melting of semi-crystalline materials may be utilized to calculate the percent crystallinity (X_c) of the polymer phase from the Eq. (43).

$$X_c (\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (43)$$

where the X_c is the percentage crystallinity, the values of ΔH_m for different compositions of PLA/CaCO₃ nanocomposites were calculated based on the DSC experiments, while the ΔH_m for sample of 100% crystallinity is taken as 93.7 Jg⁻¹ (Jia, et al., 2017). The DSC tests were performed using DSC-4000, Perkin Elmer, instrument in temperature range of 0 to 250 °C and heating and cooling rate of 5 °C/min.

3.3.7. Molecular dynamics analyses for mechanical characterization of injection molded parts

Since the determination of characteristics of materials with experimental methods is uneconomical, time-consuming, and sometimes difficult to apply, numerical methods such as Molecular Dynamics (MD) simulations are used to identify the properties of nanoparticle reinforced polymers due to their advantages such as cost-effectiveness and safety. The MD method is based on the principle of modeling structures at the atomic level and examining the motions of atoms over time under the forces formed as a result of the defined potential energy functions. The characteristics of materials can be determined under different conditions with the MD simulations by creating the equations of motion according to Newton's second law. The present study aims to investigate the mechanical properties of PLA/CaCO₃ nanocomposites in order to comparison with the experimental results of injection molded parts. Simulated parts have no gaps in the structure, hence, FDM 3D printed parts have not chosen to comparison since the FDM 3D parts have gaps as a nature of FDM method. Injection molding method creates no or less gaps, that's why the injection molded parts are suitable to comparison with MD simulations. According to verification of experimental and numerical method, PLA/GR nanocomposites also simulated to obtain the mechanical characteristics of parts.

Molecular simulations stand out as a convenient method to compare the theoretical model's predictions with experimental results and to explain the microscopic mechanisms behind the

measured properties. Estimating the properties of materials from their chemical composition is important for the improvement of products in the industry. Significantly, before the synthesis of complex polymeric structured materials, the ability to calculate the values of important physicochemical properties from their molecular structure is of great importance at the design level. These techniques can be used to identify physical and chemical characteristics of the materials as well as to clarify the atomistic mechanisms by which these attributes are determined. Microscopical analysis techniques are crucial in nanotechnology for creating novel functional materials and studying physical events at the molecular level. Through the use of molecular simulation approaches, quantum mechanics or classical physics equations can be employed in this context to identify the characteristics and behaviors of molecule structures (Erdöl, 2021). In molecular mechanical calculations, intermolecular bonds are expressed in empirical formulas with experimentally determined potential values, and the energy of the system is obtained by calculating intramolecular and intermolecular interactions with these formulas. Briefly, MD method is a molecular simulation technique using classical mechanics.

3.3.6.1. Simulation theory and energy expression/ Forcefield

The type of atoms, initial locations and velocities, pressure, and temperature are all set before the beginning of simulation. The velocity and location of each atom are determined at all time steps, and the motion of each atom is estimated per unit time step by computing the forces exerted by other atoms interacting with it. Then, energy and force calculations can be made based on appropriate interatomic potentials under different thermodynamic conditions. Finally, all the dynamic and structural properties of the system can be obtained under the predicted pressure and temperature conditions in the equilibrated system.

Biovia Materials Studio software has been conducted to perform the molecular dynamics simulations. In this way, the large systems such as a polymer that consists thousands of monomers can be simulated practically (Dassault Systemes , 2017). The term "classical simulation methods" refers to a variety of potentials (or forcefields) and distribution generating techniques that are accessible. In molecular dynamics, the process of solving Eq. (44), which represents the Newton's equation of motion, using an empirical fit to the potential energy surface $E(R)$.

$$-\frac{dV}{dR} = m \frac{d^2r}{dt^2} \quad (44)$$

In the present study, the potential energy of molecules which is the expression of the interactions between bound atoms, was calculated using the condensed-phase optimized molecular potentials for atomistic simulations (COMPASS) force field, many different types of materials, including polymers, reinforced polymers, organic and inorganic molecules, can have interatomic interactions that can be precisely explained by this force field (Sun, Chen, Cui, Zhang, & Du, 2018). This force field describes the potential energy surface of the molecule could be described according to Eqs. (45) - (48) (Dassault Systemes , 2017).

$$E_{total} = E_{valence} + E_{crossterm} + E_{nonbond} \quad (45)$$

Eq. (45) represents the total potential energy surface of the molecule by terms of valence ($E_{valence}$), cross-term ($E_{crossterm}$) and non-bond ($E_{nonbond}$) interaction energies. The coordinates of a structure combined with a forcefield form an expression of energy. This energy expression equation describes the potential energy surface of the structure as a function of its atomic coordinates. The potential energies of the system are determined from both bonded and nonbonded energies. Non-bond interactions involve the van der Waals (vdW), Coulomb and hydrogen bond (h_{bond}) terms.

$$E_{valence} = E_{bond} + E_{angle} + E_{torsion} + E_{oop} + E_{UB} \quad (46)$$

The valence energy consists of the bond-stretching E_{bond} , two-bond angle E_{angle} , a dihedral bond-torsion $E_{torsion}$, out-of-plane interactions E_{oop} , and a Uray-Bradley term which is an interaction between two atoms bonded to an another atom E_{UB} , respectively.

$$E_{nonbond} = E_{vdW} + E_{Coulomb} + E_{hbond} \quad (47)$$

which $E_{nonbond}$ term represents the interactions between non-bonded atoms and consists of the van der Waals energy E_{vdW} , the Coulomb electrostatic energy $E_{Coulomb}$, and the hydrogen bond energy E_{hbond} , respectively.

$$\begin{aligned} E_{cross-term} = & E_{bond-bond} + E_{angle-angle} + E_{bond-angle} \\ & + E_{end\ bond-torsion} + E_{middle\ bond-torsion} + E_{angle-torsion} \\ & + E_{angle-angle\ torsion} \end{aligned} \quad (48)$$

which $E_{cross-term}$ represents the cross-term interacting energy, and it consists of the stretch-stretch interactions between two nearby atoms $E_{bond-bond}$, an interaction of bend-bend between two valence angles $E_{angle-angle}$, an interaction of stretch-bend between two bond angle and one of its bonds $E_{bond-angle}$, an interaction of stretch-torsion between a dihedral angle and one of its end bonds $E_{end\ bond-torsion}$, an interaction of stretch-torsion between a dihedral angle and its middle bond $E_{middle\ bond-torsion}$, an interaction of bend-torsion between a dihedral angle and one of its valence angles $E_{angle-torsion}$, and an interaction of bend-bend-torsion interactions between a dihedral angle and its two valence angles $E_{angle-angle\ torsion}$, respectively.

The equations of motion are integrated by the velocity-Verlet integrator technique using the NVT (constant volume canonical) and NPT (isothermal-isobaric) ensembles algorithms with the time step of 1 fs to ensure the stability of the system and reduce the temperature fluctuations during simulations. In addition, the radial distribution function (RDF) was applied to analyze the details of PLA/ CaCO₃ interactions in the atomistic level. RDF provides an estimation of the possibility of finding another atom at a specified distance from a reference atom, as explained by Eq. (49):

$$g(r)_{A-B} = \left(\frac{n_B/4\pi r^2 dr}{N_B/V} \right) \quad (49)$$

where $g(r)$ is the radial distribution function, n_B denotes the number of B atoms surrounding A atoms at a distance r , N_B is the total number of B atoms and V is the volume of the system.

3.3.6.2. Statistical ensembles

The microscopic state of the system, including atomic locations, velocities, and accelerations, is revealed via MD simulations. The system's microscopic and macroscopic states are combined in great detail in these simulations using statistical mechanics. The microscopic state of the system is combined with observable macroscopic data, such as pressure, temperature, or energy state, in statistical mechanics and provides the molecular analysis of the microscopic circumstances within an atomic system (Meller, 2001). Integrating Newton's equations of motion enables the study of a system's constant-energy surface. The majority of natural phenomena, however, take place when a system is subjected to external pressure and/or exchanges heat with its surroundings. In these circumstances, the system's total energy is no longer conserved, necessitating the use of enlarged varieties of molecular dynamics. Temperature and pressure may be controlled using a variety of techniques. These variables determine thermodynamic state of the system and are controllable by statistical ensembles. The thermodynamic ensembles handled by Materials Studio include the constant-temperature, constant-pressure ensemble (NPT), the constant-energy, constant-volume ensemble (NVE), the constant-pressure, constant-enthalpy ensemble (NPH), and the constant-temperature, constant-volume ensemble (NVT) (Dassault Systemes, 2017).

which N is the number of atoms in the system, E the system's total energy, V the system's volume, T the system's temperature, and P the system's pressure. For instance, the letters in an NPT assembly stand for constant atomic number (N), pressure (P), and temperature (T). In this study, NPT and NVT ensembles have conducted for the analyses.

3.3.6.3. Simulation model

The atomistic models of CaCO_3 and GR reinforced nanocomposites were constructed with Materials Studio. Calcite unit cell, a member of carbonate minerals, is the most stable polymorph of CaCO_3 is built to construct the CaCO_3 nanoparticles. As shown in Figure 3.20 (a), this unit cell has a hexagonal structure with dimensions of $a=b=4.99\text{\AA}$, $c=17.061\text{\AA}$ and angles of $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$. The spherical CaCO_3 nanoparticle is automatically built as a nanocluster of calcites, with radius of $10\text{\AA}$, energetically minimized and geometrically optimized using forcite COMPASS simulation as represented in Figure 3.20 (b). Like CaCO_3

nanoparticles, to construct the graphene nanoparticles, graphite hexagonal unit cell is a crystalline form of carbon element, is built first. As shown in Figure 3.21 (a), this hexagonal unit cell has a structure with the dimensions of $a=b=2.459\text{\AA}$, $c=6.800\text{\AA}$ and angles of $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$. The spherical graphene nanoparticle is automatically built as a nanocluster of graphites, with radius of with radius of $10\text{\AA}$, energetically minimized and geometrically optimized using forcite COMPASS simulation as represented in Figure 3.21 (b).

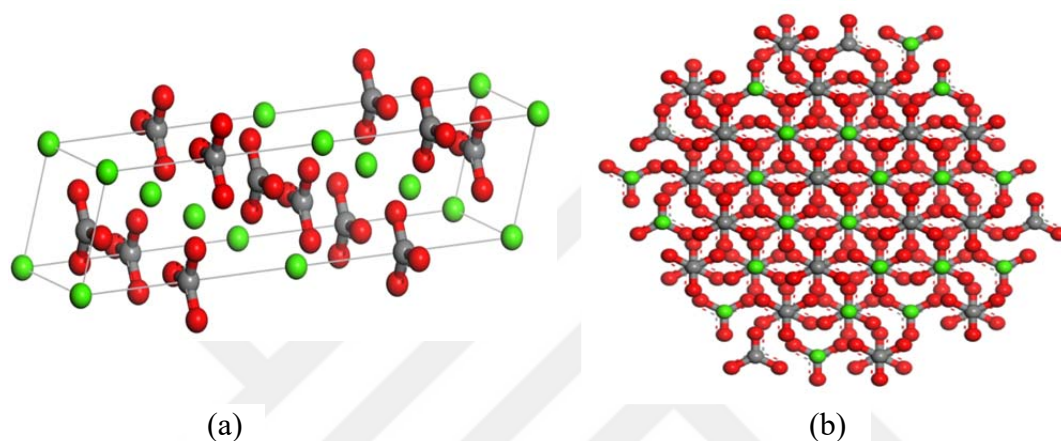


Figure 3.20. Construction of CaCO_3 nanoparticle: a) calcite hexagonal unit-cell, b) CaCO_3 spherical nanocluster.

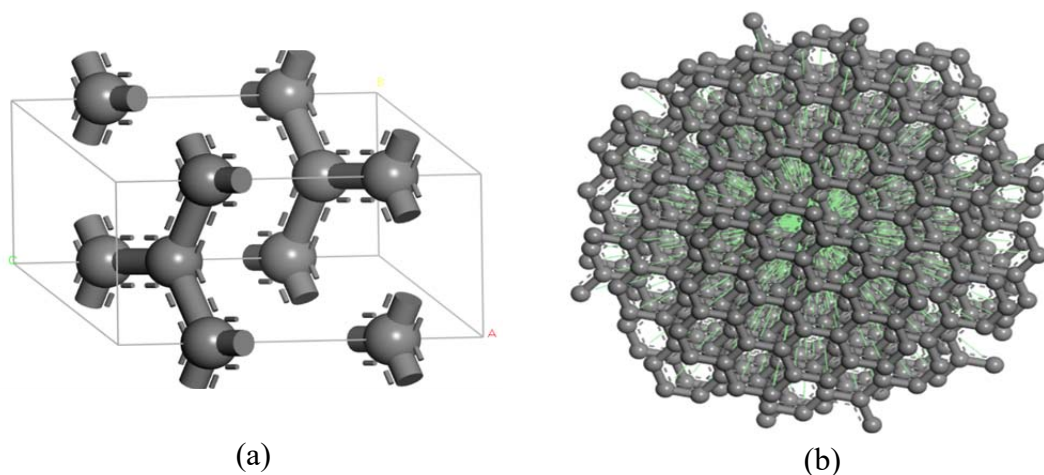


Figure 3.21. Construction of graphene nanoparticle: a) graphite hexagonal unit-cell, b) graphene spherical nanocluster.

Figure 3.22 (a) shows the lactic acid monomers have been created to construct PLA polymer matrix with sketching tools employed in Materials Studio. PLA molecule structure is very

simple than the other polymers (for ex. PBT), this property reduces the computational time, so PLA molecule becomes an effective choice in a large class of polymer materials. Since the interfacial mechanical performance of polymers is crucial, PLA homopolymers have been constructed in different molecular chain lengths that range between 20 and 40 although studies have been observed investigating this effect. Based on the molecular dynamics results, the length of molecular chain has a negligible effect to improve the mechanical performance of PLA polymers. In order to save the computational cost and time, the molecular model and geometrically optimized structural model of PLA constructed with 20 repeat unit chain lengths and the corresponding length of $\sim 74.98\text{\AA}$ are shown in Figure 3.22 (a) and Figure 3.22 (b).

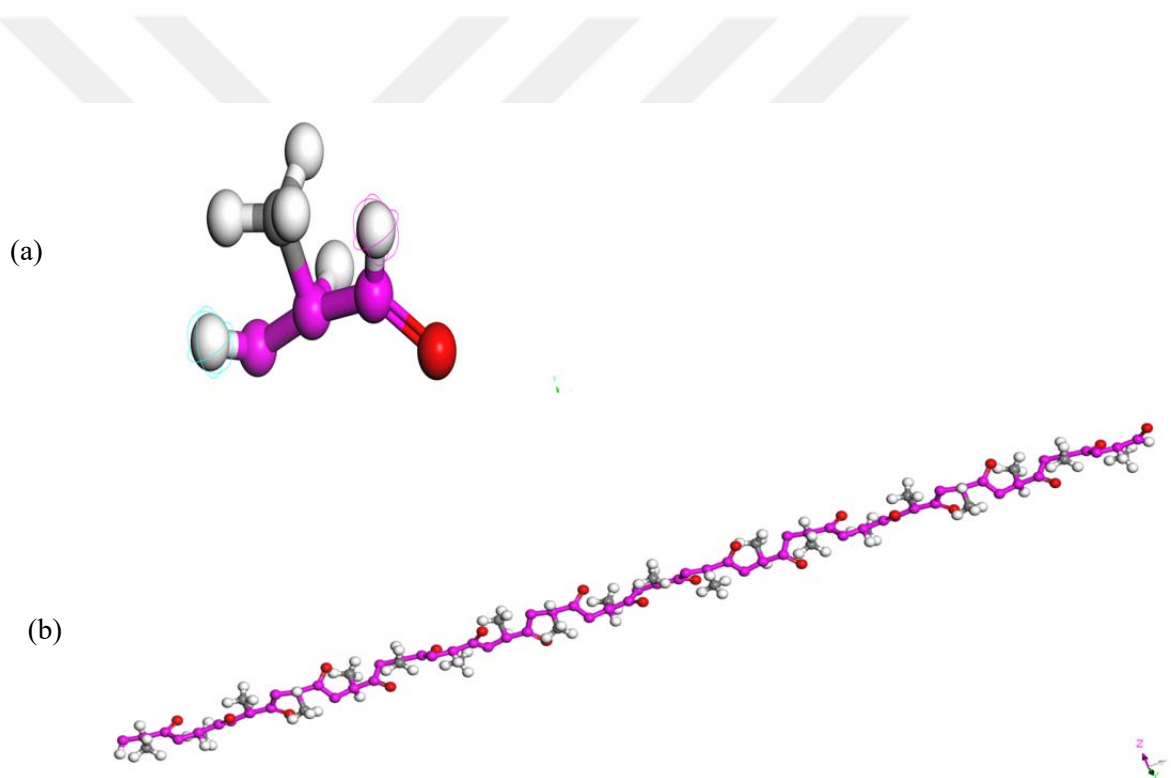


Figure 3.22. A perspective of the atomistic models of; a) lactic acid monomer and b) Optimized molecular model of isotactic PLA homopolymer.

Figure 3.22 (a) shows the lactic acid monomers have been created to construct PLA homopolymer molecules to construct RVEs of PLA/CaCO₃ and PLA/GR nanocomposites with sketching tools available in Materials Studio.

Then, in order to prevent the development of excessive energy in the amorphous cell, the periodic boxes of RVEs have been constructed with the initial target density of 1.25 g/cc. All simulated cells employed 3-dimensional periodic boundary conditions, and each cubic cell's molecules were dispersed randomly. At the same time, the dimensions of RVE boxes are set based on different weight fractions of CaCO_3 and GR nanoparticles in the PLA polymer matrix. Figure 4.23 (a) and (b) represents the PLA matrix containing 5wt% CaCO_3 and graphene nanospheres placed at the center of the periodic box and the PLA polymer molecules are packed around these nanospheres. In order to calculate the mechanical properties of nanocomposites, first isothermal-isobaric (NPT) and canonical (NVT) ensembles have been conducted to obtain equilibrium-stated final configuration of RVEs which are used to calculation of required properties.

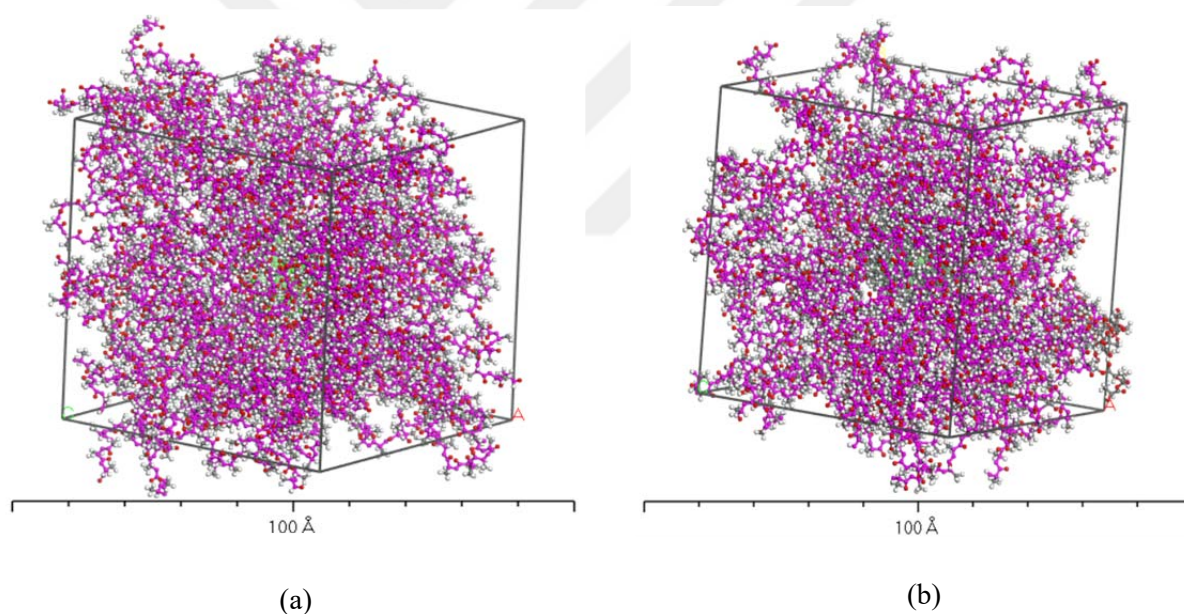


Figure 3.23. Initial RVE boxes of PLA nanocomposites with initial target densities of 1.25 g/cc; a) Initial configuration of packed 5wt% PLA/ CaCO_3 cell and b) Initial configuration of packed 5wt% PLA/GR cell.

3.3.6.4. Calculation of mechanical properties

This study aims to reveal the mechanical properties of PLA/ CaCO_3 and PLA/GR nanocomposites on an atomic scale with MD simulations. This approach allowed for the

determination of the mechanical characteristics of nanocomposites, including their elasticity and shear modulus, as well as the investigation of how their mechanical properties changed at different weight ratios. The RVEs is subjected through a variety of procedures prior to the mechanical analysis in order to get the required density value, and the system is then brought to equilibrium using statistical ensembles. In this approach, the RVEs is able to represent the actual material structure, and the generated RVEs are utilized to identify the force field that will be employed most frequently. Figure 3.25 represents the energy variation of PLA molecule during geometry optimization process. Geometry optimization process must be applied to PLA and nanoparticles before packing and after packing, RVEs should be optimized geometrically before statistical ensembles. Following this phase in the process, the structure is run at NPT conditions under circumstances of constant pressure and constant temperature until the desired density value is reached. As already mentioned above, the COMPASS force field was employed in this investigation.

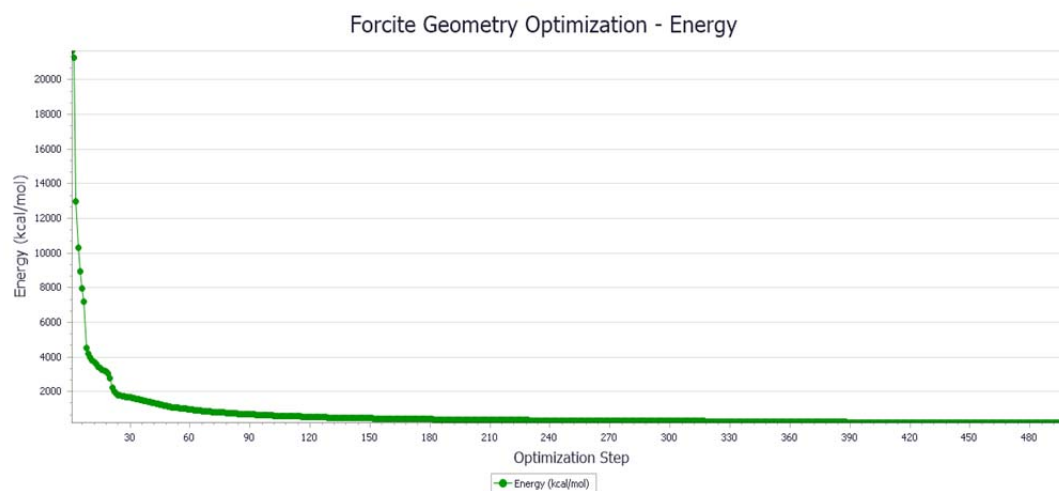


Figure 3.24. Energy variation of the PLA molecule during the geometry optimization process.

The mechanical properties of the RVEs were calculated using the Forcite module available in Materials Studio software. The elastic stiffness constants C_{ij} required for the calculation of the mechanical properties were obtained with constant strain of $0.003\text{\AA}^\circ$ to the RVEs. The

fluctuation equations are used in various ensembles, holding the simulation cell constant and computing the stiffness constants in accordance with Eq. (50), while taking into account the entropic effects (Seyedzavvar, Boğa, Akar, & Pashmforoush, 2021).

$$C_{ij} = C_{ij}^{\beta} + C_{ij}^k + C_{ij}^f \quad (50)$$

where C_{ij}^{β} , C_{ij}^k , and C_{ij}^f are represent the Born, kinetics and stress fluctuation. Eqs. (51) – (54) represent the constants of mechanical properties (Seyedzavvar, Boğa, Akar, & Pashmforoush, 2021).

$$\lambda = \frac{1}{3}(C_{11} + C_{22} + C_{33}) - \frac{2}{3}(C_{44} + C_{55} + C_{66}) \quad (51)$$

$$\mu = \frac{1}{3}(C_{44} + C_{55} + C_{66}) \quad (52)$$

$$E = \mu \left(\frac{3\lambda + 2\mu}{\lambda + \mu} \right) \quad (53)$$

$$G = \mu, \nu = \left(\frac{\lambda}{2(\lambda + \mu)} \right) \quad (54)$$

where G is the shear modulus.

4. RESULTS AND DISCUSSIONS

This present master's thesis is based on the manufacturing of pure, 0.5 and 1 wt% CaCO_3 reinforced PLA thermoplastic filaments and the production of test specimens in different printing parameters with FDM 3D printing. The aims of this study are to (i) expand the use of polymer-based nanocomposite parts with superior thermo-mechanical properties and fracture behaviors by using a rapid and cost-effective FDM technology and (ii) produce polymer-based nanocomposite parts by utilizing the injection molding process to investigate the effectiveness of MD simulations in forecasting the mechanical performance of parts through the comparison of mechanical properties of produced parts with the results of molecular dynamics (MD) simulations. In order to accomplish the first objective, polylactic acid (PLA), one of the foremost biodegradable polymers, was chosen as the matrix material, while calcium carbonate (CaCO_3) nanoparticles were used as reinforcement materials. For this purpose, the PLA/ CaCO_3 nanocomposite filaments, containing different weight ratios (0, 0.5, and 1 wt%) of nanoparticles in the matrix, have been synthesized by melt-blending technique using a twin-screw extruder system. These filaments were used to produce samples by FDM technique with different printing parameters to study the effects of nanoparticles and printing parameters on the mechanical properties and fracture behavior of the PLA nanocomposites under mixed-mode fracture loadings. In this regard, this study investigates the effects and significance of these different parameters, which are called printing speed, weight fractions of nanoparticle addition, layer thickness, filling ratio, and internal architecture, on the fracture characteristics and mechanical behavior of FDM 3D printed PLA and PLA/ CaCO_3 nanocomposites. To this end, the analysis of the Taguchi L_{27} design has been conducted based on the experimental results to determine the optimized levels of factors by which the maximum level of material properties could be obtained. Thus, it has been determined which combination can be used in further FDM 3D printing of PLA-based materials, or which factor level will be appropriate. A response surface methodology (RSM) was employed to model and predict the mechanical and mixed-mode fracture properties of the PLA-based nanocomposites produced in different weight ratios and different FDM printing parameters. The produced samples were subjected to uniaxial tensile tests for mechanical characterization. Mixed-mode fracture behavior of the synthesized samples were studied by applying mixed-mode loadings on the pre-cracked samples using an in-lab developed fixture mounted on the

uniaxial tensile test machine. Finite element simulations are employed to simulate the crack opening on such specimens and calculate the geometry shape functions of the fracture samples at different loading angles. Finally, after the experimental procedures, scanning electron microscopy (SEM) examinations have been conducted on the fractured surfaces of the test samples to reveal the fracture morphology of parts and validate the presence of nanoparticles. In addition, differential scanning calorimetry (DSC) analyses are conducted to determine the variations in the glass transition and heat capacity of the PLA polymer by the incorporation of CaCO_3 nanoparticles in the PLA matrix.

Secondly, uniaxial tensile test specimens of PLA and PLA/ CaCO_3 nanocomposites have been produced with the injection molding process to verify the MD simulations. Material Studio software is employed to investigate the physical behavior of injection molded PLA/ CaCO_3 nanocomposites in different weight ratios (1, 3, and 5wt%) and to research the details of interactions between the molecules and nanoparticles on an atomic scale. For the reason that the molecular dynamics simulations verify the experimental results, graphene (GR) reinforced PLA nanocomposites were simulated to predict the mechanical properties of injection molded PLA/GR in different weight fractions. It has been observed that Materials Studio software provides accurate results in estimating the mechanical properties of materials. This chapter represents and evaluates the results from experimental and molecular dynamics analyses.

4.1. Mechanical properties

Uniaxial tensile test procedure have been conducted to better understand of mechanical characteristics of pure and reinforced PLA thermoplastic polymers produced with FDM 3D printing and injection molding. Details of characterization conditions and methodological approach are described in Chapter 3.

4.1.1. Results of uniaxial tensile tests

Mechanical properties such as modulus of elasticity (E), yield strength, and Poisson's ratio give an idea about brittleness and plastic behavior of PLA and PLA-based nanocomposites. Table 4.1 represents the experimental results of mechanical properties of PLA/ CaCO_3 nanocomposites fabricated under different FDM parameters according to the Taguchi L_{27} table. These values were determined using uniaxial tensile tests, all of the experiments were

carried out at room temperature using a Shimadzu AGS-X tensile testing machine with 100 kN load cell for displacement and force measurement, running with a constant cross head speed of 1mm/min, respectively. Figure 4.1 represents the stress-strain diagram of the Taguchi experimental run 23 which performed the highest mechanical properties in this study. The approach to the calculation procedure of tensile properties was described in Chapter 3.

Table 4.1. Experimental results of mechanical properties of PLA/CaCO₃ nanocomposites fabricated under different FDM parameters according to Taguchi L_{27} scheme.

Experimental run	Modulus of elasticity (MPa)	Poisson's ratio	Yield strength (MPa)
1	721	0.495	9.6
2	1368	0.297	10.9
3	740.68	0.323	10.15
4	1276	0.391	17.2
5	1976	0.346	21.5
6	1350	0.315	15.3
7	3504	0.402	41.5
8	2908	0.278	40.5
9	3497	0.339	37
10	2888	0.336	35
11	2929	0.374	27
12	3168	0.392	28.8
13	1067	0.555	13.5
14	1396	0.279	16.2
15	1119	0.359	14.6
16	1592	0.397	20.3
17	2392	0.308	22.3
18	1385	0.330	15.4
19	1250	0.627	16.3
20	2171	0.428	19.1
21	2038	0.265	14.2
22	3856	0.374	43
23	3868	0.370	43.5
24	3760	0.391	41
25	995	0.462	13.5
26	1352	0.257	12.8
27	853	0.339	10.4

4.1.1.1. Effects of printing parameters on the mechanical properties of PLA and PLA-based nanocomposites

The effects of the printing speed on the mechanical properties of PLA/CaCO₃ nanoparticles are depicted through Figure 4.1 while the layer thickness and filling ratio are kept at their middle ranges.

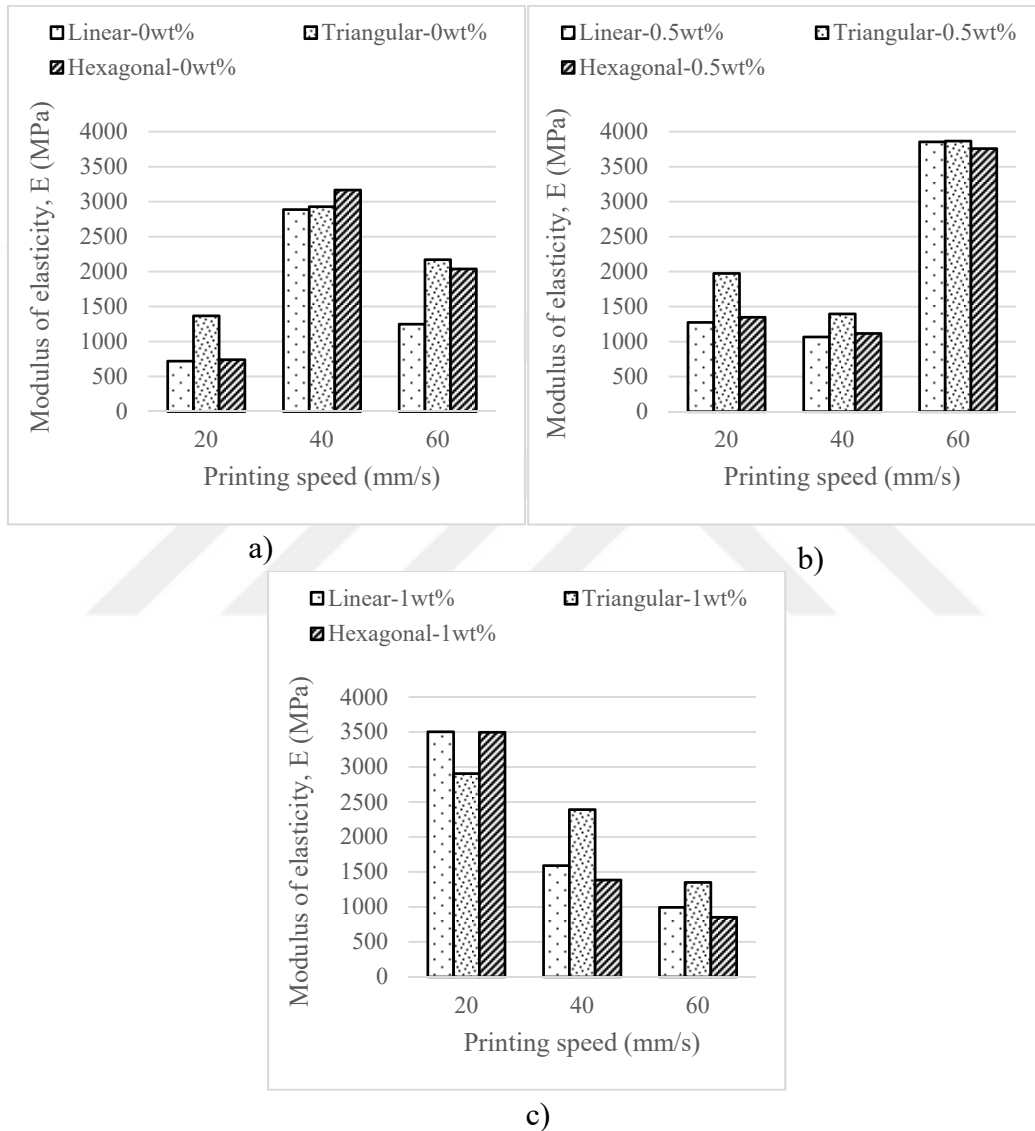


Figure 4.1. Effects of printing speed (mm/s) on E values of a) pure b) 0.5 wt% CaCO₃ c) 1 wt% CaCO₃ PLA parts printed in different internal architectures.

Although the experimental analyses indicate a more pronounced influence of the printing speed on the mechanical properties of the fabricated nanocomposites, the effect of this parameter on the leading time was not substantial in this study. In general, different printing

speed values have resulted in with different reactions on the mechanical properties of pure and reinforced parts. In particular, as can be seen in Table 4.2 and Figure 4.1 a), pure PLA parts printed at 40 mm/s have the best modulus of elasticity (E). However, increasing the printing speed over 40 mm/s weakens the mechanical properties for pure and 1 wt% CaCO_3 reinforced PLA parts. In contrast, as can be seen from Figure 4.1, 60 mm/s printing speed has resulted in the highest mechanical properties in 0.5 wt% CaCO_3 reinforced parts, while it has the weakest results in 1 wt% CaCO_3 reinforced PLA parts. However, in general, the FDM 3D printed PLA and PLA-based nanocomposites possess better tensile characteristics, especially when the printing speed is 60 mm/s. These observations could be related to the effects of the printing speed, as the relative movement speed between the printing nozzle and the platform, on the binding between the deposited printing beads and the formation of an air gap between them. Higher printing speeds, generally over 60 mm/s, would result in less stable prints and the presence of air in PLA and composite samples which significantly contribute to the creation of flaws in the printed samples. Additionally, when printing speed is increased, the mechanical strength of the stacked macromolecule chains decreases. On the other hand, when the printing speed is around to 60 mm/s, the melting material that is extruded from the nozzle has adequate time to bond with the adjacent printed component, enhancing the overall performance of manufactured components.

The results of experiments and statistical modeling of the effects of filling ratio on the mechanical performance of PLA/ CaCO_3 nanoparticles are illustrated through Figure 4.2, while the printing speed and layer thickness are kept at their middle ranges. It is a fact that if the material has fewer gaps than the others, the mechanical properties of the material will be result in higher values. The filling ratio value of printing determines the amount of gaps into the parts. As can be seen from Figure 4.2, in all pure, 0.5 wt% and 1 wt% reinforced parts, a 100% filling ratio has the best mechanical properties. As expected, the CaCO_3 reinforcement increased the ultimate tensile strength and modulus of elasticity values of pure PLA parts in all internal architectures. Overall, 0.5 wt% CaCO_3 amount has resulted in better mechanical properties in modulus of elasticity and yield strength, the reason of this situation could be related to the dispersion of nanoparticles in the PLA polymer matrix.

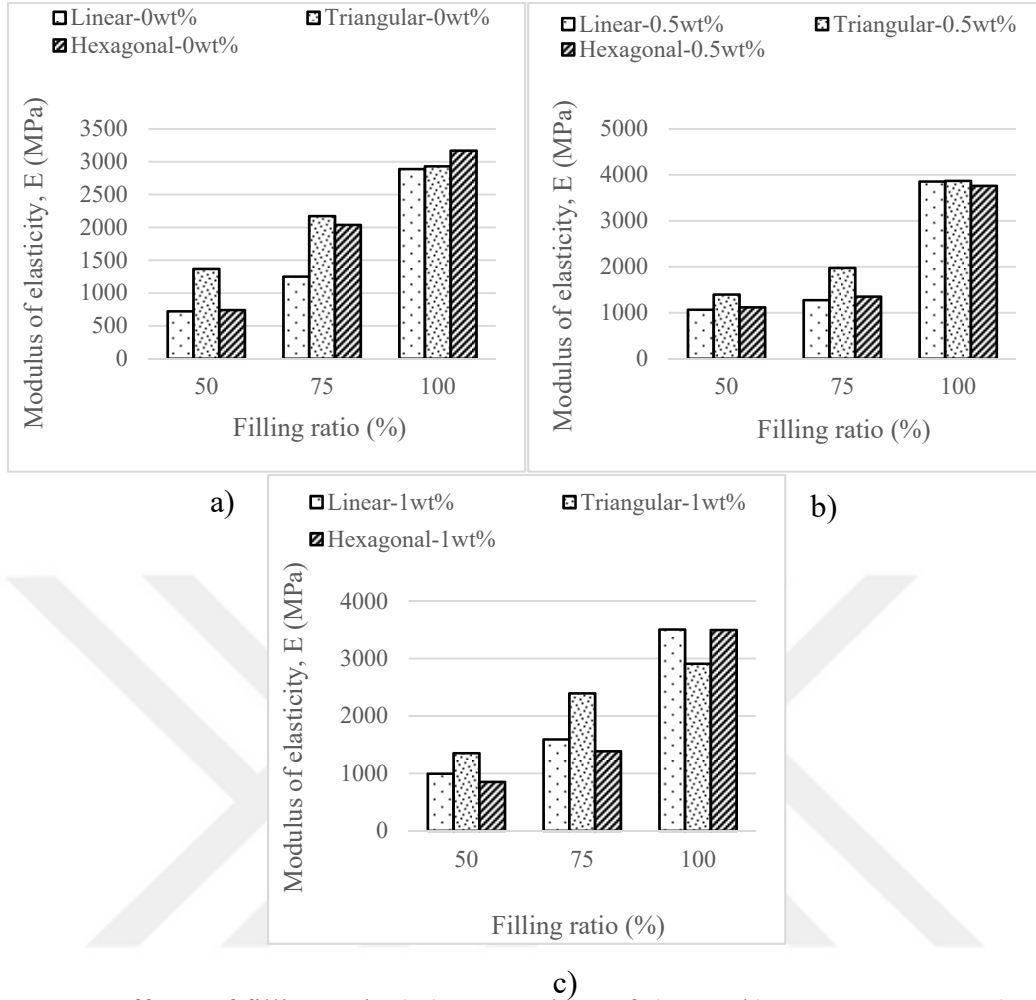


Figure 4.2. Effects of filling ratio (%) on E values of a) pure b) 0.5 wt% CaCO_3 c) 1 wt% CaCO_3 PLA parts printed in different internal architectures.

The internal architecture of parts includes the raster orientation of printed layers. In the investigation of the internal architecture, triangular internal architecture has the highest E value with 1368 MPa in pure PLA parts printed at 20 mm/s, which is higher than the lowest value of the parts printed with linear architecture by about 47%. However, pure PLA parts printed with linear and hexagonal architectures at 20 mm/s have closer E values. Pure PLA parts printed in a hexagonal structure at 40 mm/s have the highest E value with 3168 MPa, and parts printed in linear and triangular structures have closer E values. 0.5 wt% CaCO_3 /PLA parts printed with triangular structure at 60 mm/s have the highest E value with 3868 MPa. Mostly, PLA nanocomposite parts printed with linear internal architecture have the lowest mechanical properties while the triangular shows the highest.

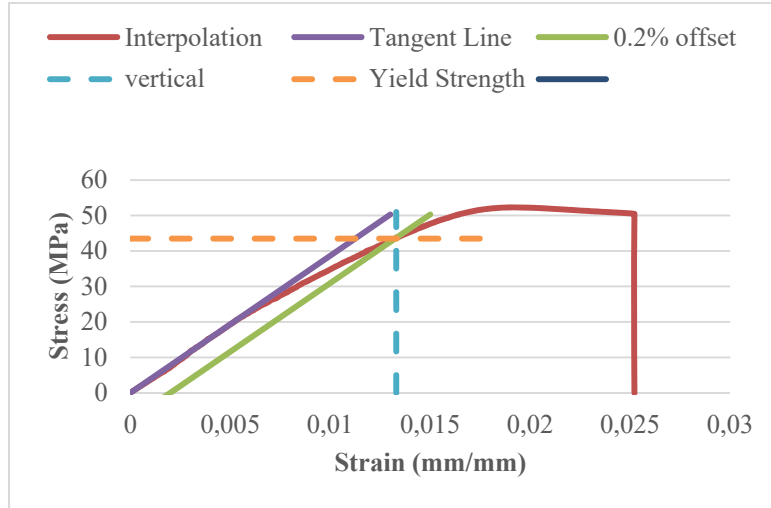


Figure 4.3. Stress-strain diagram of the experimental run number 23.

4.1.2. ANOVA of modulus of elasticity (E) for printed PLA/CaCO₃ nanocomposites

After the input and output variables have been specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the modulus of elasticity values. Figure 4.4 shows the best sequence of parameters in order to obtain the highest modulus of elasticity in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for modulus of elasticity (E) values was found as 0.5 wt% CaCO₃ reinforced triangular internal architected parts printed at 60 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. The printed parts with this sequence will have the highest rigidity, which resulted in the smallest elastic strain in this study. These observations demonstrate that the triangular pattern is the most resistant to deformation, which is also the most stiff structure.

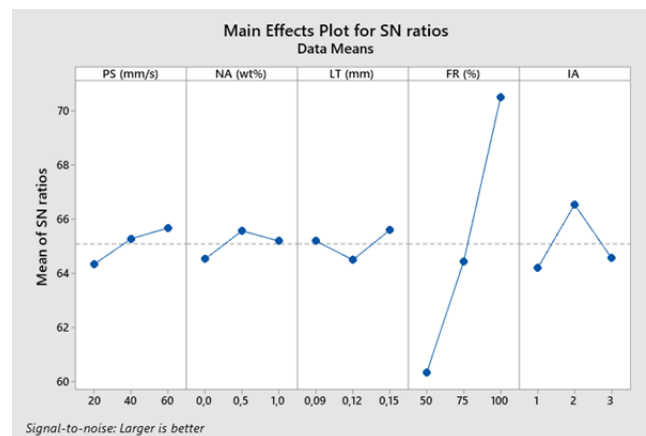


Figure 4.4. S/N ratios from Taguchi analysis for E .

Additionally, in order to investigate the significance of each input variables (parameters), which are printing speed (mm/s), weight fraction of CaCO₃ nanoparticles (%), layer thickness (mm), filling ratio (%), and internal architecture, p-values of the analysis of variance (ANOVA) were conducted. To this point, the statistical program Design Expert was used. This type of analysis is necessary to understand the behavior of independent variables and their interactions with one another. Based on the statistical parameters of p-value and adjusted R², the highest polynomial order was obtained. The lowest p-value and the highest adjusted R², which are lower than 0.0001 and greater than 0.9, respectively, were chosen based on the results of an ANOVA for different orders of polynomials. A high R² value is an assessment of the fit degree and a strong correlation between experimental and projected outcomes, while a low p-value demonstrates statistical significance for the associated response. A response surface methodology (RSM) was employed to model and predict the mechanical and mixed-mode fracture properties of the PLA-based nanocomposites produced in different weight ratios and different FDM printing parameters. 3D response surface graphs of significant parameters according to interactions between each other have been plotted to better understand their reactions.

Table 4.2. ANOVA for modified modified quadratic model of modulus of elasticity (*E*) of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.720E+07	9	3.022E+06	29.83	< 0.0001	significant
A-PS (mm/s)	1.594E+06	1	1.594E+06	15.74	0.0010	
B-NA (%)	80577.04	1	80577.04	0.7956	0.3849	
C-LT (mm)	37718.67	1	37718.67	0.3724	0.5498	
D-FR (%)	3.427E+06	1	3.427E+06	33.83	< 0.0001	
E-IA	6.255E+05	2	3.128E+05	3.09	0.0718	
AB	4.739E+05	1	4.739E+05	4.68	0.0451	
BC	1.864E+06	1	1.864E+06	18.40	0.0005	
A ²	3.711E+05	1	3.711E+05	3.66	0.0726	
Residual	1.722E+06	17	1.013E+05			
Cor Total	2.892E+07	26				
R ² , 0.9405; adjusted R ² , 0.9089; predicted R ² , 0.8450; adequate precision, 15.7084						

A response surface methodology (RSM) was employed to model and predict the mechanical properties such as modulus of elasticity and yield strength of the PLA-based nanocomposites produced in different weight ratios and with different FDM printing parameters. Design of

experiments (DOE) and response surface methodology (RSM) with an orthogonal array of the Taguchi method have been conducted to obtain optimum input parameters for the best mechanical properties of parts. Table 4.2 represents the ANOVA for the modified quadratic model of modulus of elasticity (E) of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. However, E (internal architecture) is an input variable that has p-value greater than 0.05. In order to keep the hierarchy of the models and to increase the overall significance and predictability of the model, E (internal architecture) is kept as a variable in the quadratic models in this study. The model F-value of 29.83 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A , D , AB , and BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the modulus of elasticity of PLA and PLA-based nanocomposites. The most important factors influencing the E of PLA-based nanocomposites were found as printing speed (mm/s) and filling ratio (%) with probability values of $p = 0.0010$ and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition (AB) and nanoparticle addition $\times$ layer thickness (BC) were also found to be significant with probability values of $p = 0.0451$ and $p = 0.0005$, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is near to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9405 suggested that 94.05% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.8450 is in reasonable agreement with the Adjusted R^2 of 0.9089; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the modulus of elasticity are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 15.708 indicates an adequate signal. This model can be used to navigate the design space.

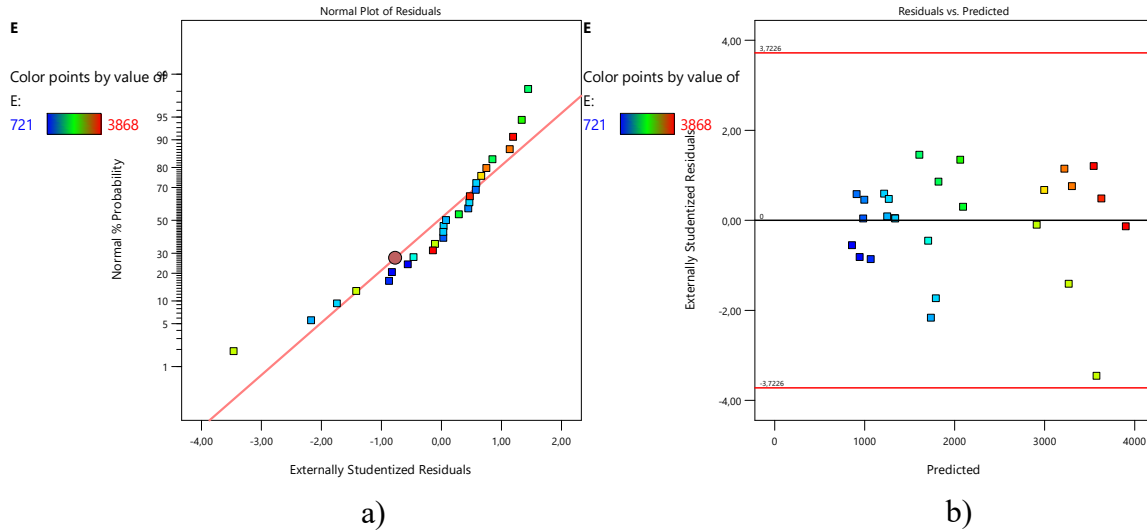


Figure 4.5. a) Normal plot of residuals b) residuals vs predicted plot of modulus of elasticity (E) of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.5 represents the normal of residuals and residuals vs. predicted plots for modulus of elasticity (E) values of PLA and PLA-based nanocomposites from uniaxial tensile tests. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to the investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of modulus of elasticity E values shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy. 3D surface diagrams show the interactive effects of input parameters on the response variable. According to Table 4.2, the interactions between AB and BC were found significant. To better understand the interaction between these parameters, 3D response surface graphs have been plotted.

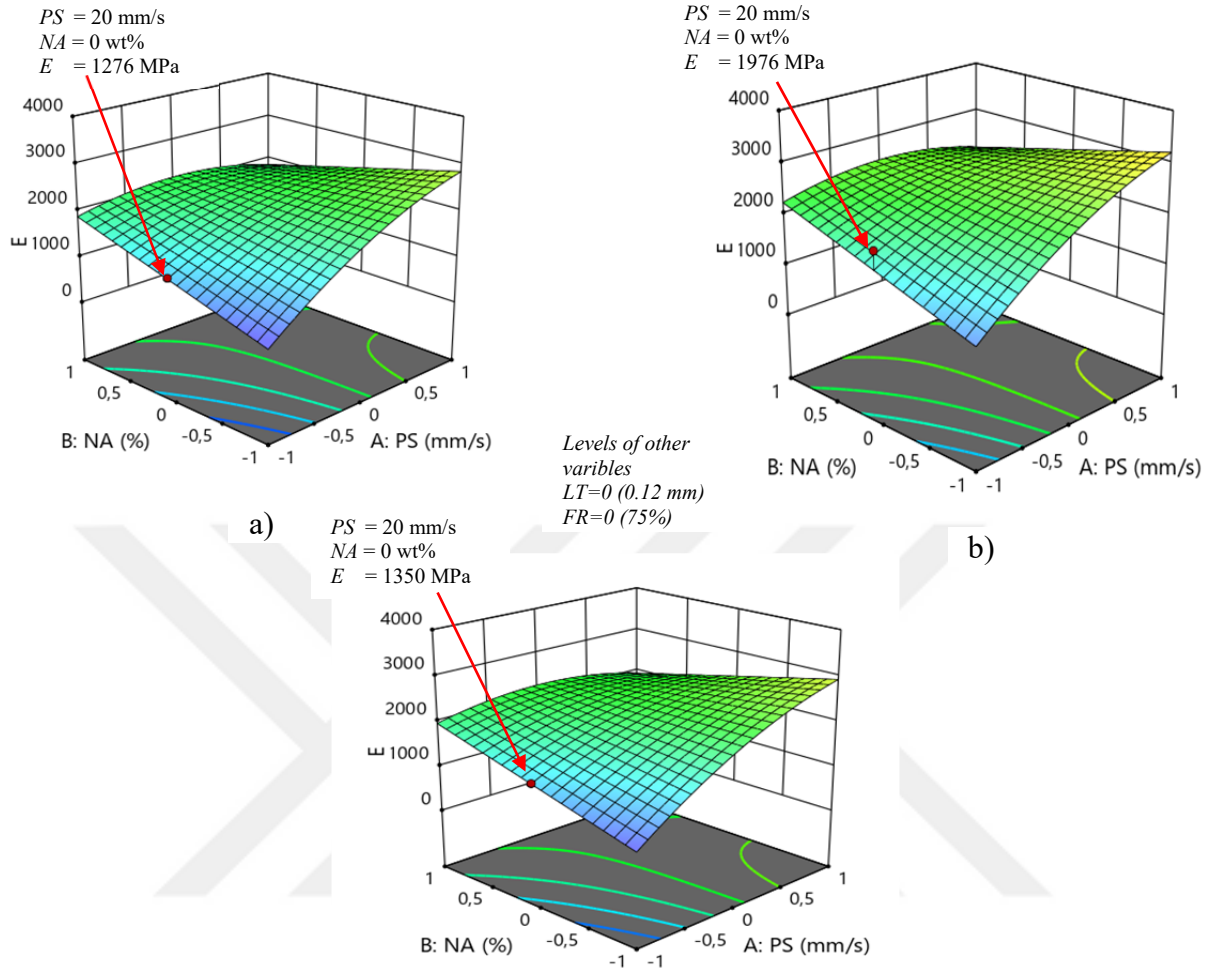


Figure 4.6. 3D response surface plot for PS (mm/s) and NA (%) of modulus of elasticity (E) of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.6 represents the interaction between printing speed (mm/s) and nanoparticle addition (%) of parts printed in linear, triangular, and hexagonal internal architectures on the modulus of elasticity E value from uniaxial tests. As can be seen from this figure, parts printed in triangular internal architecture yield the highest E value. Furthermore, the parts printed with linear internal architecture have the lowest modulus of elasticity value. These observations could be related to the gradual fracturing of macro-sized printed beads with linear internal architecture due to the addition of nanoparticles in the matrix material, which constrained their ability to elongate and absorb energy. Additionally, it can be observed that the printing speed needs to be decreased with increasing nanoparticle concentration in the matrix in all types of internal architectures to keep the mechanical strength of the 3D printed nanocomposites.

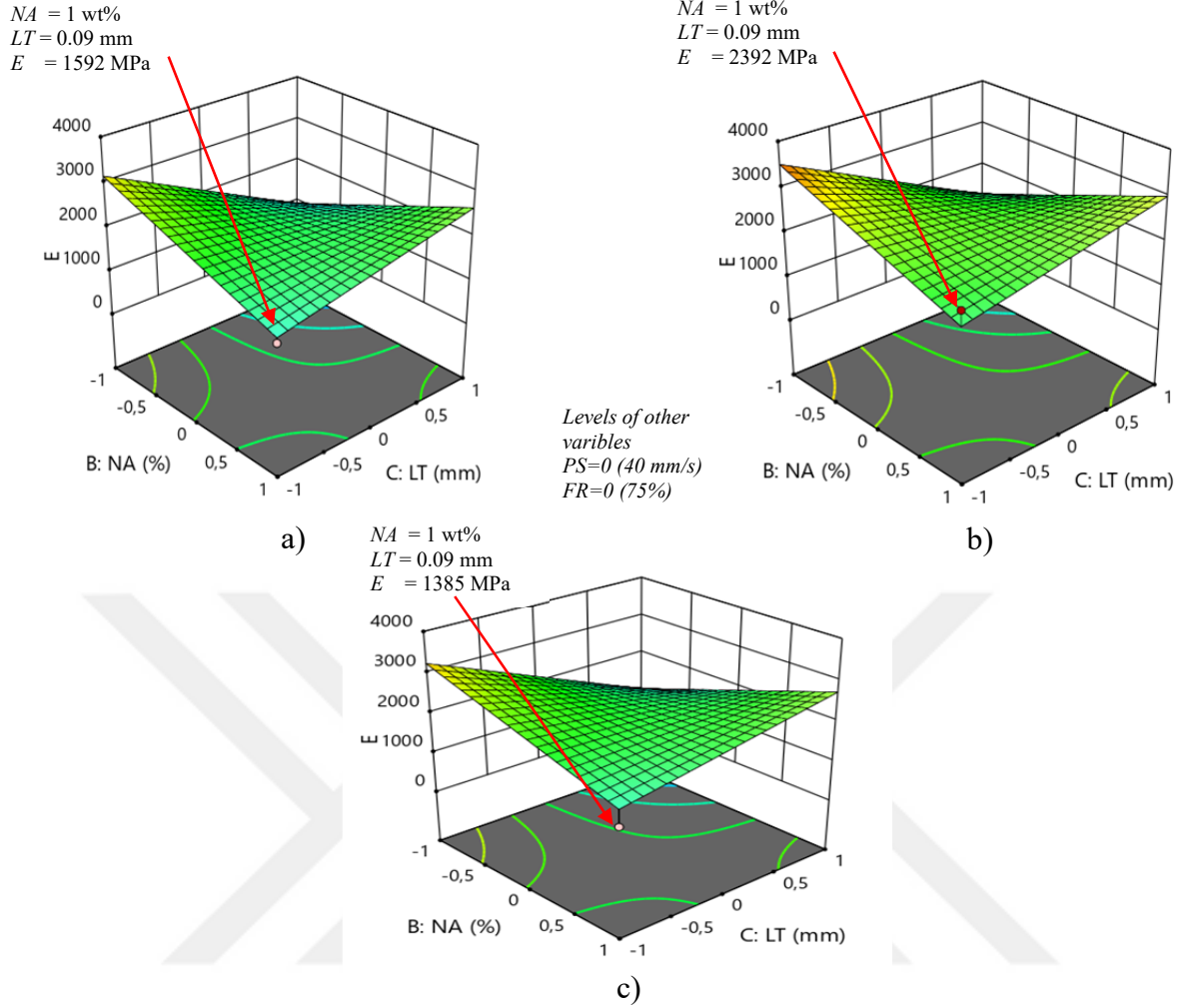


Figure 4.7. 3D response surface plot for NA (%) and LT (mm) of modulus of elasticity (E) of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.7 represents the interaction between nanoparticle addition (%) and layer thickness of parts printed in linear, triangular, and hexagonal internal architectures for the modulus of elasticity (E) value from uniaxial tests. As can be seen from position in diagrams in the figure, parts printed with triangular internal architecture yield the highest E value. This figure shows the printing speed change according to nanoparticle addition at different internal architectures in tensile tests. As can be seen from the figure, it can be observed that the layer thickness should be decreased with the increase of nanoparticle addition in linear, triangular, and hexagonal architectures to maintain the mechanical strength of fabricated nanocomposite samples.

4.1.3. ANOVA of yield strength for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the yield strength values. Figure 4.8 shows the best sequence of parameters in order to obtain the highest yield strength in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for yield strength values was found as, 0.5 wt% CaCO₃ reinforced triangular internal architected parts printed at 60 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest yield strength, resulting in the highest stress beyond their plastic deformation. As a consequence of its geometry, a typical loading causes tension and compression to act concurrently on the parts that have a triangular internal architecture, so that the triangular internal architecture improves the reinforcing effects of nanoadditives on the mechanical response of 3D printed samples. The probable causes about the phenomena in the 0.5 wt% reinforced parts have been explained in the analysis of modulus of elasticity.

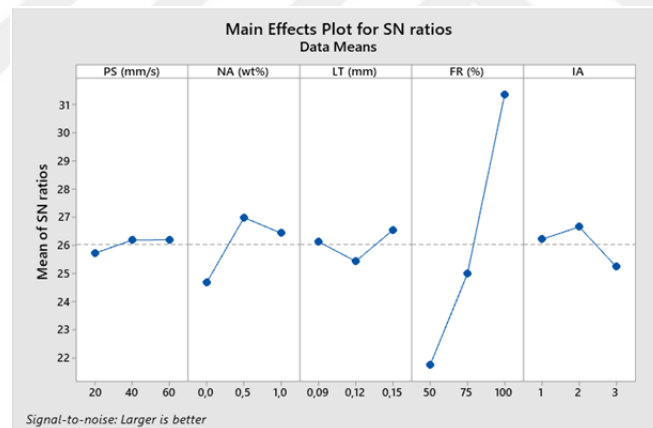


Figure 4.8. S/N ratios from Taguchi analysis for the yield stress.

A response surface methodology (RSM) was employed to model and predict the mechanical properties such as modulus of elasticity and yield strength of the PLA-based nanocomposites produced in different weight ratios and different with FDM printing parameters. Design of experiments (DOE) and response surface methodology (RSM) with an orthogonal array of the Taguchi method have been conducted to obtain optimum input parameters for the best mechanical properties of parts.

Table 4.3. ANOVA for modified quadratic model of yield stress of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3447.43	9	383.05	81.03	< 0.0001	significant
A-PS (mm/s)	154.48	1	154.48	32.68	< 0.0001	
B-NA (%)	63.96	1	63.96	13.53	0.0019	
C-LT (mm)	15.72	1	15.72	3.33	0.0858	
D-FR (%)	68.27	1	68.27	14.44	0.0014	
E-IA	47.14	2	23.57	4.99	0.0198	
AB	70.51	1	70.51	14.92	0.0013	
AC	124.04	1	124.04	26.24	< 0.0001	
BC	104.14	1	104.14	22.03	0.0002	
Residual	80.37	17	4.73			
Cor Total	3527.80	26				
R ² , 0.9772; adjusted R ² , 0.9652; predicted R ² , 0.9454; adequate precision, 27.0350						

Table 4.3 represents the ANOVA for the modified quadratic model of the yield strength of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. The model F-value of 81.03 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, D, E, AB, AC, and BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the yield strength of PLA and PLA-based nanocomposites. The most important factors influencing the yield strength of PLA based nanocomposites were found as printing speed (mm/s), nanoparticle addition (%), filling ratio (%) and internal architecture, with probability values of $p < 0.0001$, $p = 0.0019$, $p = 0.0014$ and $p = 0.0198$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition (AB), printing speed $\times$ layer thickness (AC), and nanoparticle addition $\times$ layer thickness (BC) were also found to be significant with probability values of $p = 0.0013$, $p < 0.0001$ and $p = 0.0002$, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9772 suggested that 97.72% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.9454 is in reasonable agreement with the Adjusted R^2 of 0.9652; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the yield strength are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 27.035 indicates an adequate signal. This model can be used to navigate the design space.

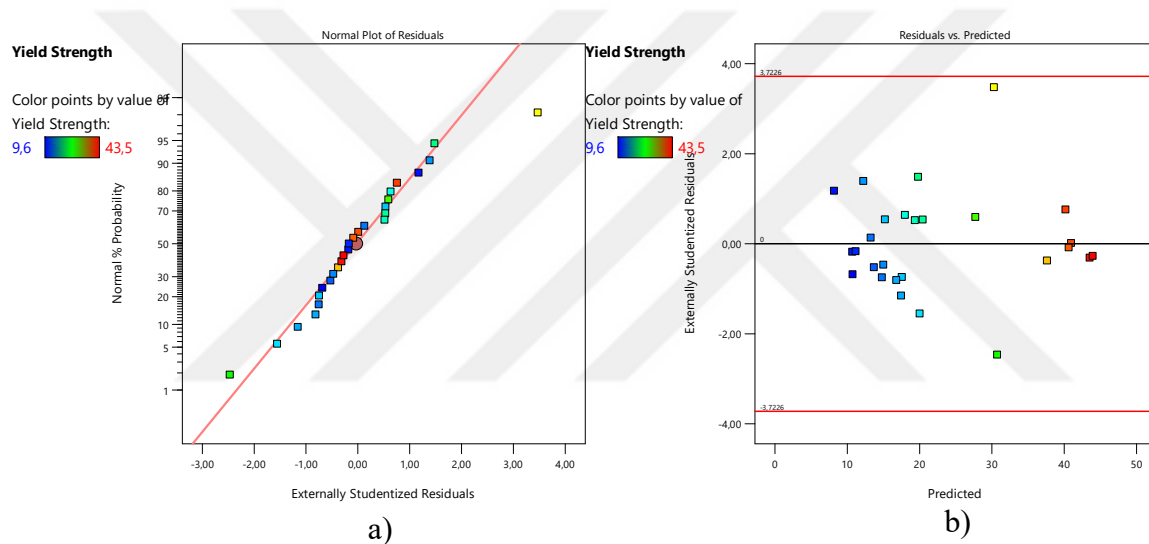


Figure 4.9. a) Normal plot of residuals b) residuals vs predicted plot of yield stress of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.9 represents the normal of residuals and residuals vs. predicted plots for the yield stress values of PLA and PLA-based nanocomposites from uniaxial tensile tests. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of yield stress values shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy. 3D surface diagrams show the interactive effects of input parameters on the response variable. According to Table 4.3, the interactions between AB, AC and BC were

found significant. To better understand the interaction between these parameters, 3D response surface graphs have been plotted.

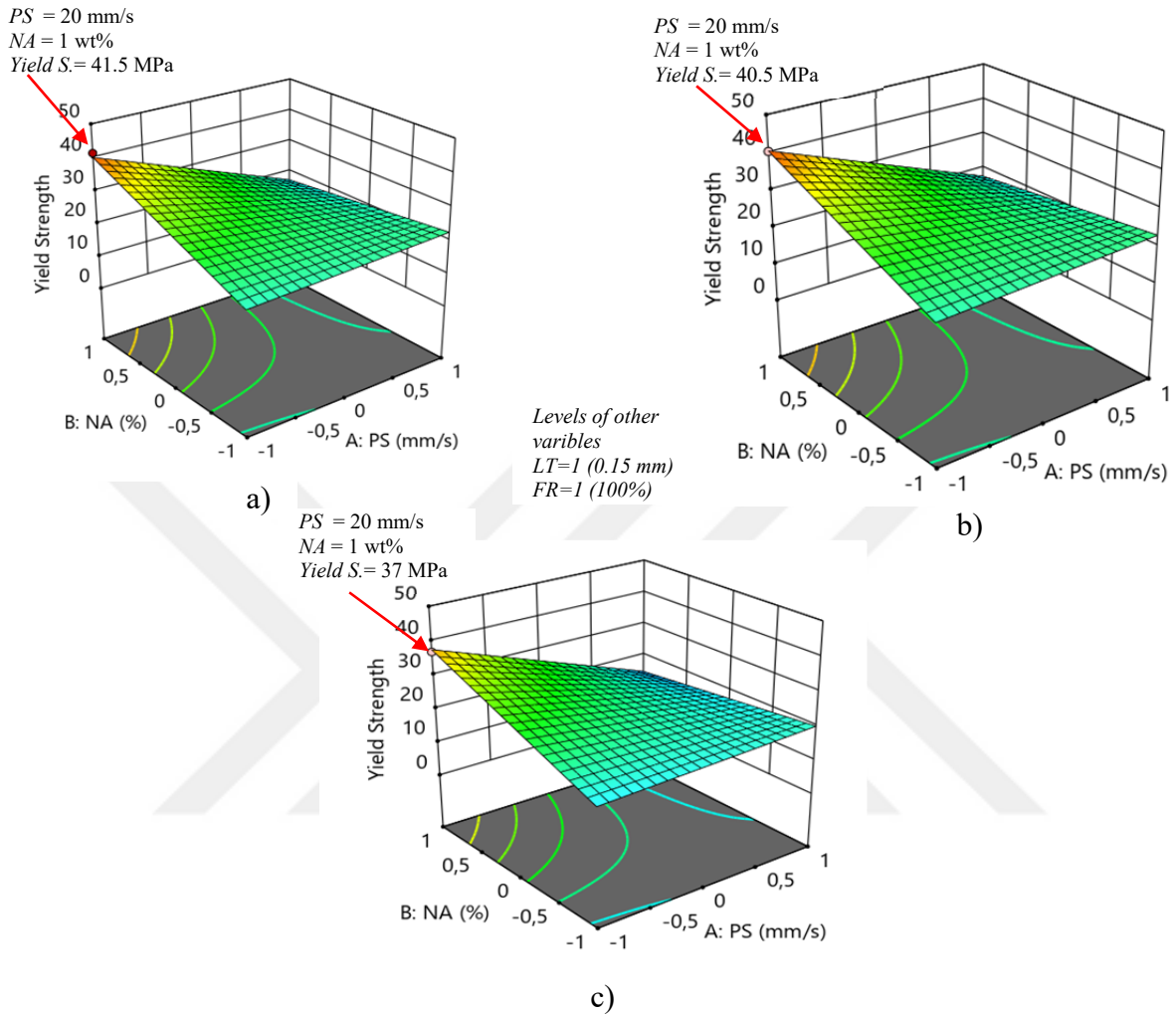


Figure 4.10. 3D response surface plot for PS (mm/s) and NA (%) of yield stress of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.10 represents the interaction between printing speed (mm/s) and nanoparticle addition (%) of parts printed in linear, triangular and hexagonal internal architectures on the yield stress value from uniaxial tests. As can be seen from these figures, parts printed with linear internal architecture have the highest yield stress value. In comparison to other two filling patterns, linear internal architecture with a cross deposition structure of printed beads at $\pm 45^\circ$ assures that polymer molecules are oriented along the shear loading that may arise during tensile testing, and it may absorb the most energy before breaking. Additionally, it can

be observed that the printing speed needs to be decreased with the increase of nanoparticle addition in all types of internal architectures.

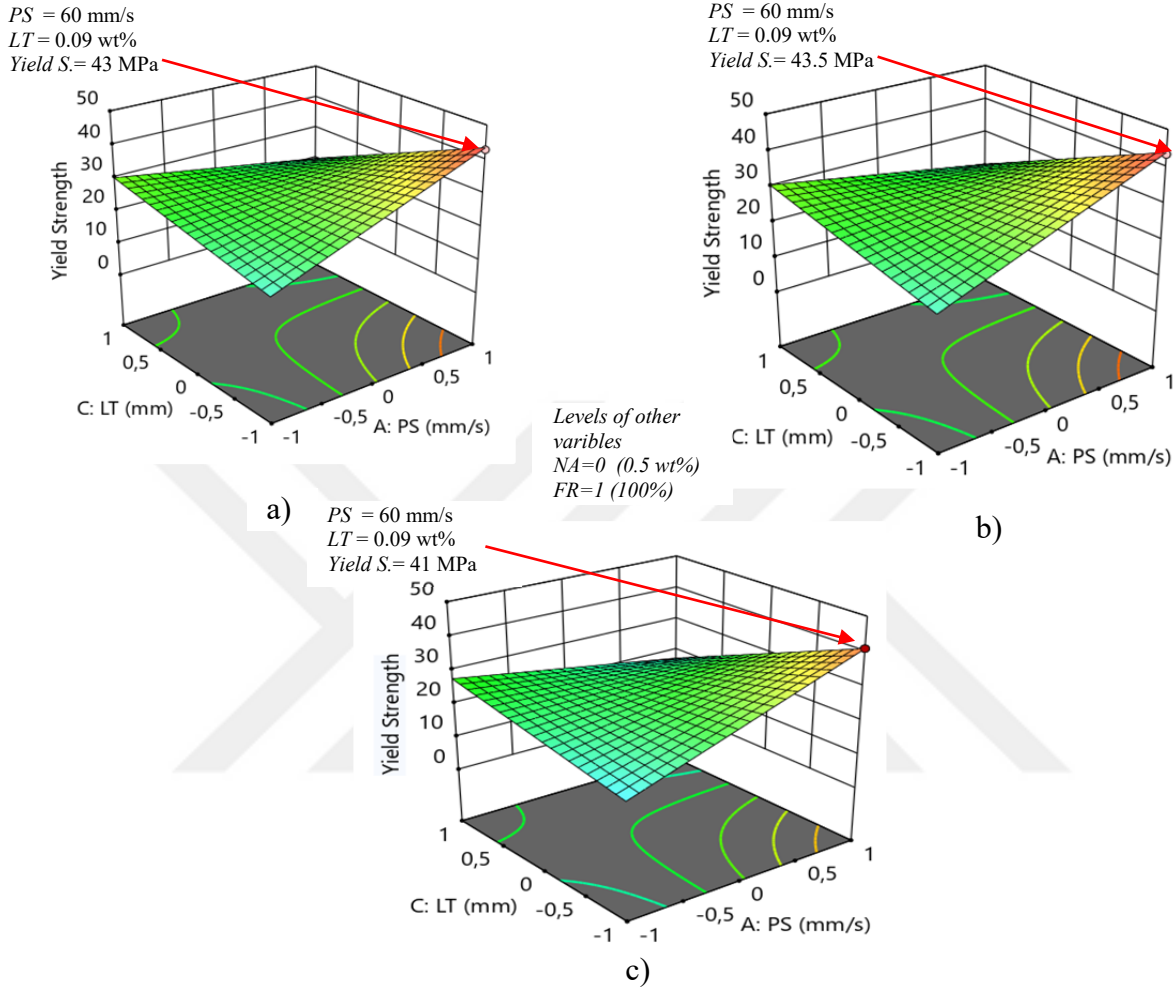


Figure 4.11. 3D response surface plot for PS (mm/s) and LT (mm) of yield stress of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.11 represents the interaction between the printing speed (mm/s) and layer thickness (mm) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for the yield strength of parts. The 3D response surfaces have less fluctuation, in other words, they have more smooth surfaces, parts printed with linear internal architecture yields the highest yield strength value, triangular and hexagonal parts have slight differences. The explanation of this situation mentioned above. This figure shows the printing speed change according to layer thickness at different internal architectures. As can be seen from this figure, it can be observed that the layer thickness should be decreased with the

increase of the printing speed in linear, triangular and hexagonal architectures to keep the mechanical performance of the parts. It can be said that the mechanical properties of parts increases with the increment of printing speed.

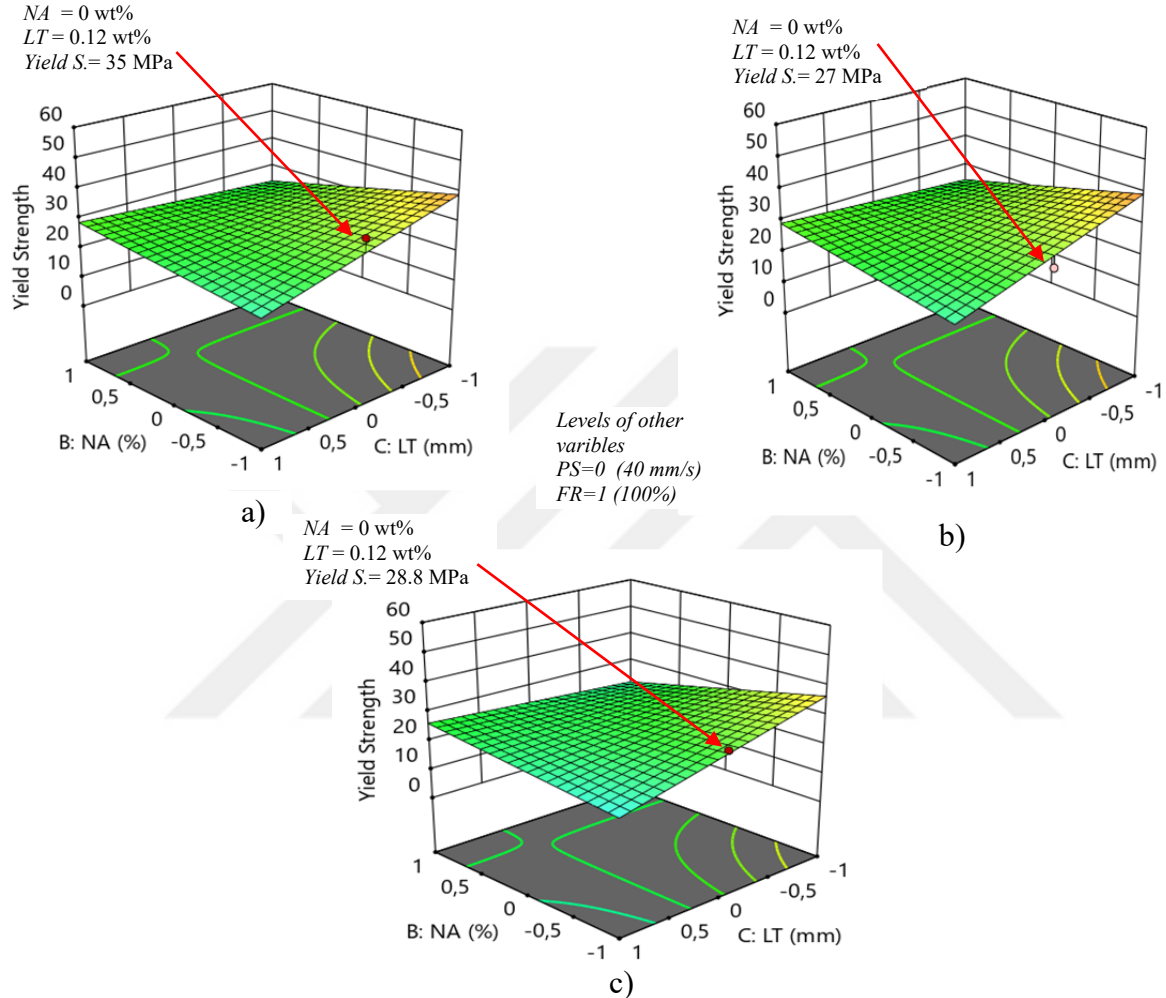


Figure 4.12. 3D response surface plot for NA (%) and LT (mm) of yield stress of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.12 represents the interaction between the nanoparticle addition (%) and layer thickness (mm) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for yield stress values. As can be seen in red areas and their position in diagrams in this figure, parts printed with linear internal architecture yields the highest yield stress value, triangular and hexagonal parts have slight differences. This figure shows the nanoparticle addition change according to layer thickness at different internal architectures. As can be seen from Figure 4.12, it can be observed that the layer thickness

should be decreased with the increase of nanoparticle addition in linear, triangular and hexagonal architectures. It can be said that the fracture properties of parts increases with the increment of nanoparticle addition.

4.2. Fracture tests results

Fracture tests of parts under Mode I, Mode I/II and Mode II loadings were carried out at room temperature using a Shimadzu AGS-X tensile testing machine, with a special fixture mounted onto the machine. Table 4.4 represents the experimental results of fracture properties of PLA/CaCO₃ nanocomposites fabricated under different FDM parameters according to the Taguchi L_{27} table. The approach to the calculation procedure of tensile properties was described in Chapter 3.

Table 4.4. Experimental results of fracture properties of PLA/CaCO₃ nanocomposites fabricated under different FDM parameters according to Taguchi L_{27} scheme.

	0°			45°				90°		
Exp erim ental run	P_C	K_I	J_I	P_C	K_I	K_{II}	J_T	P_C	K_{II}	J_{II}
1	913	0.91	1.157	530	0.36	0.48	0.5	755	0.63	0.546
2	699	0.69	0.351	794	0.54	0.72	0.592	830	0.69	0.345
3	518	0.51	0.355	630	0.43	0.57	0.688	600	0.5	0.334
4	1566	1.57	1.939	1080	0.73	0.98	1.174	1240	1.03	0.832
5	874	0.88	0.391	1240	0.84	1.13	0.999	1790	1.48	1.112
6	783	0.78	0.449	1130	0.77	1.03	1.215	1550	1.27	1.203
7	3710	3.81	4.136	2800	1.9	2.54	2.873	3590	2.98	2.53
8	3260	3.28	3.697	2190	1.5	2	2.152	3270	2.68	2.466
9	3380	3.44	3.383	2410	1.63	2.19	2.133	3320	2.74	2.149
10	3130	3.17	3.478	2350	1.59	2.13	2.455	3140	2.59	2.316
11	2130	2.16	1.6	1780	1.21	1.62	1.389	2130	1.75	1.044
12	2050	2.1	1.396	1900	1.29	1.73	1.463	2200	1.82	1.046
13	1150	1.15	1.249	780	0.53	0.71	0.732	750	0.63	0.367
14	1011	1	0.718	1207	0.82	1.1	1.34	915	0.76	0.409
15	910	0.91	0.737	825	0.56	0.75	0.781	1120	0.93	0.768
16	1920	1.94	2.354	1420	0.96	1.29	1.627	1730	1.43	1.293
17	1183	1.19	0.59	1420	0.96	1.29	1.087	1780	1.45	0.876
18	1118	1.11	0.897	990	0.67	0.9	0.909	1550	1.28	1.177
19	1300	1.31	1.366	1020	0.69	0.93	1.068	1030	0.86	0.59
20	1230	1.25	0.719	1125	0.76	1.02	0.749	1340	1.12	0.58
21	1020	1.01	0.82	1050	0.71	0.95	1.145	1070	0.88	0.626
22	2920	2.99	2.321	2540	1.72	2.31	2.149	3426	2.84	2.093
23	2660	2.72	1.918	2320	1.57	2.11	1.787	2950	2.45	1.554
24	2820	2.89	2.225	2560	1.74	2.32	2.238	2950	2.46	1.604
25	1090	1.1	1.22	780	0.53	0.71	0.785	790	0.66	0.443
26	760	0.75	0.416	900	0.61	0.82	0.769	835	0.69	0.351
27	765	0.76	0.678	755	0.51	0.69	0.859	960	0.79	0.735

4.2.1. K_I fracture toughness in the Mode-I loading

The effects of the printing speed on the mode-I fracture toughness of PLA/CaCO₃ nanoparticles are depicted through Figure 4.13, while the layer thickness and filling ratio are kept at their middle ranges.

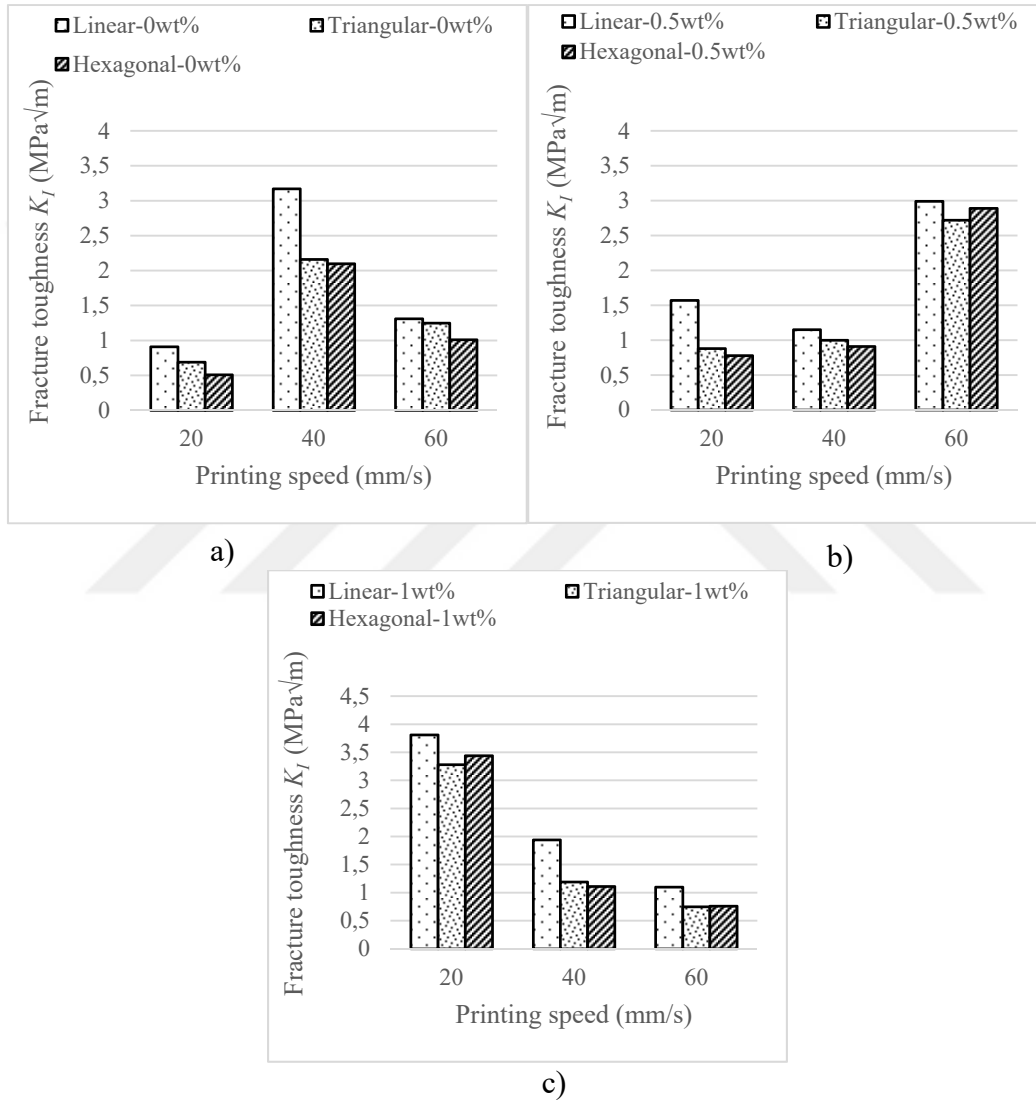


Figure 4.13. Effects of printing speed (mm/s) on K_I fracture toughness in the Mode-I values of a) pure b) 0.5 wt% CaCO₃/PLA and c) 1 wt% CaCO₃/PLA parts printed in different internal architectures.

In the investigation of the effects of the printing speed on the mode-I fracture toughness (K_I) of pure PLA parts, similar to the modulus of elasticity of fabricated samples, parts printed at

40 mm/s have the best fracture toughness results in opening mode with 3.17 MPa√m. In pure PLA parts, while the linear architecture has the best result at 40 mm/s, hexagonal structure printed at 20 mm/s resulted in the lowest value with 0.51 MPa√m. In pure PLA parts, changing the architecture from hexagonal to linear while increasing the printing speed from 20 mm/s to 40 mm/s, increases the K_I fracture toughness value by about 84%. However, increasing the printing speed from 40 mm/s to 60 mm/s while changing the structure from linear to hexagon, decreases K_I by about 68%. Unlike the results of E , in all printing speeds, linear architecture has the highest fracture toughness, in which the part printed at 40 mm/s is the highest, and it is followed by the parts printed at 60 mm/s. This may be caused by the linear internal architecture with a cross deposition structure of printed beads at $\pm 45^\circ$ assures that polymer molecules are oriented along the shear loading that may arise during mixed-mode testing, and it may absorb the most energy before breaking. Overall, pure PLA parts printed at 20 mm/s speed have the lowest fracture toughness values in the Mode-I loading. As can be seen from figure, 0.5 wt% CaCO₃ reinforced PLA parts printed at 60 mm/s printing speed has the highest fracture toughness values in the Mode-I loading. In 60 mm/s, linear architecture has the highest toughness value with 2.99 MPa√m while the hexagonal parts printed at 20 mm/s is the lowest. From the Figure 4.13, results for 1 wt% CaCO₃ reinforced PLA parts, linear part printed at 20 mm/s printing speed has the highest fracture toughness values for the Mode-I loading with 3.81 MPa√m, while the triangular and hexagonal parts printed at 60 mm/s have the lowest with 0.75 and 0.76 MPa√m. This situation might be shows the negative effects of higher printing speed on the adhesion behavior of molten layers resulted in different architectures. The reason for this may be that the interfacial interactions between the components of the nanocomposites are the primary factor underlying the property changes. For instance, the filler, which is meant to be stiff and strong, carries the majority of the load or stress placed on the matrix, whereas the polymer matrix, which is tougher but less strong, only efficiently transfers the load to the filler if the interfacial contacts are sufficiently strong.

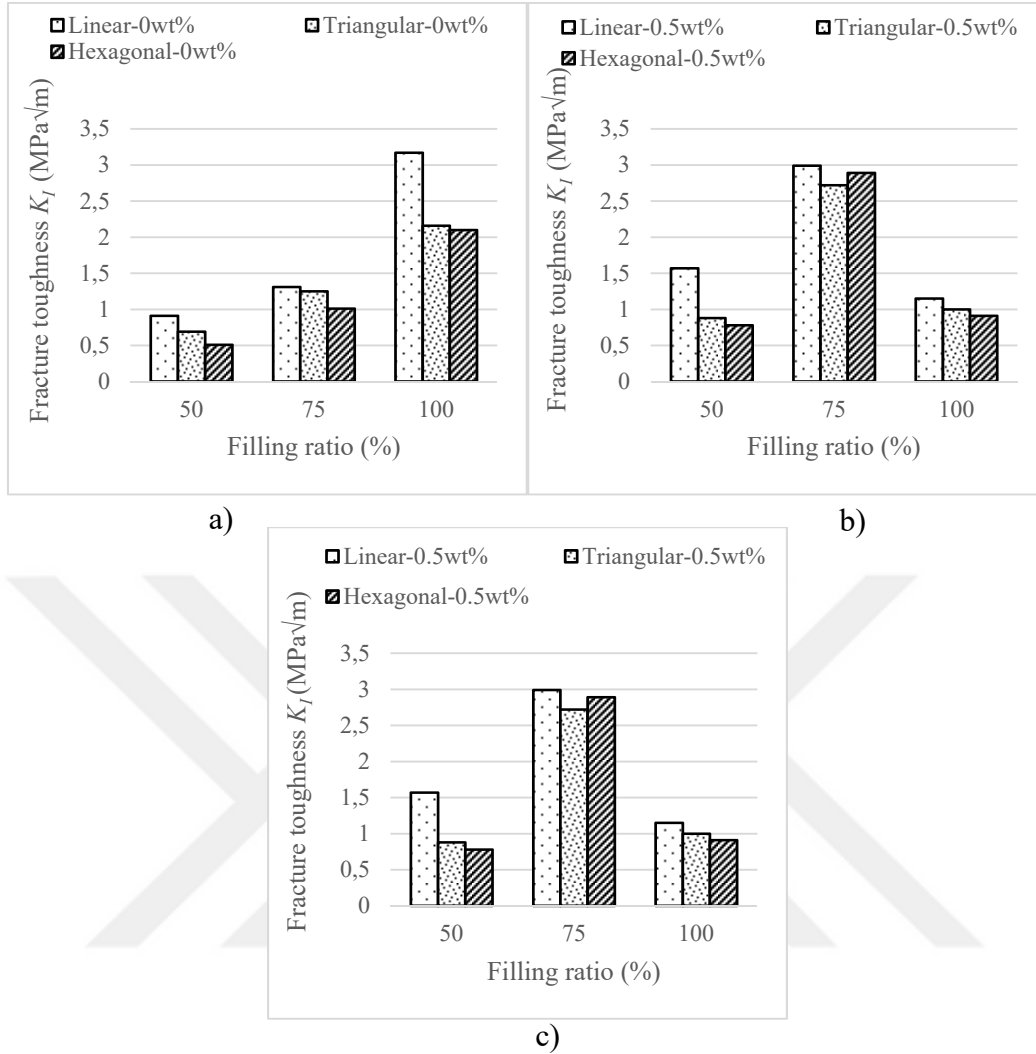


Figure 4.14. Effects of filling ratio (%) on K_I fracture toughness in the Mode-I loading values of a) pure b) 0.5 wt% CaCO₃/PLA and c) 1 wt% CaCO₃/PLA parts printed in different internal architectures.

The results of experiments and statistical modeling of the effects of filling ratio on the fracture performance of PLA/CaCO₃ nanoparticles are illustrated through Figure 4.14, while the printing speed and layer thickness are kept at their middle ranges. As can be seen from Figure 4.14, pure PLA parts printed in linear architecture with 100% filling ratio has the best fracture toughness. But overall, all the architectures printed at 100% filling ratio have the highest fracture toughness results in pure parts. This is an expected situation for pure parts, since they have no reinforcement, the fewer gaps in the parts will achieve better results in fracture properties. Fracture toughness values have resulted in different concentrations of 0.5 wt% and

1 wt% reinforced parts, overall, while the amount of reinforcement increases, the lower filling ratios have achieved better results in the Mode-I fracture toughness values. In order to see and better understand the dispersion of nanoparticles and the gaps and molten filaments in the parts, data from SEM examinations would help. Figure 4.15 represents the SEM images of pure PLA triangular structured parts printed at 20 mm/s printing speed, 0.09 mm layer thickness, and 50% filling ratio. The primary drawback of using PLA is its innate brittleness. The impact fracture surface of PLA displays straight crack propagation lines, as would be expected in a brittle polymer. The specimen is easy to shatter with less energy because of these straight lines, which also encourage further growth. It can be clearly seen that printed layers have good accuracy while printing. In x50 magnification, the adhesion of layers in the triangular architecture looks almost perfect, but in x500, the gaps of layers can be seen clearly. This gaps could be reduced version of 40 mm/s or 60 mm/s printing speeds because in 20 mm/s speed, molten materials have enough time to bond with the previous layer. Even in the lowest printing speed, the gaps between layers are inevitable due to the nature of FDM 3D printing. As can be seen in x50 magnification, in triangular structure, layers of specimens printed perpendicular to Mode-I loading. In this situation, the important point is the strength of the adhesion behavior of materials, not the strength of molten layers directly. This situation can be evaluated with SEM results from Figures 4.15 - 4.17, the interactions between layers of molten filaments have fewer gaps and they have better adhesion.

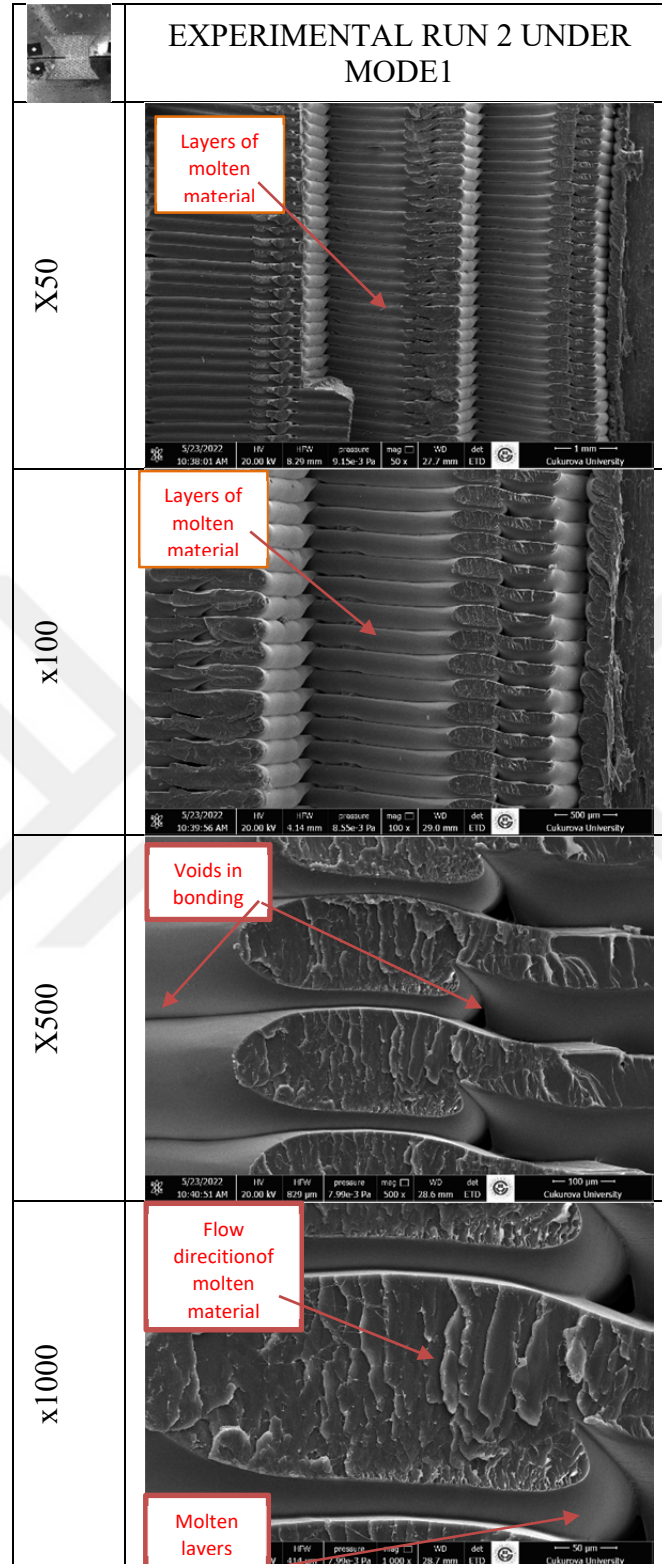


Figure 4.15. SEM images in different magnifications of internal layers of pure triangular PLA parts printed at 20 mm/s printing speed, 0.09 mm layer thickness and 50% filling ratio (Taguchi Experimental Run 2) under Mode-I loading.

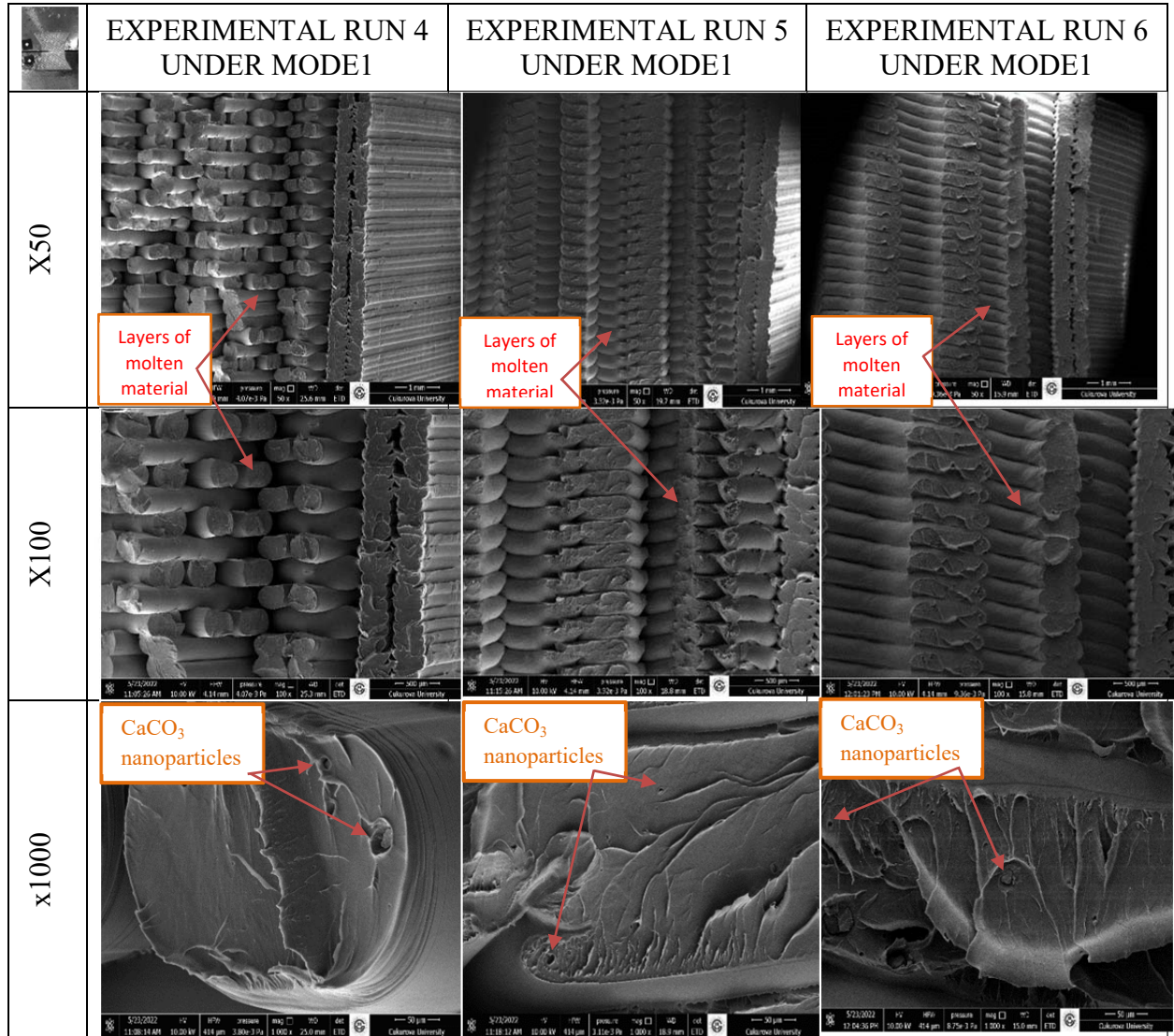


Figure 4. 16. SEM images in different magnifications of internal layers of a) 0.5 wt% CaCO_3 linear PLA parts printed at 20 mm/s printing speed, 0.12 mm layer thickness and 75% filling ratio (Taguchi Experimental Run 4), b) 0.5 wt% CaCO_3 triangular PLA parts printed at 20 mm/s printing speed, 0.12 mm layer thickness and 75% filling ratio (Taguchi Experimental Run 5), c) 0.5 wt% CaCO_3 hexagonal PLA parts printed at 20 mm/s printing speed, 0.12 mm layer thickness and 75% filling ratio (Taguchi Experimental Run 6), under Mode-I loading at x50, 100 and 1000 magnifications.

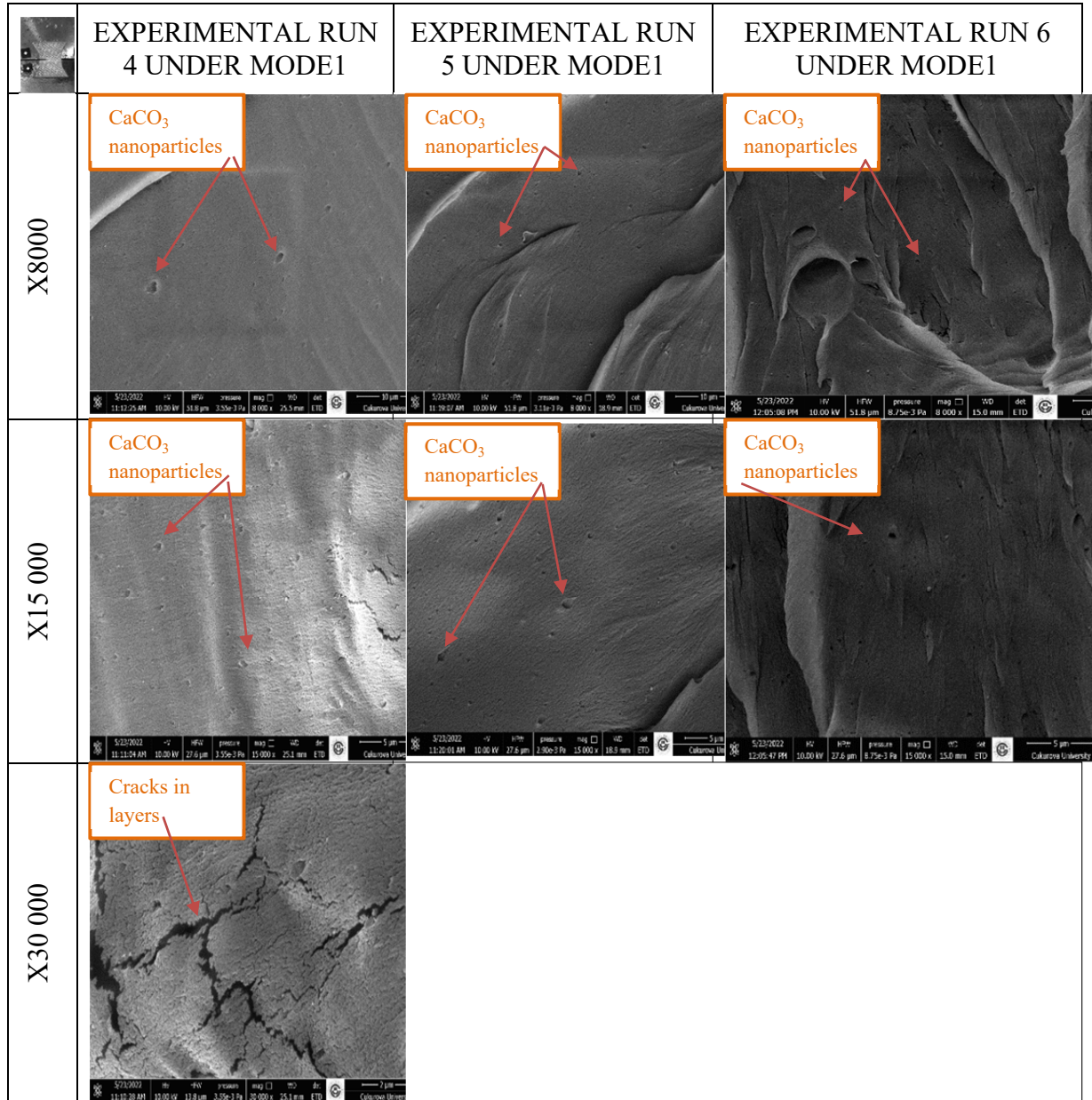
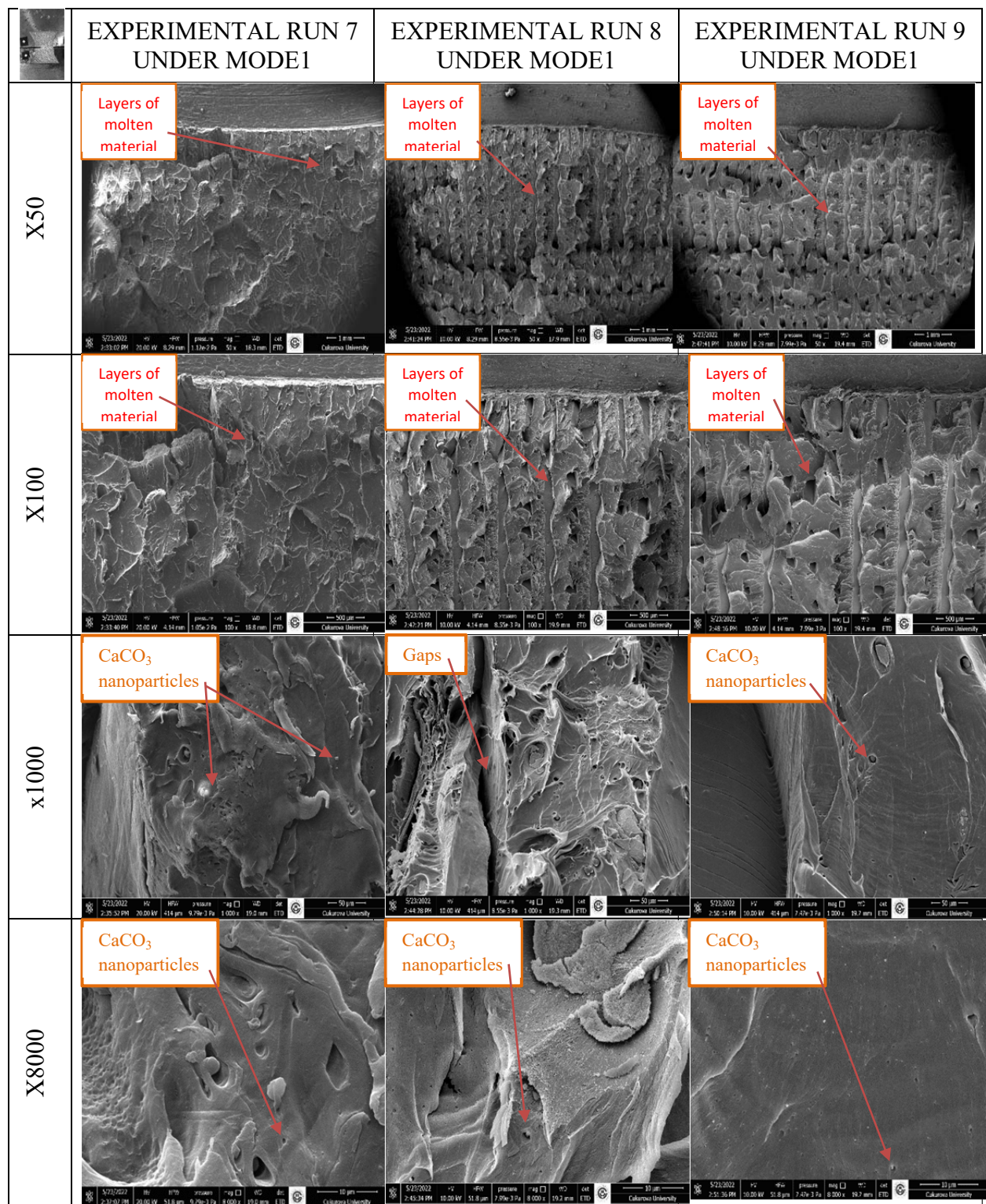


Figure 4.17. SEM images in different magnifications of internal layers of a) 0.5 wt% CaCO_3 linear PLA parts printed at 20 mm/s printing speed, 0.12 mm layer thickness and 75% filling ratio (Taguchi Experimental Run 4), b) 0.5 wt% CaCO_3 triangular PLA parts printed at 20 mm/s printing speed, 0.12 mm layer thickness and 75% filling ratio (Taguchi Experimental Run 5), c) 0.5 wt% CaCO_3 hexagonal PLA parts printed at 20 mm/s printing speed, 0.12 mm layer thickness and 75% filling ratio (Taguchi Experimental Run 6), under Mode-I loading at x8000, 15000 and 30000 magnifications.

Figures 4.16 and 4.17 represent the SEM images in different magnifications of internal layers of 0.5 wt% CaCO_3 PLA parts linear, triangular and hexagonal internal architectures and printed at 20 mm/s printing speed, 0.12 mm layer thickness and 75% filling ratio under Mode-I loading. The effects and differences of internal architectures and nanoparticle addition can be observed for the interpretation of morphological structure of specimens. Brittle behavior of PLA has been targeted to be prevented with nanoparticle reinforcements. PLA/ CaCO_3 nanocomposites have similar fracture surfaces to pure PLA, which represented in Figure 4.15. In all situations for this three types of specimens, even with the addition of 0.5 wt% of nanoparticles, specimens showed brittle behavior. A significant proportion of the fracture propagation lines are clear and extensive. In comparison to pure PLA, the surfaces of the nanocomposites are rougher. The presence of nanoparticles has led to the development of tiny fractures that point in various directions. It can be seen from x100 magnifications that linear internal architecture has +45/-45 sequence. This situation can be resulted best shearing stress in parts. Besides, the gaps between layers can be seen clearly, this situation reduces the strength of materials. In triangular and hexagonal architectures, layers of specimens printed perpendicular to Mode-I loading. In this situation, the important point is the strength of the adhesion behavior of materials, not the strength of molten layers directly. As can be seen from x1000, x8000, x15000 magnifications, CaCO_3 nanoparticles have dispersed perfectly into the PLA polymer matrix. Porosity and gaps cause the weakened mechanical and fracture characteristics of FDM 3D printed parts.



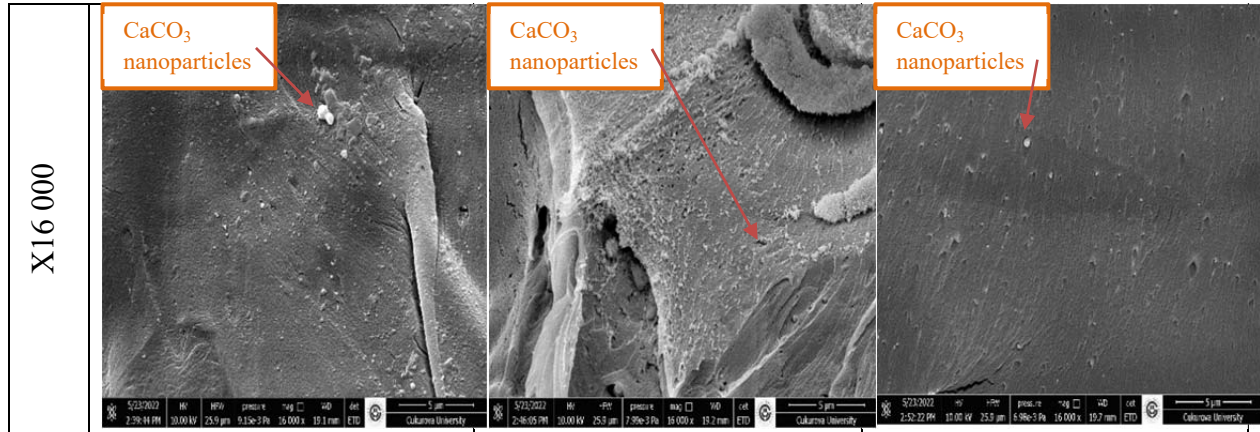


Figure 4.18. SEM images in different magnifications of internal layers of a) 1 wt% CaCO_3 linear PLA parts printed at 20 mm/s printing speed, 0.15 mm layer thickness and 100% filling ratio (Taguchi Experimental Run 7), b) 1 wt% CaCO_3 triangular PLA parts printed at 20 mm/s printing speed, 0.15 mm layer thickness and 100% filling ratio (Taguchi Experimental Run 8), c) 1 wt% CaCO_3 hexagonal PLA parts printed at 20 mm/s printing speed, 0.15 mm layer thickness and 100% filling ratio (Taguchi Experimental Run 9), under Mode-I loading.

Figure 4.18 represents the SEM images in different magnifications of internal layers of 1 wt% CaCO_3 PLA parts linear, triangular and hexagonal internal architectures and printed at 20 mm/s printing speed, 0.15 mm layer thickness and 100% filling ratio under Mode-I loading. The effects and differences of internal architectures and nanoparticle addition can be observed for the interpretation of morphological structure of specimens. As can be seen from SEM results in Figures 4.16 - 4.18, polymer matrix interacted with nanoparticle surfaces and intertwined around such nanoparticles, this situation could be increased the load bearing capacity of polymers. In the comparison between 0.5 wt% CaCO_3 reinforced parts from Figures 4.16 and 4.17, the surfaces of the nanocomposites are rougher and addition of 1 wt% CaCO_3 provides more ductile behavior of triangular parts. From x50 and x100 magnifications, linear structured parts have printed almost no voids than other two structures. This situation may be provided by lower printing speed because the molten filaments have enough time to bond with the previous layer and design nature of these three architectures. Parts printed with hexagonal internal architecture exhibit more brittle fracture behavior and a relatively straight fracture surface. Even the 1 wt% CaCO_3 nanoparticles are quantitatively more in the matrix, they have showed good dispersion into the PLA matrix. This situation strengthens the material to the loadings.

4.2.1.1. ANOVA of K_I fracture toughness in the Mode-I for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the mode-I fracture toughness (K_I) values. Figure 4.19 shows the best sequence of parameters in order to obtain the highest mode-I fracture toughness (K_I) in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the mode-I fracture toughness (K_I) values was found as, 1 wt% CaCO₃ reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. According to the Taguchi analysis and experimental results, it can be concluded that the addition of nanoparticles by 1 wt% into the PLA matrix has resulted in better Mode-I fracture toughness characteristics. Printed parts with this sequence will have the highest toughness in the opening mode, resulted in highest strain energy release rate in this study.

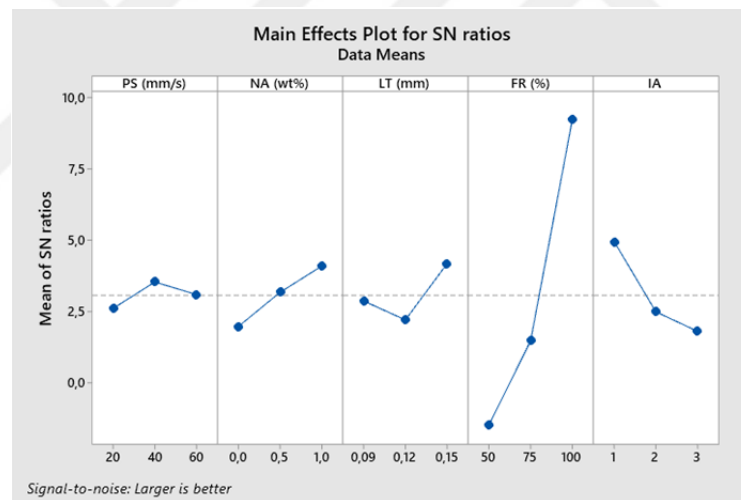


Figure 4.19. S/N ratios from Taguchi analysis for K_I fracture toughness in the Mode-I loading.

A response surface methodology (RSM) was employed to model and predict the fracture properties of the PLA-based nanocomposites produced in different weight ratios and different FDM printing parameters. Design of experiments (DOE) and response surface methodology (RSM) with an orthogonal array of the Taguchi method have been conducted to obtain optimum input parameters for the best fracture characteristics of parts.

Table 4.5. ANOVA for modified quadratic model of K_I fracture toughness in the Mode-I of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	25.59	9	2.84	70.17	< 0.0001	significant
A-PS (mm/s)	0.3859	1	0.3859	9.52	0.0067	
B-NA (%)	0.7846	1	0.7846	19.36	0.0004	
C-LT (mm)	0.5220	1	0.5220	12.88	0.0023	
D-FR (%)	2.24	1	2.24	55.25	< 0.0001	
E-IA	1.26	2	0.6286	15.52	0.0001	
AB	0.7823	1	0.7823	19.31	0.0004	
BC	3.10	1	3.10	76.56	< 0.0001	
A ²	0.8788	1	0.8788	21.69	0.0002	
Residual	0.6888	17	0.0405			
Lack of Fit	0.6310	16	0.0394	0.6823	0.7564	not significant
Pure Error	0.0578	1	0.0578			
Cor Total	26.27	26				
R ² , 0.9738; adjusted R ² , 0.9599; predicted R ² , 0.9330; adequate precision, 26.9402						

Table 4.5 represents the ANOVA for modified quadratic model of K_I fracture toughness in the Mode-I of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. The model F-value of 70.17 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AB, BC, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The Lack of Fit F-value of 0,68 implies the Lack of Fit is not significant relative to the pure error. There is a 75.64% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good, the model should be fitted. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the K_I fracture toughness in the Mode-I loading of PLA and PLA-based nanocomposites. The most important factors influencing K_I fracture toughness in the Mode-I of PLA based nanocomposites were found as printing speed (mm/s), nanoparticle addition (%), layer thickness (mm), filling ratio (%), and internal architecture with probability values of $p = 0.0067$, $p = 0.0004$, $p = 0.0023$, $p < 0.0001$ and $p = 0.0198$, respectively. It was also noticed that the interaction effects between printing speed $\times$

nanoparticle addition (AB), and nanoparticle addition $\times$ layer thickness (BC) were also found to be significant with probability values of $p = 0.0004$ and $p < 0.0001$, respectively. The quadratic effects of the printing speed was also found to be significant with p value of 0.0002, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9738 suggested that 97.38% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.9330 is in reasonable agreement with the Adjusted R^2 of 0.9599; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the K_I fracture toughness in the Mode-I are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 26.940 indicates an adequate signal. This model can be used to navigate the design space.

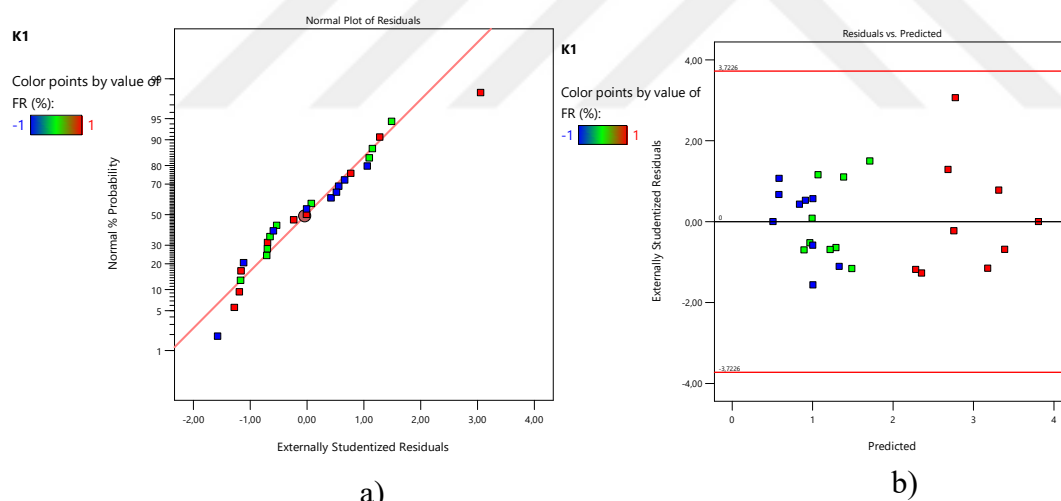


Figure 4.20. a) Normal plot of residuals b) residuals vs predicted plot of K_I fracture toughness in the Mode-I of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.20 indicates the normal of residuals and residuals vs. predicted plots for K_I fracture toughness of PLA and PLA-based nanocomposites in the Mode-I loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The

plot of predicted values vs. residuals of K_I fracture toughness in the Mode-I loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy. 3D surface diagrams show the how input parameters affect each other. According to Table 4.5, the interactions between AB and BC were found significant. To better understand the interaction between these parameters, 3D response surface graphs have been plotted.

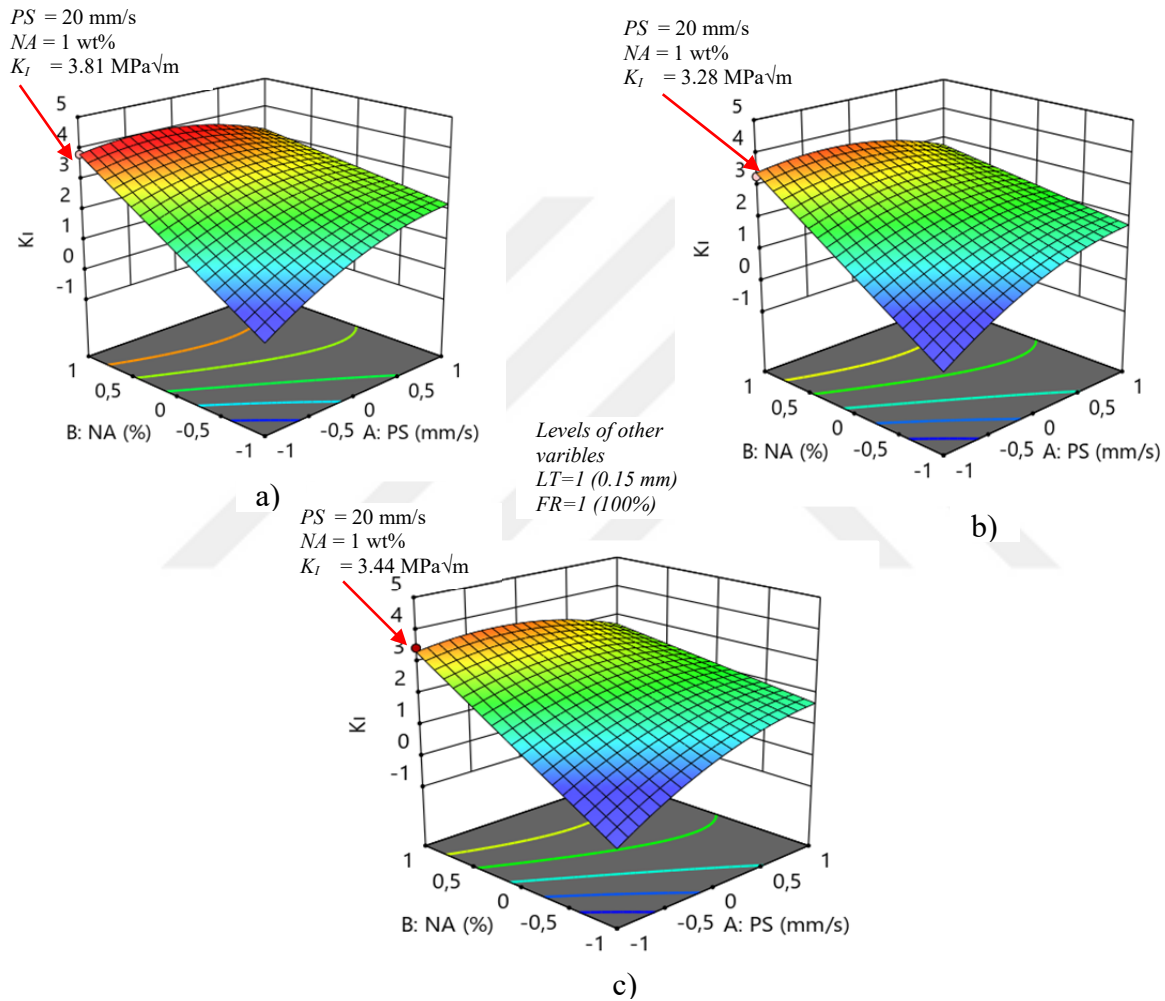


Figure 4.21. 3D response surface plot for PS (mm/s) and NA (%) of K_I fracture toughness in the Mode-I of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.21 represents the interaction between printing speed (mm/s) and nanoparticle addition (%) of parts printed in linear, triangular and hexagonal internal architectures for K_I fracture toughness in the Mode-I loading. As can be seen in red areas and their position in diagrams in this figure, parts printed with linear internal architecture yields the highest

fracture toughness value. As can be seen from this figure, the printing speed needs to be decreased with the increase of nanoparticle addition in linear, triangular and hexagonal architectures to elevate the fracture toughness of fabricated nanocomposites in the Mode-I loading.

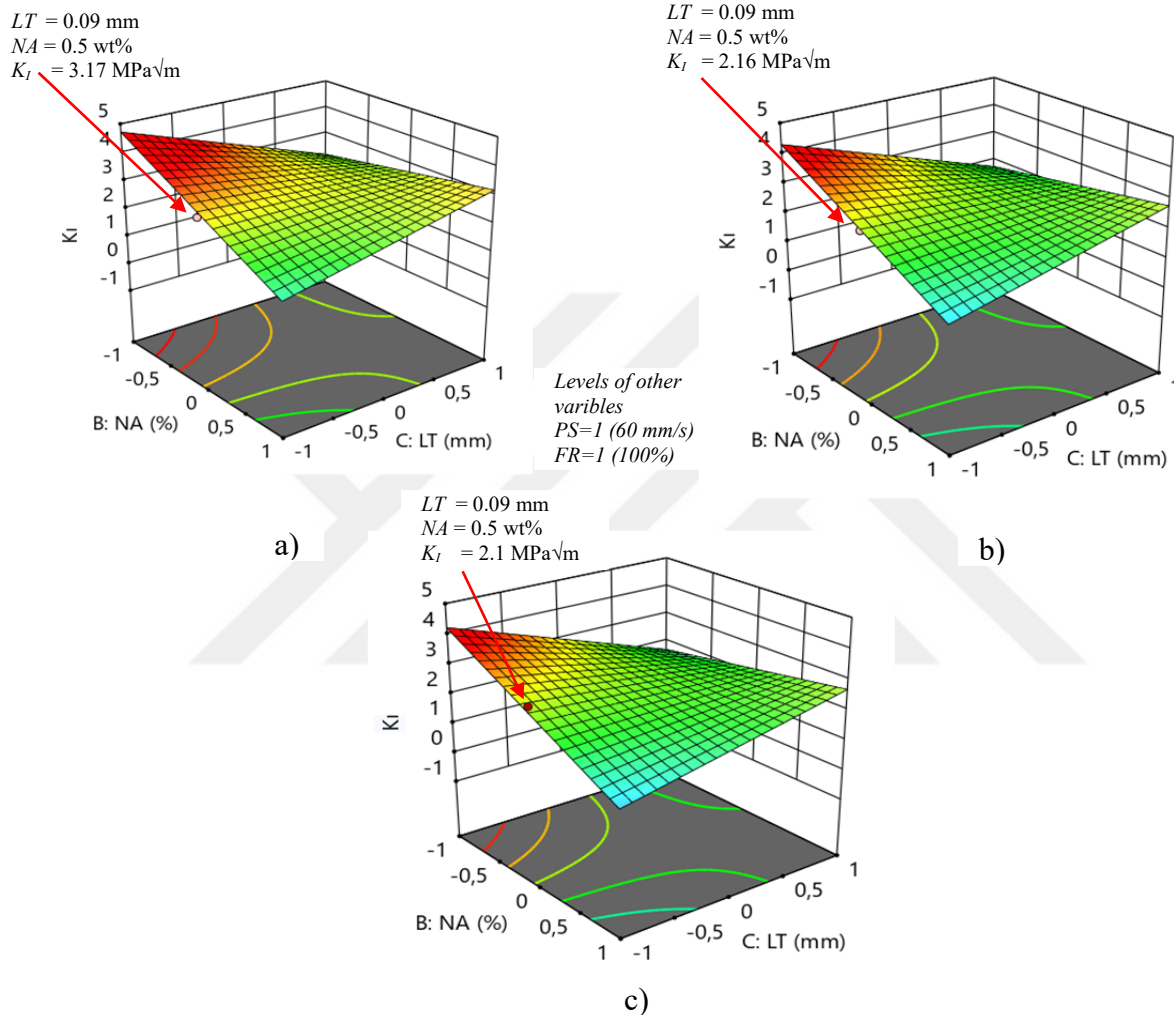


Figure 4.22. 3D response surface plot for NA (%) and LT (mm) of K_I fracture toughness in the Mode-I of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.22 represents the interaction between the nanoparticle addition (%) and layer thickness (mm) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_I fracture toughness in the Mode-I loading. As can be seen in red areas and their position in diagrams in this figure, parts printed with linear internal architecture yields the highest fracture toughness value, hexagonal parts have the lowest. This situation could be related to the fracture mechanism of printed beads of hexagonal internal

architecture. This situation evaluated with SEM results in Figure 4.18, sample printed with hexagonal internal architecture shows less ductile behavior with macro-sized printed beads, also in linear architecture, the interactions between layers of molten filaments have fewer gaps and they have better adhesion. This figure shows the nanoparticle addition change according to layer thickness at different internal architectures in the Mode-I loading. As can be seen from this figure, it can be observed that the layer thickness should be decreasing noticeably with the increase of nanoparticle addition in linear, triangular and hexagonal architectures to maintain a high fracture toughness of fabricated samples under mode-I loading. It can be said that the fracture properties of parts increases with the increment of nanoparticle addition.

4.2.2. ANOVA of P_C critical load in the Mode-I loading for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the critical load (P_C) values in the Mode-I. Figure 4.23 shows the best sequence of parameters in order to obtain the highest critical load in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the critical load (P_C) values in the Mode-I was found as, 1 wt% CaCO₃ reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest critical load in the opening mode in this study.

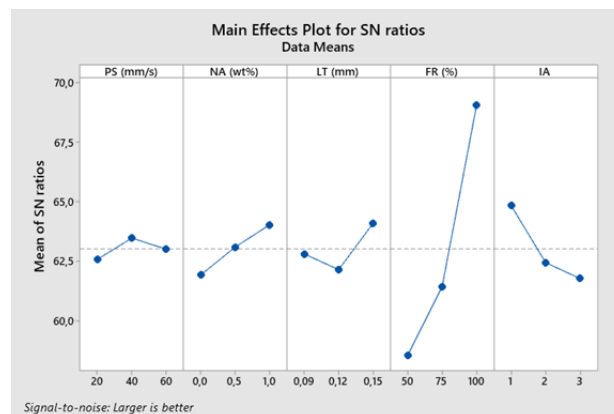


Figure 4.23. S/N ratios from Taguchi analysis for critical load P_C in the Mode-I.

Table 4.6. ANOVA for modified quadratic model of critical load (P_C) in the Mode-I of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.426E+07	9	2.696E+06	76.47	< 0.0001	significant
A-PS (mm/s)	5.093E+05	1	5.093E+05	14.45	0.0014	
B-NA (%)	9.781E+05	1	9.781E+05	27.75	< 0.0001	
C-LT (mm)	6.603E+05	1	6.603E+05	18.73	0.0005	
D-FR (%)	2.282E+06	1	2.282E+06	64.73	< 0.0001	
E-IA	1.264E+06	2	6.322E+05	17.93	< 0.0001	
AB	5.452E+05	1	5.452E+05	15.47	0.0011	
BC	2.776E+06	1	2.776E+06	78.74	< 0.0001	
A ²	7.118E+05	1	7.118E+05	20.19	0.0003	
Residual	5.993E+05	17	35252.52			
Cor Total	2.486E+07	26				
R ² , 0.9759; adjusted R ² , 0.9631; predicted R ² , 0.9386; adequate precision, 28.1947						

Table 4.6 represents the ANOVA for modified quadratic model of critical load (P_C) of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. The model F-value of 76.47 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AB, BC, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the critical load (P_C) in the Mode-I of PLA and PLA-based nanocomposites. The most important factors influencing critical load (P_C) in the Mode-I of PLA based nanocomposites were found as printing speed (mm/s), nanoparticle addition (%), layer thickness (mm), filling ratio (%), and internal architecture with probability values of $p = 0.0014$, $p < 0.0001$, $p = 0.0005$, $p < 0.0001$ and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition (AB), and nanoparticle addition $\times$ layer thickness (BC) were also found to be significant with probability values of $p = 0.0011$ and $p < 0.0001$, respectively. The quadratic effects of the printing speed was also found to be significant with p value of 0.0003, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9759 suggested that 97.59% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.9386 is in reasonable agreement with the Adjusted R^2 of 0.9631; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the critical load (P_C) in the Mode-I are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 28.195 indicates an adequate signal. This model can be used to navigate the design space.

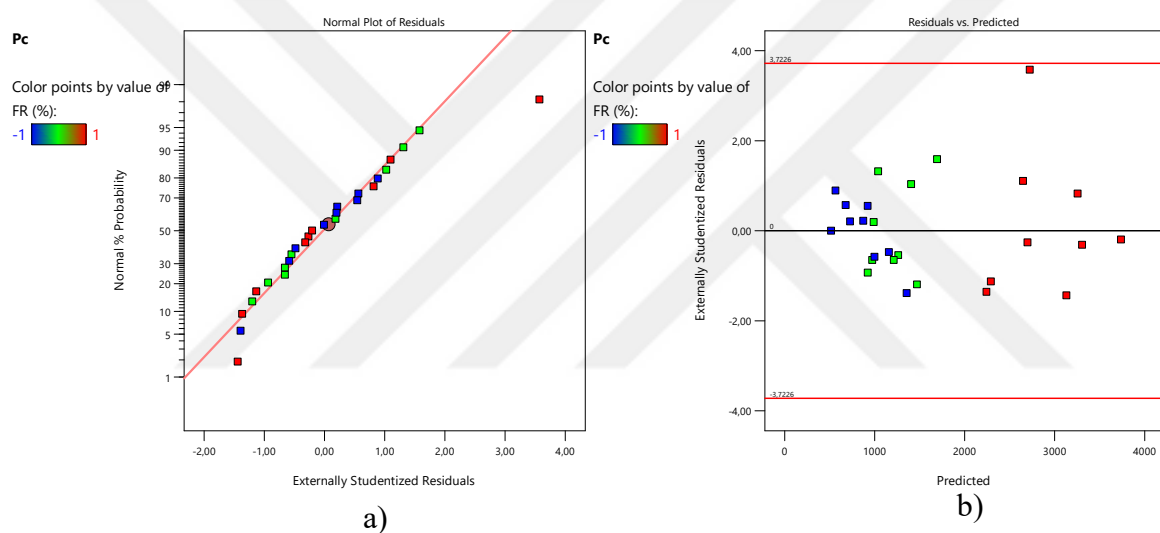


Figure 4.24. a) Normal plot of residuals b) residuals vs predicted plot of critical load (P_C) in the Mode-I of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.24 shows the normal of residuals and residuals vs. predicted plots for critical load P_C of PLA and PLA-based nanocomposites in the Mode-I loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of critical load P_C in the Mode-I loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy.

4.2.3. ANOVA of J_I strain energy release rate in the Mode-I loading for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the strain energy release rate (J_I) values in the Mode-I. Figure 4.25 shows the best sequence of parameters in order to obtain the highest strain energy release rate in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the strain energy release rate (J_I) values in the Mode-I found as, 1 wt% CaCO₃ reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest strain energy release rate in the opening mode in this study.

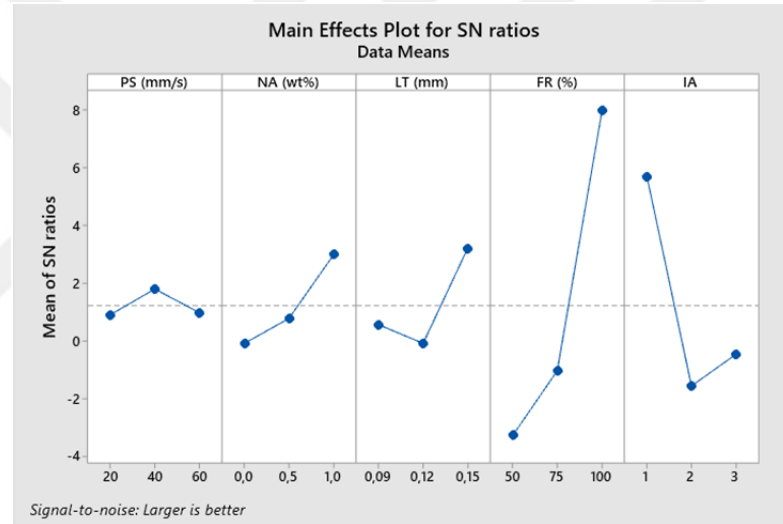


Figure 4.25. S/N ratios from Taguchi analysis for J_I in the Mode-I.

Table 4.7. ANOVA for modified quadratic model of strain energy release rate (J_I) in the Mode-I of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	28.67	7	4.10	22.68	< 0.0001	significant
A-PS (mm/s)	0.0294	1	0.0294	0.1626	0.6913	
B-NA (%)	2.09	1	2.09	11.55	0.0030	
C-LT (mm)	1.20	1	1.20	6.67	0.0182	
D-FR (%)	16.58	1	16.58	91.77	< 0.0001	
E-IA	5.43	2	2.72	15.03	0.0001	
BC	2.40	1	2.40	13.31	0.0017	
Residual	3.43	19	0.1806			
Cor Total	32.10	26				
R ² , 0.8931; adjusted R ² , 0.8537; predicted R ² , 0.7962; adequate precision, 17.7128						

Table 4.7 represents the ANOVA for modified quadratic model of the strain energy release rate (J_I) values of PLA and PLA-based nanocomposites produced at different printing parameters in the Mode-I. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. The model F-value of 22.68 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case B, C, D, E, BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the strain energy release rate (J_I) in the Mode-I of PLA and PLA-based nanocomposites. The most important factors influencing strain energy release rate (J_I) in the Mode-I of PLA based nanocomposites were found as nanoparticle addition (%), layer thickness (mm), filling ratio (%), and internal architecture with probability values of $p = 0.0030$, $p = 0.0182$, $p < 0.0001$ and $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC) was also significant with probability values of $p = 0.0017$ respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.8931 suggested that 89.31% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.7962 is in reasonable agreement with the Adjusted R^2 of 0.8537; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the strain energy release rate (J_I) in the Mode-I are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 17.713 indicates an adequate signal. This model can be used to navigate the design space.

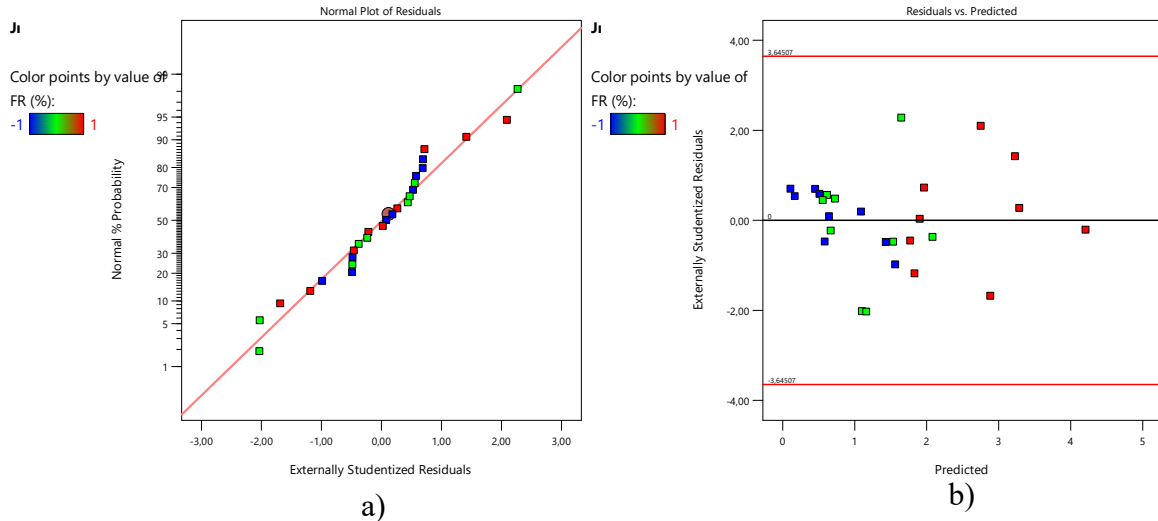


Figure 4.26. a) Normal plot of residuals b) residuals vs predicted plot of strain energy release rate (J_I) in the Mode-I of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.26 shows the normal of residuals and residuals vs. predicted plots for critical strain energy release rate J_I of PLA and PLA-based nanocomposites in the Mode-I loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of critical strain energy release rate J_I in the Mode-I loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy.

According to all Taguchi analyses for K_I , P_C , and J_I from figures 4.23, 4.27, and 4.29, the best parameters in order to obtain the best fracture characteristics in the Mode-I loading are all the same. The best factors provide the best characteristics in the Mode-I are, 40 mm/s printing speed, 1 wt% CaCO_3 addition, 0.15 mm layer thickness, and 100% filling ratio, and linear internal architecture. This phenomena could be explained that in the printing process, molten layers have enough time to bond with each other and solidify in 40 mm/s speed, and as explained before, linear internal architecture with a cross deposition structure of printed beads at $\pm 45^\circ$ assures that polymer molecules are oriented along the shear loading that may arise during tensile testing, and it may absorb the most energy before breaking.

4.2.4. K_I fracture toughness in the Mode-I/II loading

The effects of the printing speed on the fracture toughness (K_I) in the Mode-I/II of PLA/CaCO₃ nanoparticles are depicted through Figure 4.27, while the layer thickness and filling ratio are kept at their middle ranges.

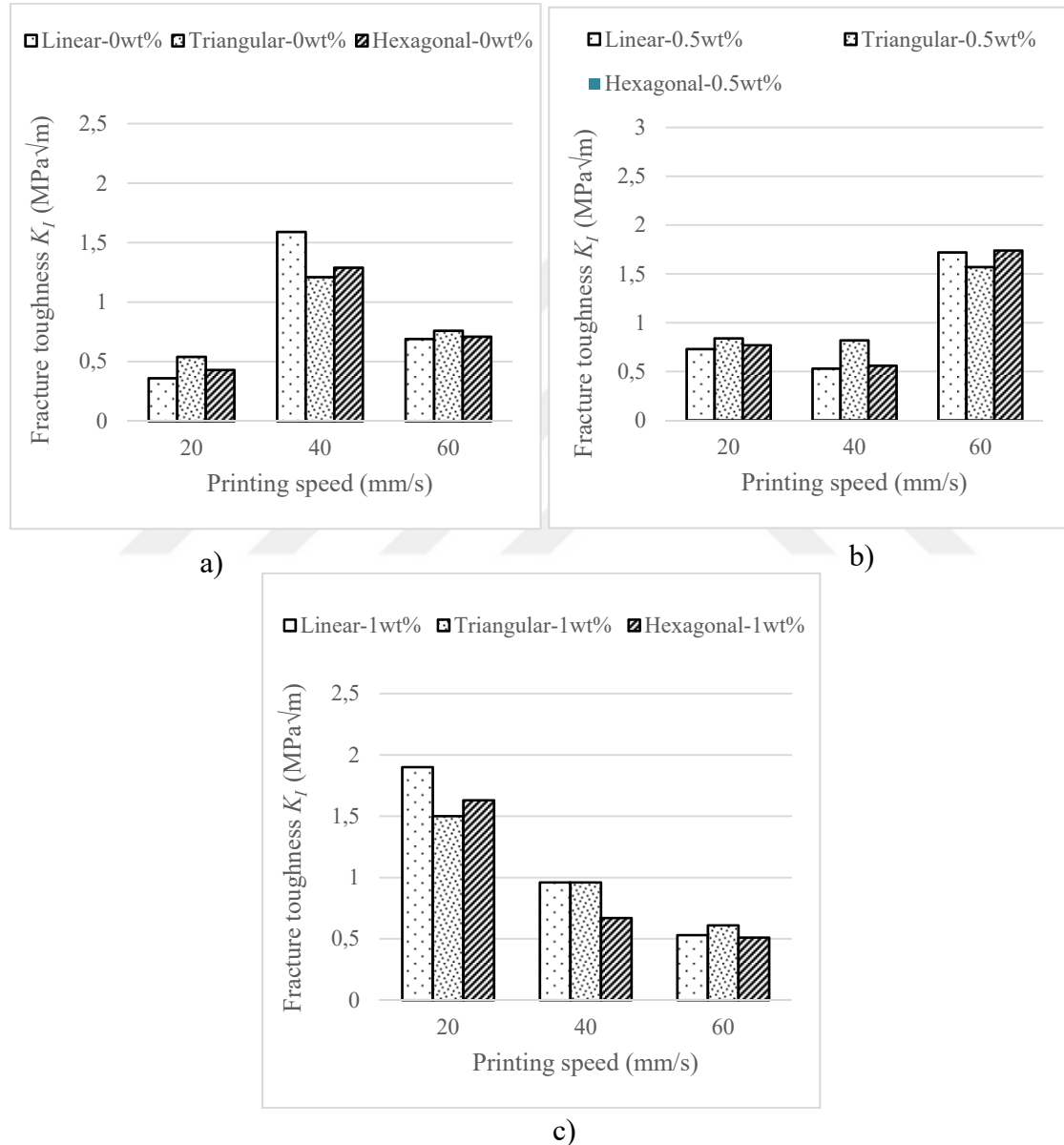


Figure 4.27. Effects of printing speed (mm/s) on K_I fracture toughness in mixed-mode values of a) pure b) 0.5 wt% CaCO₃ and c) 1 wt% CaCO₃ PLA parts printed in different internal architectures.

Figure 4.27 (a) represents the effects of the printing speed on the K_I fracture toughness of pure PLA parts in the Mode I/II loading. Similarly in K_I fracture toughness in the Mode-I loading, pure parts printed at 40 mm/s have the best fracture toughness results in the mixed mode loading with 1.59 MPa√m. In pure PLA, while the linear architecture has the best result in 40 mm/s, it also resulted in the lowest value in pure PLA parts with 0.36 MPa√m. In linear architecture for pure PLA parts, increasing the printing speed from 20 mm/s to 40 mm/s, increases the K_I fracture toughness value by about 77%. However, increasing the speed from 40 mm/s to 60 mm/s, decreases K_I by about 57%. This situation might be shows the negative effects of higher printing speed on the adhesion behavior of molten layers. In the investigation of results the reinforced specimens in detail, the effects of the printing speed on the K_I fracture toughness of 0.5 wt% CaCO₃/PLA parts in the Mode I/II loading, hexagonal structured part printed at 60 mm/s has the highest fracture toughness value in the mixed-mode loading with 1.74 MPa√m. This situation could be related with to the 3D stress distribution at the crack tip brought on by the strong contact between the nanoparticles and the polymer molecules, which increased the fracture loading in parts printed in hexagonal internal architecture. Parts printed at 20 and 40 mm/s speeds have almost no difference in toughness results but linear part printed at 40 mm/s has the lowest toughness value with 0.53 MPa√m, with a slight difference from hexagonal structured part. Figure 4.27 c), shows the effects of the printing speed on the K_I fracture toughness of 1 wt% CaCO₃/PLA parts in the Mode I/II loading. Linear parts printed at 20 mm/s has the highest K_I value in mixed-mode loading with 1.90 MPa√m. Hexagonal structure with 60 mm/s has the lowest with 0.51 MPa√m. That means the increasing printing speed from 20 mm/s to 60 mm/s, decreases the K_I of PLA parts reinforced with 1 wt% CaCO₃ in mixed-mode loading by about 73%.

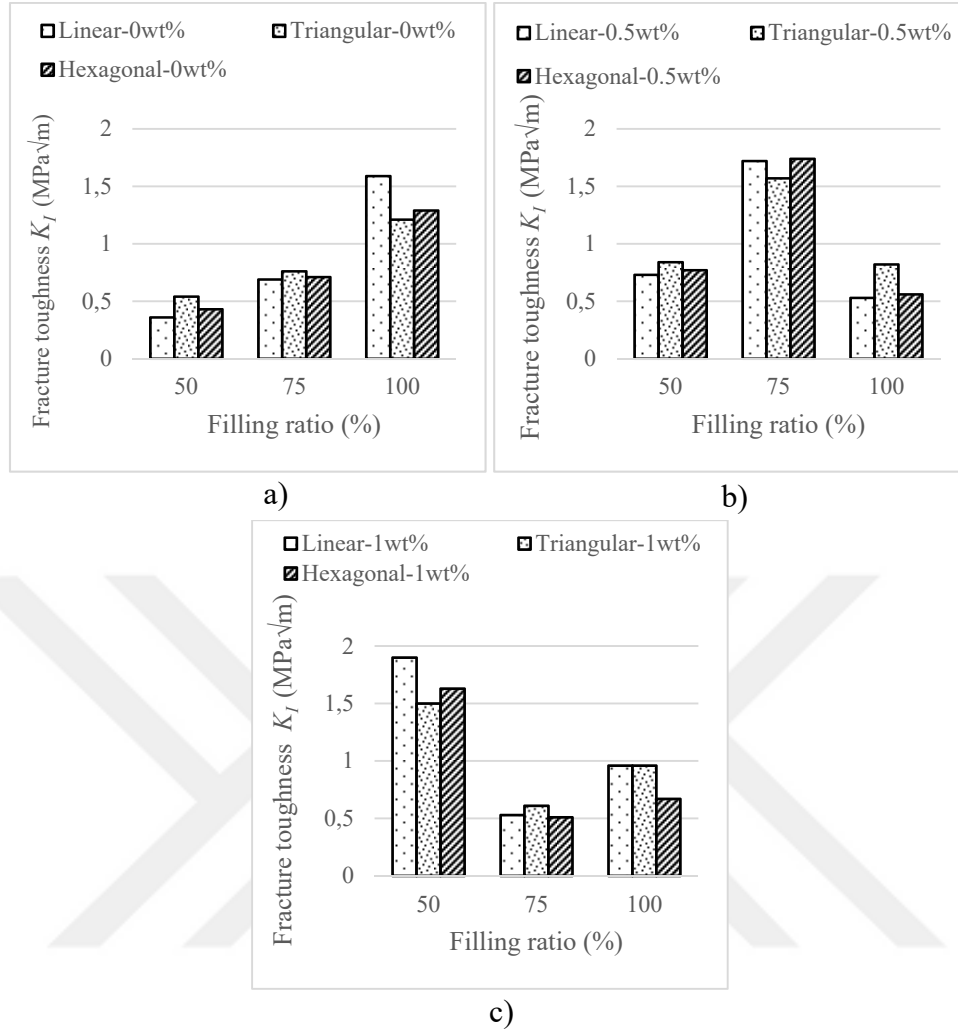


Figure 4.28. Effects of filling ratio (%) on K_I fracture toughness in mixed-mode values of a) pure b) 0.5 wt% CaCO_3 /PLA and c) 1 wt% CaCO_3 /PLA parts printed in different internal architectures.

The results of experiments and statistical modeling of the effects of filling ratio on the fracture performance of PLA/ CaCO_3 nanoparticles are illustrated through Figure 4.28, while the printing speed and layer thickness are kept at their middle ranges. As can be seen from Figure 4.28, pure PLA parts printed in linear architecture and 100% filling ratio has the best fracture toughness, but overall, all the architectures printed at 100% filling ratio have the best fracture toughness results in pure parts. Fracture toughness values have resulted in different situations for 0.5 wt% and 1 wt% reinforced parts, overall, while the amount of reinforcement increases, the lower filling ratios have achieved better results in the Mode-I/II fracture toughness values.

4.2.4.1. ANOVA of K_I fracture toughness in the Mode-I/II loading for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the mode-I/II fracture toughness (K_I) values. Figure 4.29 shows the best sequence of parameters in order to obtain the highest mode-I/II fracture toughness (K_I) in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the mode-I/II fracture toughness (K_I) values was found as, 1 wt% CaCO₃ reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest toughness in the mixed mode loading, resulted in highest strain energy release rate in this study.

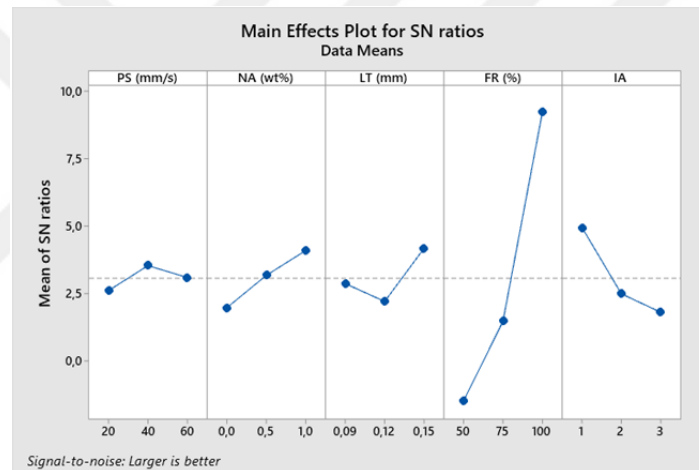


Figure 4.29. S/N ratios from Taguchi analysis for K_I fracture toughness in the Mode I/II loading.

Table 4.8. ANOVA for modified quadratic model of K_I fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5.70	12	0.4748	62.81	< 0.0001	significant
A-PS (mm/s)	0.1614	1	0.1614	21.35	0.0004	
B-NA (%)	0.0565	1	0.0565	7.48	0.0161	
C-LT (mm)	0.0594	1	0.0594	7.86	0.0141	
D-FR (%)	0.2543	1	0.2543	33.63	< 0.0001	
E-IA	0.0289	2	0.0144	1.91	0.1846	
AB	0.0662	1	0.0662	8.75	0.0104	
AC	0.0541	1	0.0541	7.16	0.0181	
BC	0.1568	1	0.1568	20.74	0.0004	
DE	0.1839	2	0.0919	12.16	0.0009	
A ²	0.0494	1	0.0494	6.53	0.0229	
Residual	0.1058	14	0.0076			
Cor Total	5.80	26				
R ² , 0.9818; adjusted R ² , 0.9661; predicted R ² , 0.9340; adequate precision, 24.3289						

Table 4.8 represents the ANOVA for modified quadratic model of K_I fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. However, E (internal architecture) is an input variable that has p-value greater than 0.05. In order to keep the hierarchy of the models and to increase the overall significance and predictability of the model, E (internal architecture) is kept as a variable in the quadratic models in this study. The Model F-value of 62.81 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AB, AC, BC, DE, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the K_I fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites. The most important factors influencing K_I fracture toughness in the Mode-I/II of PLA based nanocomposites were found as printing speed (mm/s), nanoparticle addition (%), layer thickness (mm), and filling ratio (%) with probability values of $p = 0.0004$, $p = 0.0161$, $p = 0.0141$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between

printing speed $\times$ nanoparticle addition (AB), printing speed $\times$ layer thickness (AC), and nanoparticle addition $\times$ layer thickness (BC), and filling ratio $\times$ internal architecture (DE) were also found to be significant with probability values of $p = 0.0104$, $p = 0.0181$, $p = 0.0004$ and $p = 0.0009$, respectively. The quadratic effects of the printing speed was also found to be significant with p value of 0.0229, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9818 suggested that 98.18% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.9340 is in reasonable agreement with the adjusted R^2 of 0.9661; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the K_I fracture toughness in the Mode-I/II are highly consistent. Adequate Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 24.329 indicates an adequate signal. This model can be used to navigate the design space.

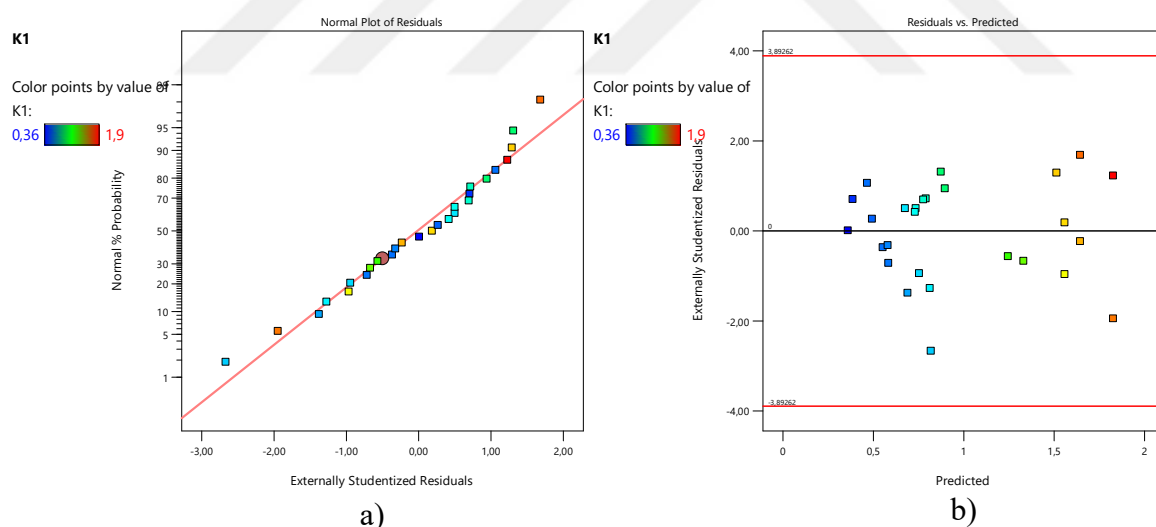


Figure 4.30. a) Normal plot of residuals b) residuals vs predicted plot of K_I fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.30 indicates the normal of residuals and residuals vs. predicted plots for K_I fracture toughness of PLA and PLA-based nanocomposites in the Mode-I/II loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals

have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of K_I fracture toughness in the Mode-I/II loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy.

Design of experiments (DOE) and response surface methodology (RSM) with an orthogonal array of the Taguchi method have been conducted to obtain optimum input parameters for the best fracture characteristics of parts in the Mode-I/II loadings. 3D surface response diagrams help to better understand to how input parameters affect each other. According to Table 4.8, the interactions between AB, AC, BC and DE were found significant. To better understand the interaction between these parameters, 3D response surface graphs have been plotted.

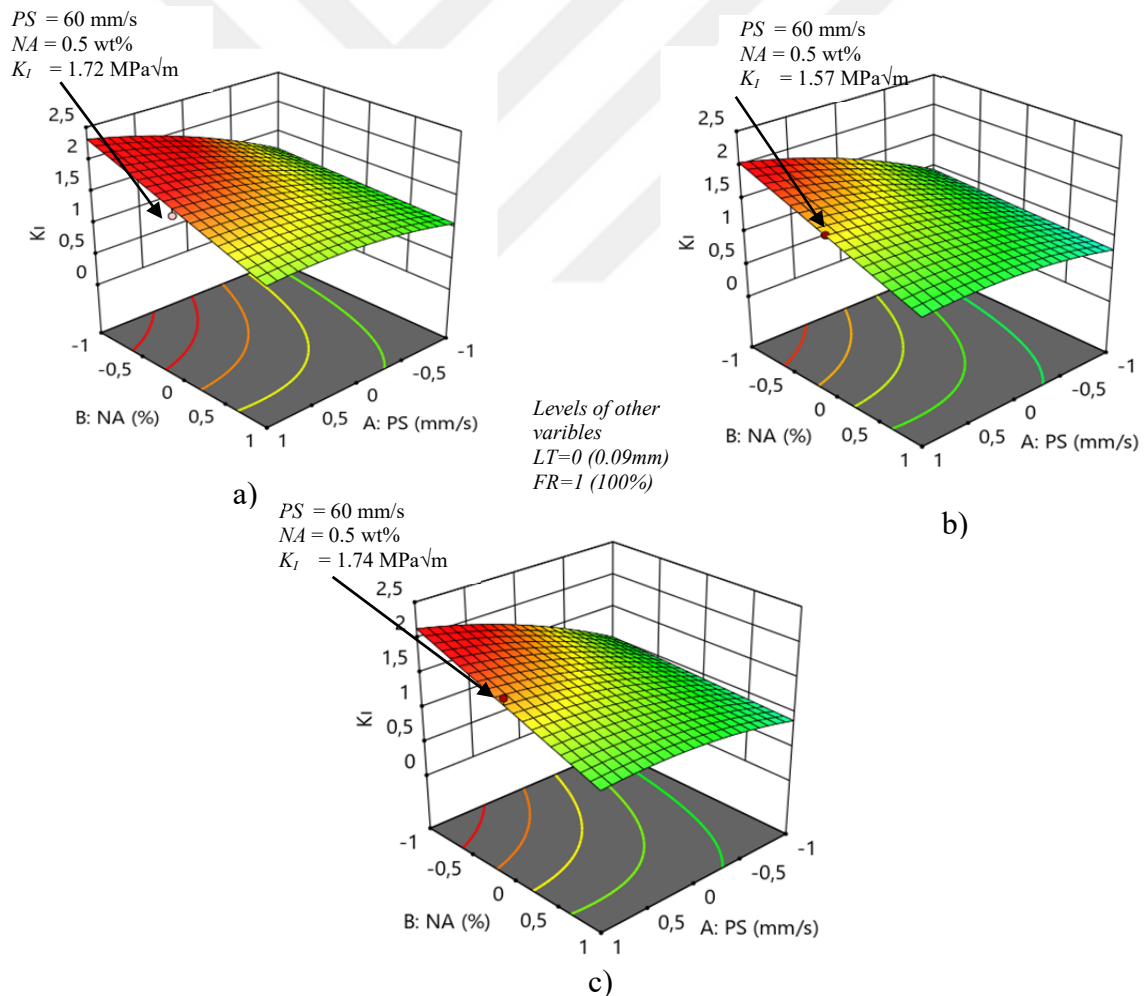


Figure 4.31. 3D response surface plot for PS (mm/s) and NA (%) of K_I fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.31 represents the interaction between printing speed (mm/s) and nanoparticle addition (%) of parts printed in linear, triangular and hexagonal internal architectures for K_I fracture toughness in the Mode-I/II loading. As can be seen in the diagrams, parts printed with linear internal architecture yields the highest fracture toughness value with a small difference. This figure shows the printing speed change according to nanoparticle addition at different internal architectures in the Mode-I/II loading. As can be seen from this figure, it can be observed that the printing speed should be increased with the decrease of nanoparticle addition in linear, triangular and hexagonal architectures for mode-I/II loading. It can be seen from figures, K_I fracture toughness increases with the increment of printing speed in the Mode I/II loading. Different fracture mechanisms of all internal architectures have been observed, this situation could be related with the elongation and failure of printed beads.

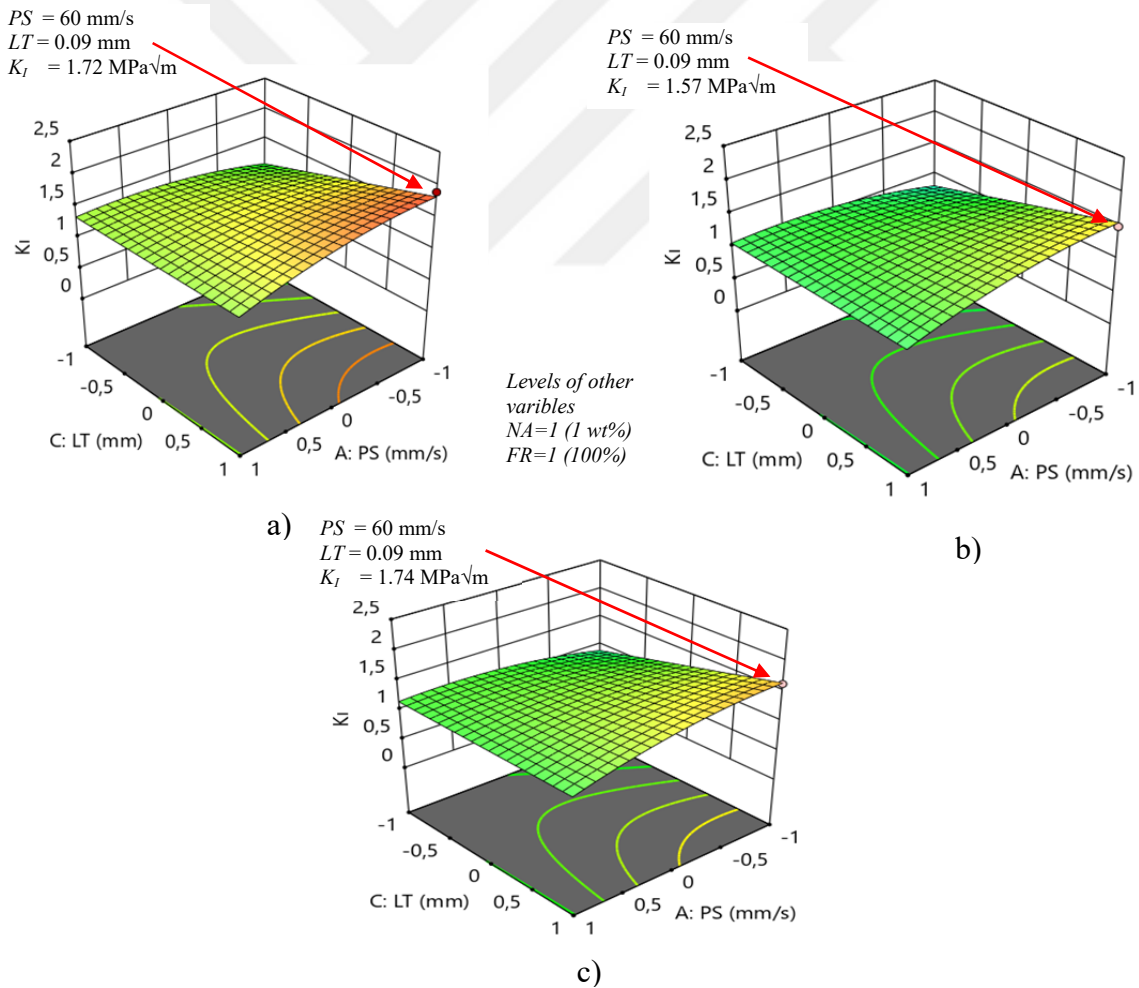


Figure 4.32. 3D response surface plot for PS (mm/s) and LT (mm) of K_I fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites printed a) linear b) triangular c) hexagonal internal architecture.

Figure 4.32 represents the interaction between the printing speed (mm/s) and layer thickness (mm) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_I fracture toughness in the Mode-I/II loading. The 3D response surfaces have less fluctuation, in other words, they have more smooth surfaces, parts printed with linear internal architecture yields the highest fracture toughness value, triangular and hexagonal parts have slight differences. The explanation of this situation mentioned above. This figure shows the printing speed change according to layer thickness at different internal architectures in the Mode-I/II loading. As can be seen from this figure, it can be observed that the printing speed needs to be increased with decreasing the layer thickness in linear, triangular and hexagonal architectures higher fracture toughness of fabricated samples in the Mode-I/II loading is achievable. It can be said that the fracture properties of parts increases with the increment of printing speed.

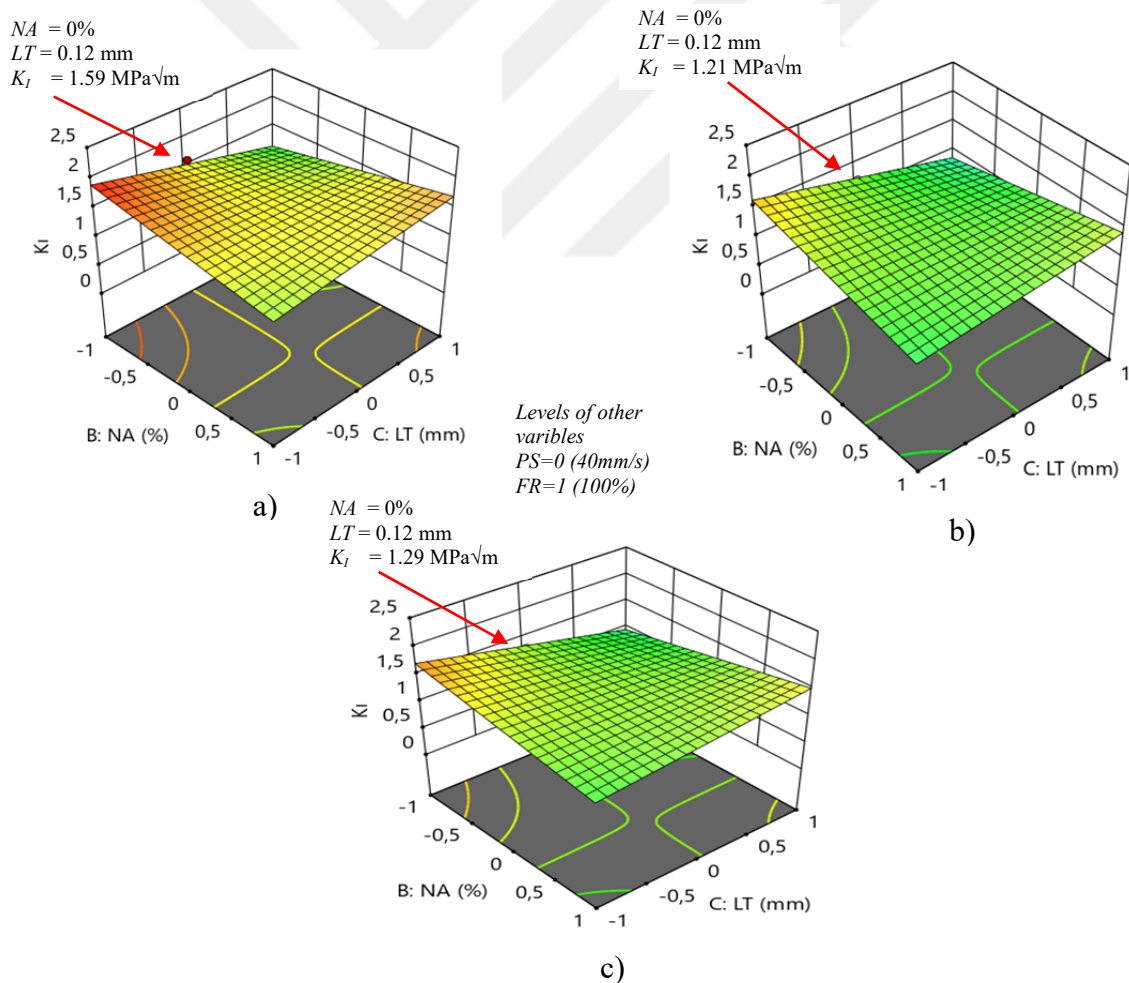


Figure 4.33. 3D response surface plot for NA (%) and LT (mm) of K_I fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.33 represents the interaction between the layer thickness (mm) and nanoparticle addition (%) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_I fracture toughness in the Mode-I/II loading. From this figure, it can be concluded that parts printed with linear internal architecture yields the highest fracture toughness value, triangular and hexagonal parts have slight differences. This figure shows the layer thickness change according to nanoparticle addition at different internal architectures in the Mode-I/II loading. As can be seen from this figure, it can be observed that the layer thickness should be decreased with the increase of nanoparticle addition in linear, triangular and hexagonal architectures for mode-I/II loading. It can be said that the fracture properties of parts increases with the increment of nanoparticle addition.

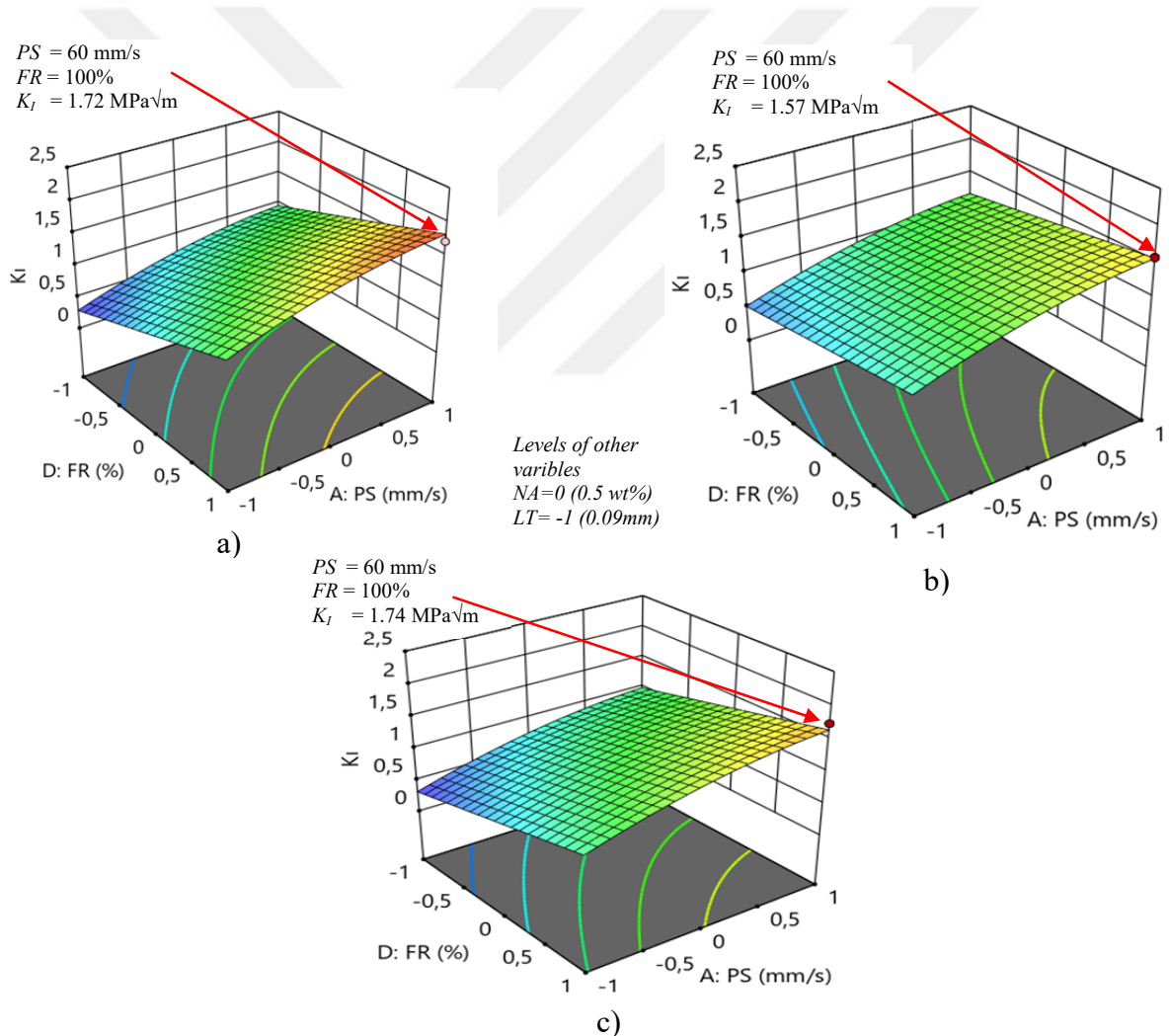


Figure 4.34. 3D response surface plot for PS (mm/s) and FR (%) of K_I fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.34 represents the interaction between the printing speed (mm/s) and filling ratio (%) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_I fracture toughness in the Mode-I/II loading. From this figure, it can be concluded that parts printed with triangular internal architecture yields the highest fracture toughness value. This figure shows the printing speed change according to filling ratio at different internal architectures in the Mode-I/II loading. As can be seen from this figure, it can be observed that increasing the printing speed at lower filling ratios while the porosity of fabricated samples increases, could portionally compensate for the reduction in fracture toughness of samples in linear, triangular and hexagonal architectures for mode-I/II loading. Overall, it can be said that the fracture properties of parts increases with the increment of printing speed.



4.2.5. K_{II} fracture toughness in the Mode-I/II loading

The effects of the printing speed on the fracture toughness (K_{II}) in the Mode-I/II of PLA/CaCO₃ nanoparticles are depicted through Figure 4.35, while the layer thickness and filling ratio are kept at their middle ranges.

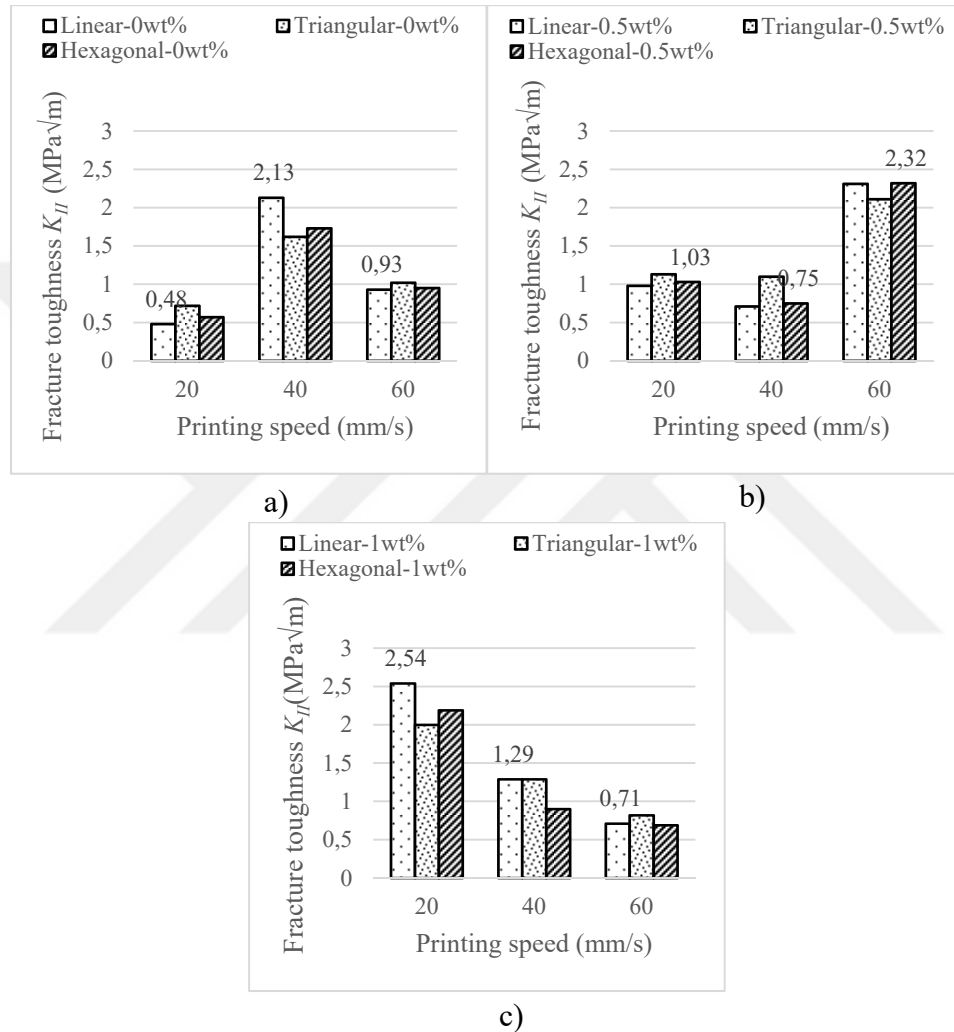


Figure 4.35. Effects of printing speed (mm/s) on K_{II} fracture toughness in mixed-mode values of a) pure b) 0.5 wt% CaCO₃/PLA and c) 1 wt% CaCO₃/PLA parts printed in different internal architectures.

Figure 4.35 (a) represents the effects of the printing speed on the K_{II} fracture toughness of pure PLA parts in the Mode I/II loading. Similar behavior can be observed in K_I fracture toughness in the current loading, linear parts printed at 40 mm/s have the best fracture toughness results in opening mode with 2.13 MPa√m. While the linear architecture has the

best result in 40 mm/s, it also resulted in the lowest value in pure PLA parts with 0.48 MPa√m. In linear architecture for pure PLA parts, increasing the printing speed from 20 mm/s to 40 mm/s, increases the K_{II} fracture toughness value by about 77%. However, increasing the speed from 40 mm/s to 60 mm/s, decreases K_{II} by about 56%. Figure 4.35 (b) shows the effects of the printing speed on the K_{II} fracture toughness of 0.5 wt% CaCO₃/PLA parts in the Mode I/II loading. With a negligible difference, linear and hexagonal structured parts printed at 60 mm/s has the highest fracture toughness value in the mixed-mode loading with 2.31 and 2.32 MPa√m, while the same patterned parts printed at 40 mm/s have the lowest K_{II} values with 0.71 and 0.75 MPa√m. Figure 4.35 (c) shows the effects of the printing speed on the K_{II} fracture toughness of 1 wt% CaCO₃/PLA parts in the Mode I/II loading. Linear parts printed at 20 mm/s has the highest K_{II} value in mixed-mode loading with 2.54 MPa√m. Hexagonal structure with 60 mm/s has the lowest with 0.69 MPa√m. That means the increasing printing speed from 20 mm/s to 60 mm/s, decreases the K_{II} of PLA parts reinforced with 1 wt% CaCO₃ in mixed-mode loading by about 73%.

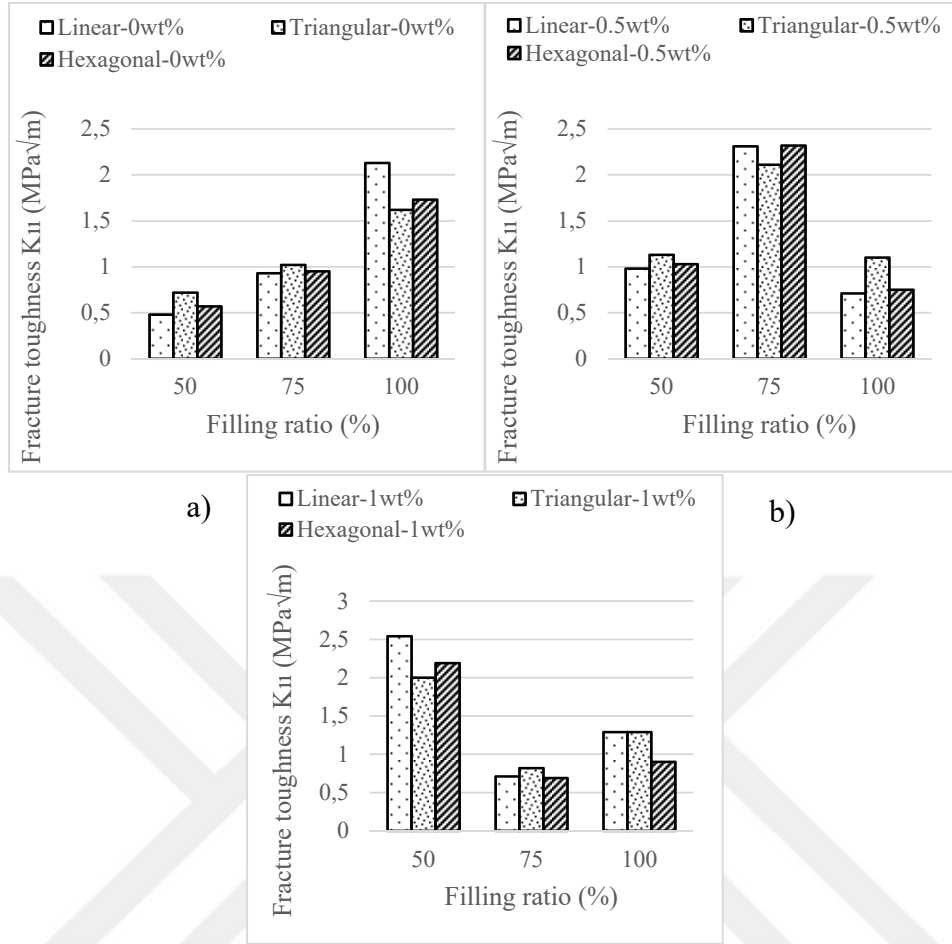


Figure 4.36. Effects of filling ratio (%) on K_{II} fracture toughness in mixed-mode values of a) pure b) 0.5 wt% CaCO_3 /PLA and c) 1 wt% CaCO_3 /PLA parts printed in different internal architectures.

The results of experiments and statistical modeling of the effects of filling ratio on the fracture performance of PLA/ CaCO_3 nanoparticles are illustrated through Figure 4.36, while the printing speed and layer thickness are kept at their middle ranges. As can be seen from Figure 4.36, pure PLA parts printed in linear architecture with 100% filling ratio has the best fracture toughness. But overall, all the architectures printed at 100% filling ratio have the best fracture toughness results in pure parts. This is an expected situation for pure parts, since they have no reinforcement, the fewer gaps in the parts will achieve better results in fracture properties. Fracture toughness values have resulted in different situations for 0.5 wt% and 1 wt% reinforced parts, overall, while the amount of reinforcement increases, the lower filling ratios have achieved better results in the Mode-I/II fracture toughness values.

4.2.5.1. ANOVA of K_{II} fracture toughness in the Mode-I/II loading for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the mode-I/II fracture toughness (K_{II}) values. Figure 4.37 shows the best sequence of parameters in order to obtain the highest mode-I/II fracture toughness (K_{II}) in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the mode-I/II fracture toughness (K_{II}) values was found as, with a slight difference, 0.5 wt% CaCO₃ reinforced triangular internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. The reason that the 0.5 wt% reinforced parts have the better results may be due to the weak zones in the 1 wt% CaCO₃/PLA matrix had forced to elongate along the mixed-mode loading direction. Printed parts with this sequence will have the highest toughness in the mixed mode loading, resulted in highest strain energy release rate in this study.

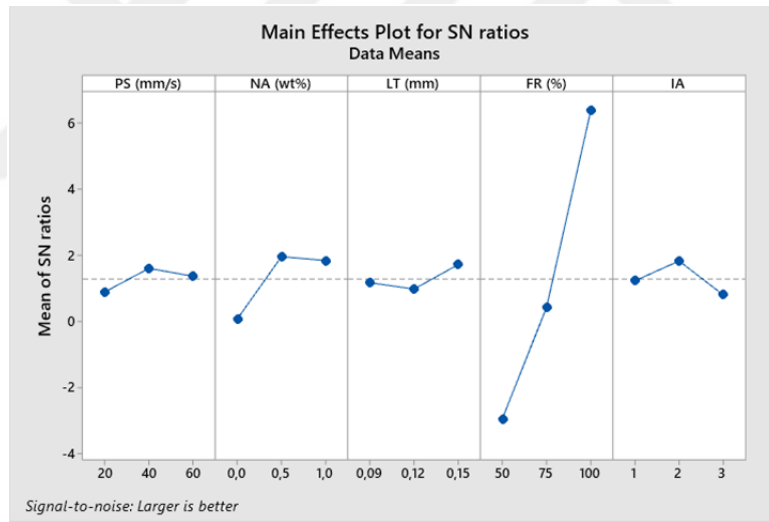


Figure 4.37. S/N ratios from Taguchi analysis for K_{II} fracture toughness in the Mode I/II loading.

Table 4.9. ANOVA for modified quadratic model of K_{II} fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	10.06	10	1.01	48.28	< 0.0001	significant
A-PS (mm/s)	0.2912	1	0.2912	13.97	0.0018	
B-NA (%)	0.0980	1	0.0980	4.70	0.0456	
C-LT (mm)	0.0022	1	0.0022	0.1066	0.7483	
D-FR (%)	1.45	1	1.45	69.59	< 0.0001	
E-IA	0.0533	2	0.0266	1.28	0.3058	
AC	0.1792	1	0.1792	8.60	0.0098	
BC	0.1318	1	0.1318	6.32	0.0230	
DE	0.3323	2	0.1662	7.97	0.0040	
Residual	0.3335	16	0.0208			
Cor Total	10.40	26				
R^2 , 0.9679; adjusted R^2 , 0.9479; predicted R^2 , 0.9136; adequate precision, 27.7261						

Table 4.9 represents the ANOVA for modified quadratic model of K_{II} fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. However, E (internal architecture) is an input variable that has p-value greater than 0.05. In order to keep the hierarchy of the models and to increase the overall significance and predictability of the model, E (internal architecture) is kept as a variable in the quadratic models in this study. The Model F-value of 48,28 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise. P-values less than 0,0500 indicate model terms are significant. In this case A, B, D, AC, BC, DE are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the K_{II} fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites. The most important factors influencing K_{II} fracture toughness in the Mode-I/II of PLA based nanocomposites were found as printing speed (mm/s), nanoparticle addition (%), and filling ratio (%) with probability values of $p = 0.0018$, $p = 0.0456$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$ layer thickness (AC), and nanoparticle addition $\times$ layer thickness (BC), and filling ratio $\times$ internal architecture

(DE) were also found to be significant with probability values of $p = 0.0098$, $p = 0.0230$ and $p = 0.0040$, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9679 suggested that 96.79% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.9136 is in reasonable agreement with the Adjusted R^2 of 0.9479; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the K_{II} fracture toughness in the Mode-I/II are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 21.726 indicates an adequate signal. This model can be used to navigate the design space.

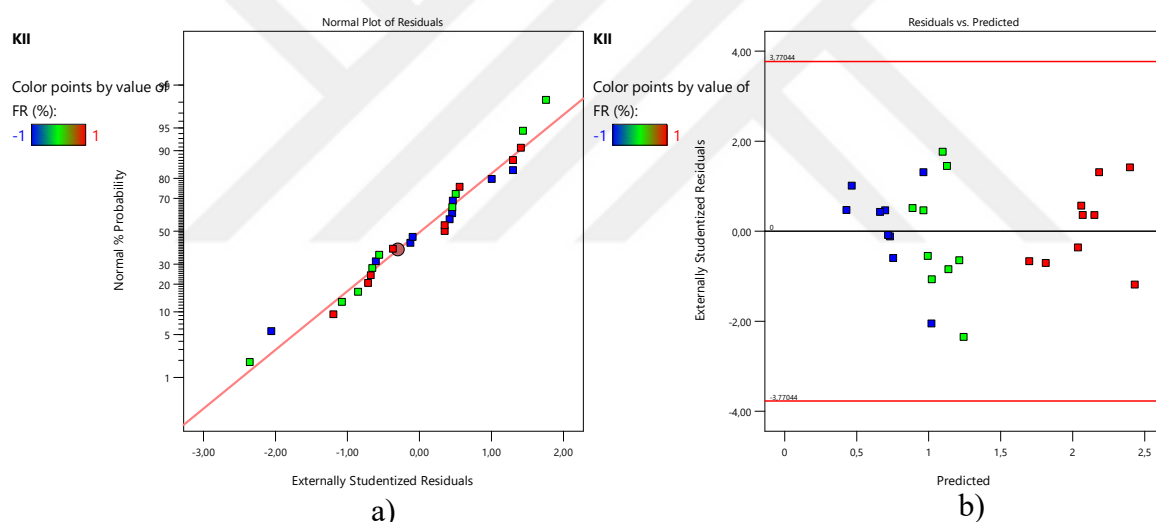


Figure 4.38. a) Normal plot of residuals b) residuals vs predicted plot of K_{II} fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.38 indicates the normal of residuals and residuals vs. predicted plots for K_{II} fracture toughness of PLA and PLA-based nanocomposites in the Mode-I/II loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of K_{II} fracture toughness in the Mode-I/II loading shows

the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy.

Design of experiments (DOE) and response surface methodology (RSM) with an orthogonal array of the Taguchi method have been conducted to obtain optimum input parameters for the best fracture characteristics of parts in the Mode-I/II loadings. 3D surface response diagrams help to better understand to how input parameters affect each other. According to Table 4.9, the interactions between AC, BC and DE were found significant. To better understand the interaction between these parameters, 3D response surface graphs have been plotted.

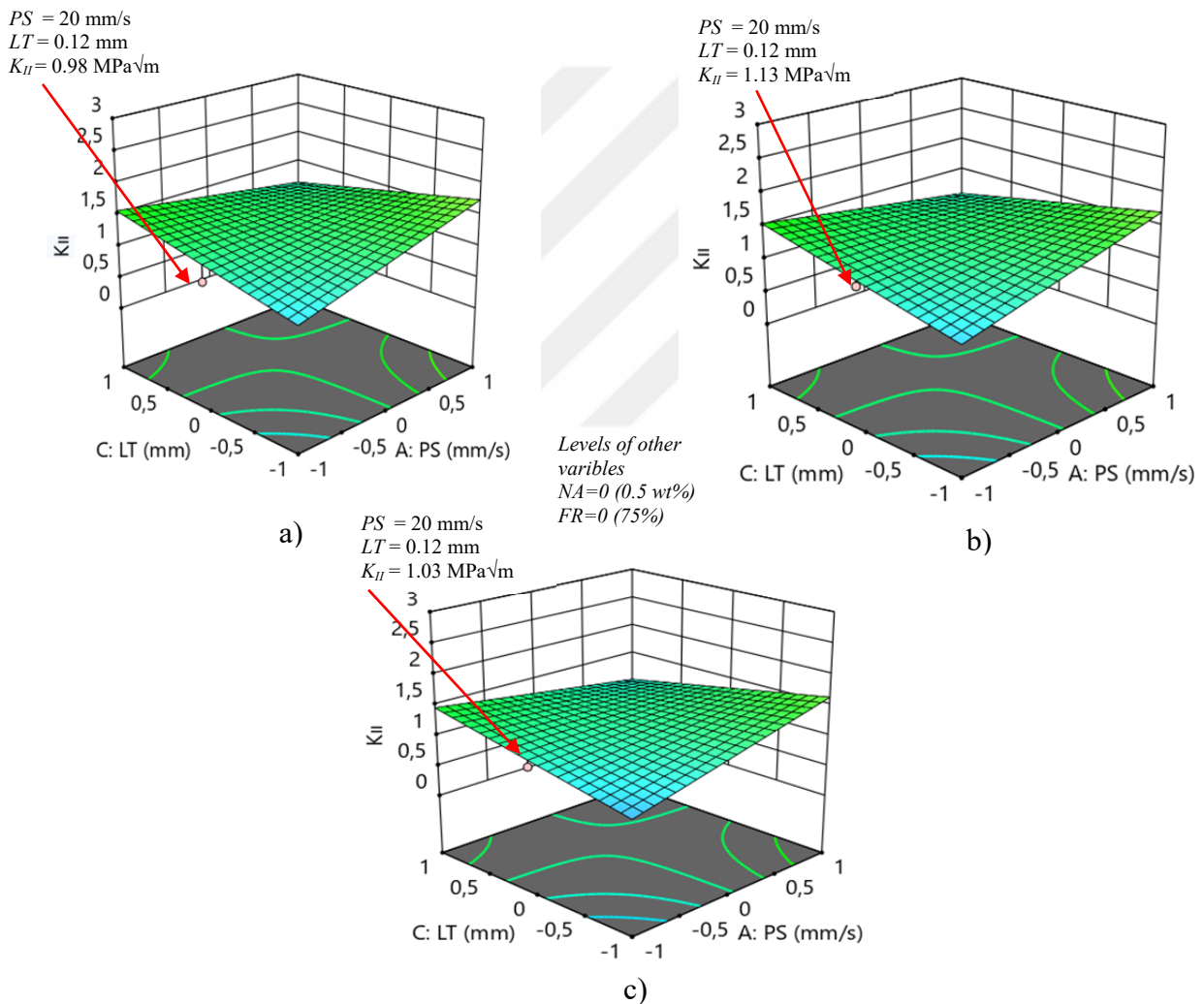


Figure 4.39. 3D response surface plot for PS (mm/s) and LT (mm) of K_{II} fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.39 represents the interaction between the layer thickness (mm) and printing speed (mm/s) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_{II} fracture toughness in the Mode-I/II loading. From this figure, it can be concluded that parts printed with linear and triangular internal architectures yield the highest fracture toughness value, and hexagonal parts have slight differences. This figure shows the layer thickness change according to printing speed at different internal architectures in the Mode-I/II loading. As can be seen from this figure, it can be observed that the printing speed should be decreasing with the increase of layer thickness in linear, triangular and hexagonal architectures to maintaining high fracture toughness of 3D printed samples under mode-I/II loading. It can be said that the fracture properties of parts increases with the increment of printing speed.

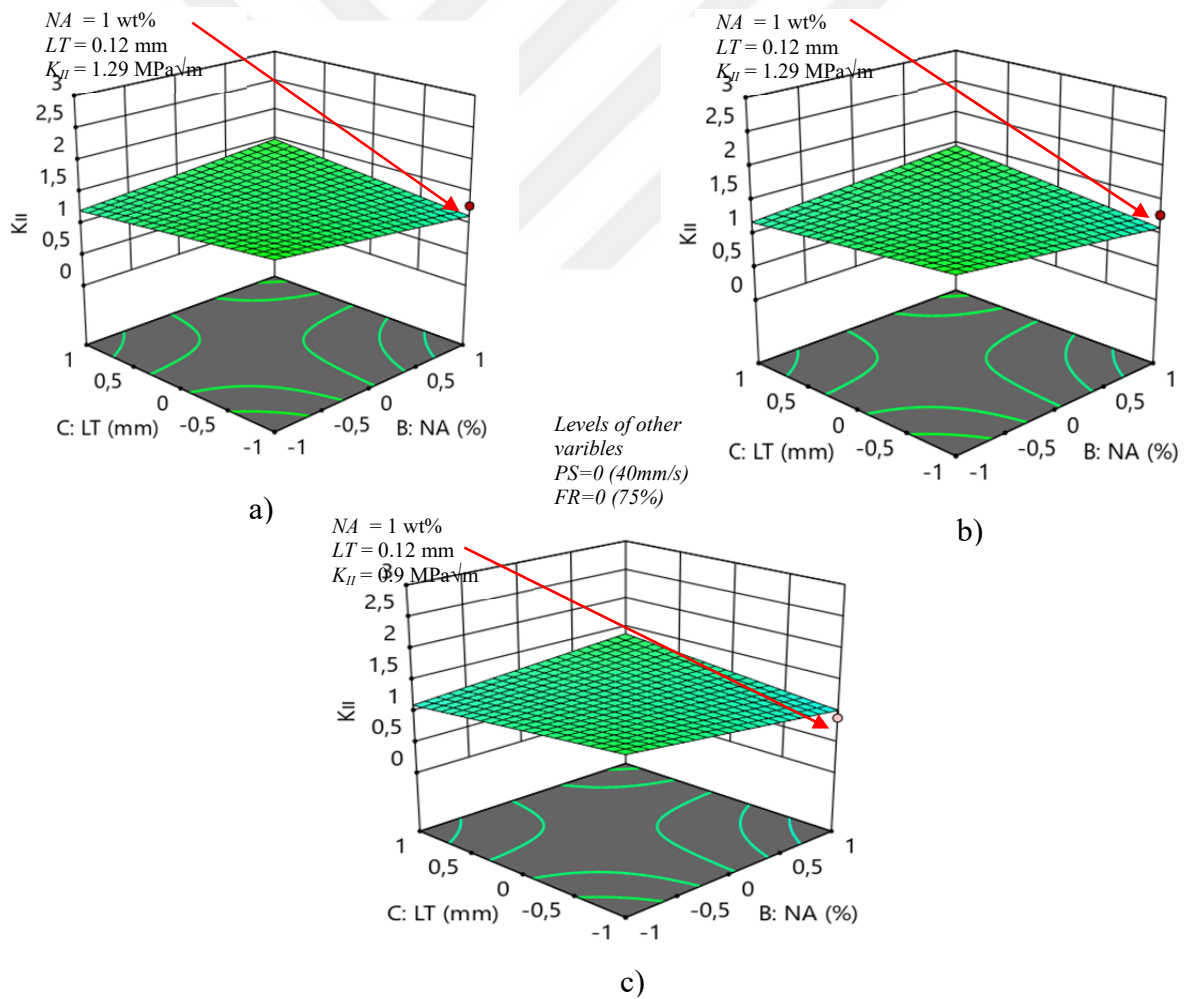


Figure 4.40. 3D response surface plot for NA (%) and LT (mm) of K_{II} fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.40 represents the interaction between the layer thickness (mm) and nanoparticle addition (%) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_{II} fracture toughness in the Mode-I/II loading. From this figure, it can be concluded that parts printed with linear and triangular internal architectures yield the highest fracture toughness value, and hexagonal parts have slight differences. The figure shows the layer thickness change according to nanoparticle addition at different internal architectures in the Mode-I/II loading. As can be seen from this figure, it can be observed that the layer thickness should be decreasing with the increase of nanoparticle addition in linear, triangular and hexagonal architectures to realize the enhancing effect of nanoadditives on the fracture toughness of fabricated samples under mode-I/II loading. It can be said that the fracture properties of parts increases with increasing of the nanoparticle concentration in the matrix.

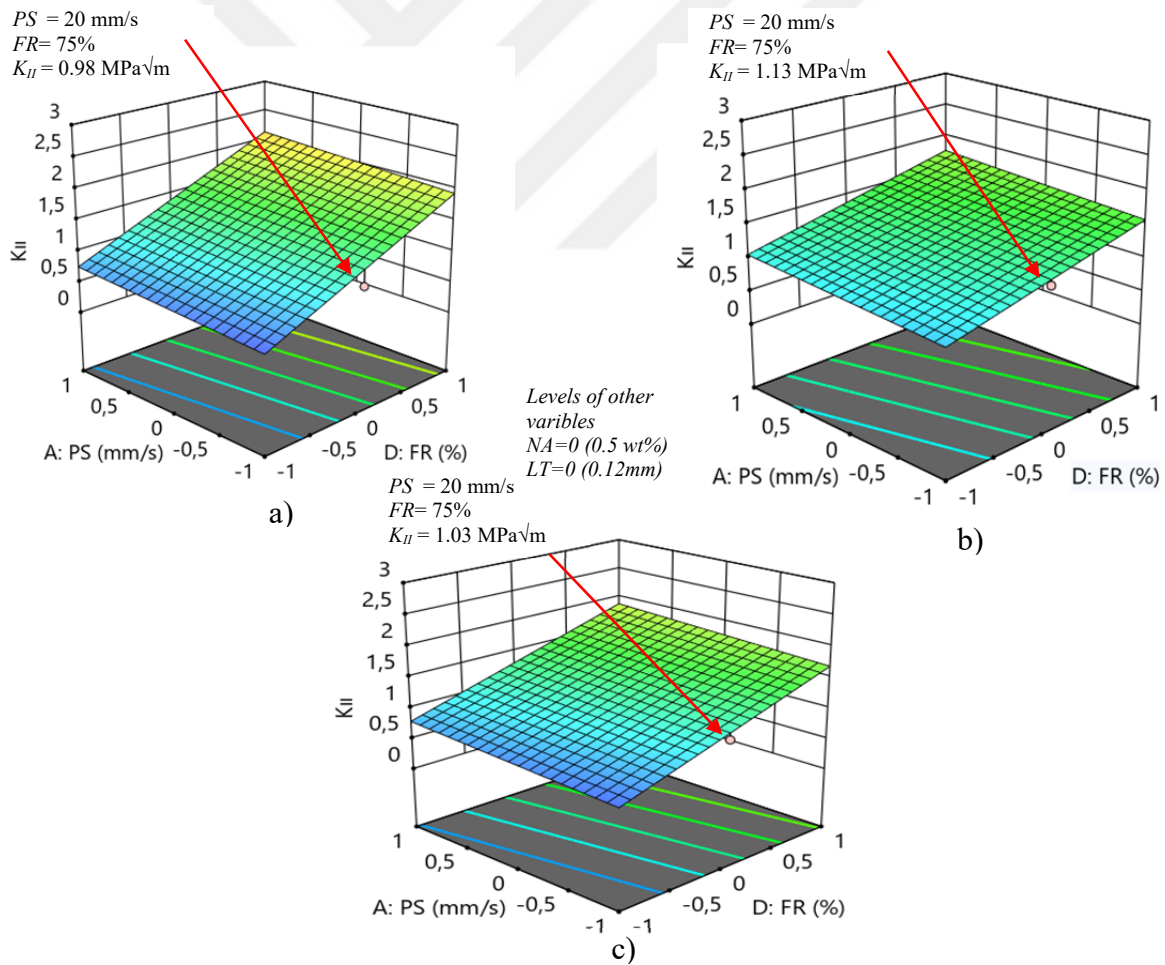


Figure 4.41. 3D response surface plot for PS (mm/s) and FR (%) of K_{II} fracture toughness in the Mode-I/II of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.41 represents the interaction between the printing speed (mm/s) and filling ratio of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_{II} fracture toughness in the Mode-I/II loading. From this figure, it can be concluded that parts printed with triangular internal architectures yield the highest fracture toughness value, linear and hexagonal parts have slight differences. This figure shows the printing speed change according to filling ratio at different internal architectures in the Mode-I/II loading. As can be seen from this figure, it can be observed that the printing speed should be decreasing with the increase of filling ratio in linear, triangular and hexagonal architectures to realize the enhancing effect of nanoadditives on the fracture toughness of fabricated samples under mode-I/II loading. It can be said that the fracture properties of parts increases with the increment of filling ratio.

4.2.6. ANOVA of P_C critical load in the Mode-I/II loading for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the critical load (P_C) values in the Mode-I/II. Figure 4.42 shows the best sequence of parameters in order to obtain the highest critical load in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the critical load (P_C) values in the Mode-I/II found as, 0.5 wt% CaCO₃ reinforced triangular internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest critical load in the mixed mode loading in this study.



Figure 4.42. Taguchi analysis for critical load (P_C) in the Mode I/II

Table 4.10. ANOVA for modified quadratic model of critical load (P_C) in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1.226E+07	11	1.114E+06	47.74	< 0.0001	significant
A-PS (mm/s)	3.530E+05	1	3.530E+05	15.13	0.0015	
B-NA (%)	3.433E+05	1	3.433E+05	14.71	0.0016	
C-LT (mm)	1.241E+05	1	1.241E+05	5.32	0.0358	
D-FR (%)	1.640E+06	1	1.640E+06	70.30	< 0.0001	
E-IA	64242.67	2	32121.33	1.38	0.2826	
AB	1.432E+05	1	1.432E+05	6.14	0.0256	
BC	9.042E+05	1	9.042E+05	38.75	< 0.0001	
DE	4.104E+05	2	2.052E+05	8.79	0.0030	
A ²	2.424E+05	1	2.424E+05	10.39	0.0057	
Residual	3.500E+05	15	23335.15			
Cor Total	1.261E+07	26				
R ² , 0.9722; adjusted R ² , 0.9519; predicted R ² , 0.9124; adequate precision, 21.2634						

Table 4.10 represents the ANOVA for modified quadratic model of critical load (P_C) in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. However, E (internal architecture) is an input variable that has p-value greater than 0.05. In order to keep the hierarchy of the models and to increase the overall significance and predictability of the model, E (internal architecture) is kept as a variable in the quadratic models in this study. The Model F-value of 47.74 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AB, BC, DE, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the critical load (P_C) in the Mode-I/II of PLA and PLA-based nanocomposites. The most important factors influencing critical load (P_C) in the Mode-I/II of PLA based nanocomposites were found as printing speed (mm/s), nanoparticle addition (%), layer thickness (mm), and filling ratio (%) with probability values of $p = 0.0015$, $p = 0.0016$, $p = 0.0358$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$

nanoparticle addition (AB), nanoparticle addition $\times$ layer thickness (BC), and filling ratio $\times$ internal architecture (DE) were also found to be significant with probability values of $p = 0.0256$, $p < 0.0001$ and $p = 0.0030$, respectively. The quadratic effects of the printing speed was also found to be significant with p value of 0.0057, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9722 suggested that 97.22% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.9124 is in reasonable agreement with the Adjusted R^2 of 0.9519; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the critical load (P_C) in the Mode-I/II are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 21.263 indicates an adequate signal. This model can be used to navigate the design space.

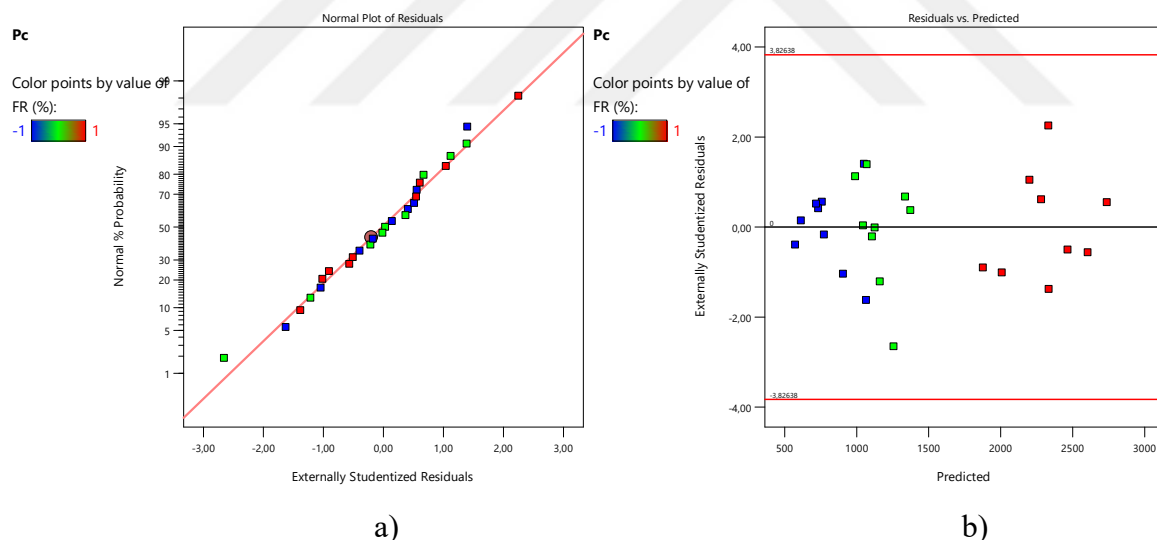


Figure 4.43. a) Normal plot of residuals b) residuals vs predicted plot of critical load (P_C) in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.43 shows the normal of residuals and residuals vs. predicted plots for critical load P_C of PLA and PLA-based nanocomposites in the Mode-I/II loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing

the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of critical load P_C in the Mode-I/II loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy.

4.2.7. ANOVA of J_T total critical strain energy release rate in the Mode-I/II loading for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the total strain energy release rate (J_T) values in the Mode-I/II. Figure 4.44 shows the best sequence of parameters in order to obtain the highest strain energy release rate in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the total strain energy release rate (J_T) values in the Mode-I/II found as, 1 wt% CaCO₃ reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest total strain energy release rate in mixed mode in this study.



Figure 4.44. Taguchi analysis for total strain energy release rate (J_T) in the Mode I/II.

Table 4.11. ANOVA for modified quadratic model of total strain energy release rate (J_T) in the Mode I/II of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	9.85	10	0.9852	17.74	< 0.0001	significant
A-PS (mm/s)	0.0867	1	0.0867	1.56	0.2294	
B-NA (%)	0.5495	1	0.5495	9.90	0.0062	
C-LT (mm)	0.1083	1	0.1083	1.95	0.1817	
D-FR (%)	7.47	1	7.47	134.47	< 0.0001	
E-IA	0.3814	2	0.1907	3.43	0.0574	
BC	0.6099	1	0.6099	10.98	0.0044	
DE	0.7009	2	0.3505	6.31	0.0095	
A ²	0.0971	1	0.0971	1.75	0.2046	
Residual	0.8884	16	0.0555			
Cor Total	10.74	26				
R ² , 0.9173; adjusted R ² , 0.8656; predicted R ² , 0.7592; adequate precision, 14.4555						

Table 4.11 represents the ANOVA for modified quadratic model of total strain energy release rate (J_T) in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. However, E (internal architecture) is an input variable that has p-value greater than 0.05. In order to keep the hierarchy of the models and to increase the overall significance and predictability of the model, E (internal architecture) is kept as a variable in the quadratic models in this study. The Model F-value of 17.74 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case B, D, BC, DE are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the total strain energy release rate (J_T) in the Mode-I/II of PLA and PLA-based nanocomposites. The most important factors influencing total strain energy release rate (J_T) in the Mode-I/II of PLA based nanocomposites were found as nanoparticle addition (%), and filling ratio (%) with probability values of $p = 0.0062$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC)

and filling ratio $\times$ internal architecture (DE) were also found to be significant with probability values of $p = 0.0044$ and $p = 0.0095$, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9173 suggested that 91.73% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.7592 is in reasonable agreement with the adjusted R^2 of 0.8656; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the total strain energy release rate (J_T) in the Mode-I/II are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 15.455 indicates an adequate signal. This model can be used to navigate the design space.

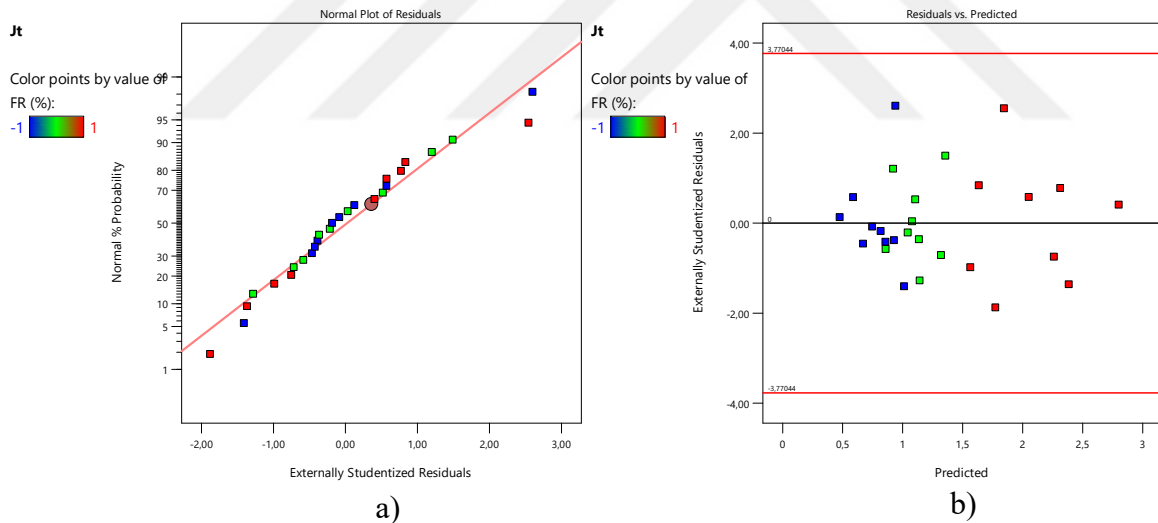


Figure 4.45. a) Normal plot of residuals b) residuals vs predicted plot of total strain energy release rate (J_T) in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.45 shows the normal of residuals and residuals vs. predicted plots for total critical strain energy release rate J_T of PLA and PLA-based nanocomposites in the Mode-I/II loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of

whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of total critical strain energy release rate J_T in the Mode-I/II loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy.

4.2.8. K_{II} fracture toughness in the Mode-II loading

The effects of the printing speed on the fracture toughness (K_{II}) in the Mode-II of PLA/ CaCO_3 nanoparticles are depicted through Figure 4.46 while the layer thickness and filling ratio are kept at their middle ranges.

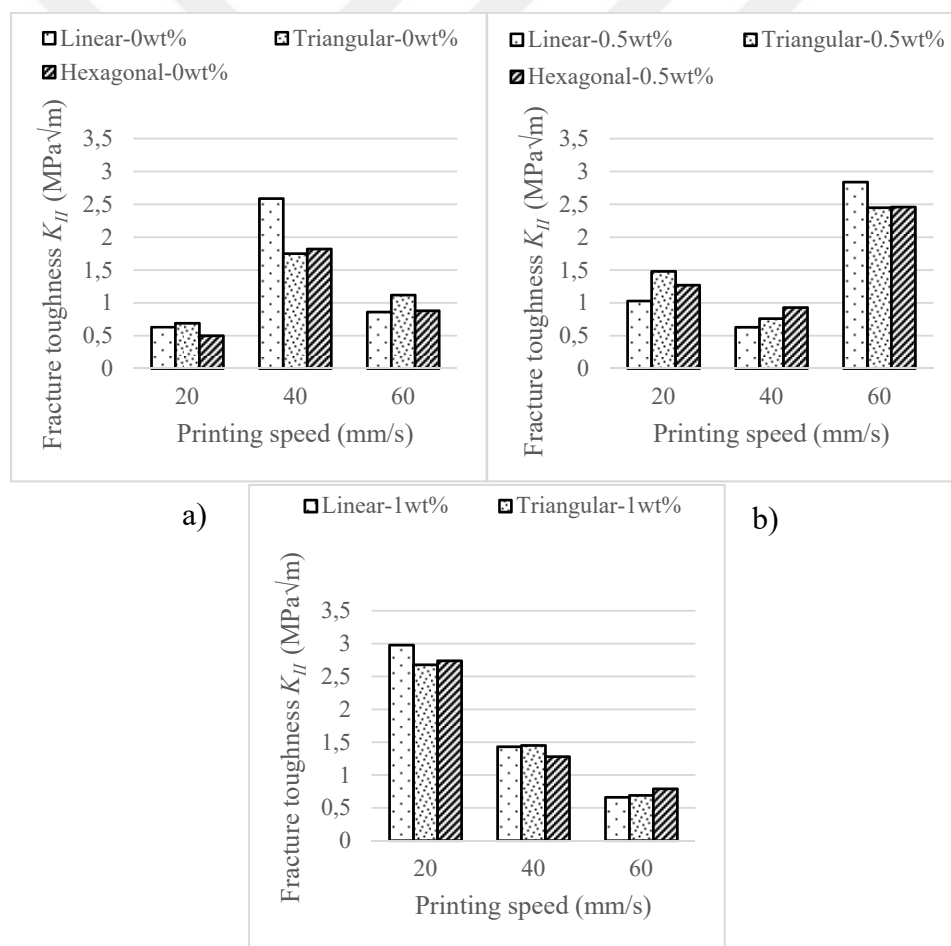


Figure 4.46. Effects of printing speed (mm/s) on K_{II} fracture toughness in the Mode-II values of a) pure b) 0.5 wt% CaCO_3 /PLA and c) 1 wt% CaCO_3 /PLA parts printed in different internal architectures.

Figure 4.46 (a) represents the effects of the printing speed on the K_{II} fracture toughness of pure PLA parts in the Mode-II loading. Similar behavior can be observed in K_{II} fracture toughness in the current loading, linear parts printed at 40 mm/s have the best fracture toughness results in the Mode-II loading with 2.59 MPa√m. While the linear architecture has the best result in 40 mm/s, hexagonal parts printed at 20 mm/s resulted in the lowest value in pure PLA parts with 0.50 MPa√m. For pure PLA parts, changing the architecture from hexagonal to linear and increasing the printing speed from 20 mm/s to 40 mm/s, increases the K_{II} fracture toughness value by about 81%. However, increasing the speed from 40 mm/s to 60 mm/s, decreases K_{II} by about 81%. Figure 4.46 (b) shows the effects of the printing speed on the K_{II} fracture toughness of 0.5 wt% CaCO₃/PLA parts in the Mode-II loading. Linear structured parts printed at 60 mm/s has the highest fracture toughness value in the mixed-mode loading with 2.84 MPa√m, while the same patterned part printed at 40 mm/s have the lowest K_{II} value 0.63 MPa√m. Figure 4.46 (c) shows the effects of the printing speed on the K_{II} fracture toughness of 1 wt% CaCO₃/PLA parts in the Mode I-II loading. Linear parts printed at 20 mm/s has the highest K_{II} value in mixed-mode loading with 2.98 MPa√m. Triangular structure with 60 mm/s has the lowest with 0.66 MPa√m. That means the increasing printing speed from 20 mm/s to 60 mm/s, and changing the architecture from linear to triangular, decreases the K_{II} of PLA parts reinforced with 1 wt% CaCO₃ in the Mode-II loading by about 78%. According to Table 4.4, fracture resistance of parts against the shear loading is decreased. This could be related with the plastic deformation ahead of the crack tip and formation of striation marks along the crack propagation path in shearing mode.

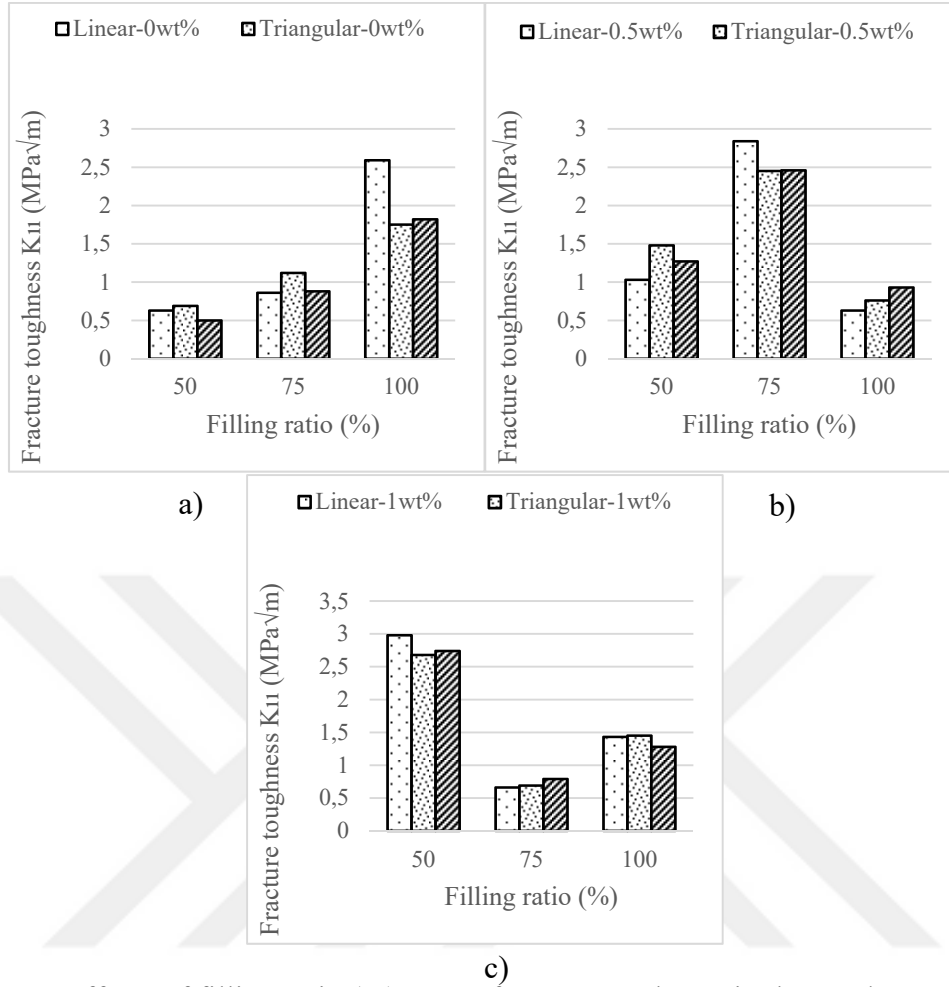


Figure 4.47. Effects of filling ratio (%) on K_{II} fracture toughness in the Mode-II values of a) pure b) 0.5 wt% CaCO₃/PLA and c) 1 wt% CaCO₃/PLA parts printed in different internal architectures.

The results of experiments and statistical modeling of the effects of filling ratio on the fracture performance of PLA/CaCO₃ nanoparticles are illustrated through Figure 4.47, while the printing speed and layer thickness are kept at their middle ranges. As can be seen from Figure 4.47, pure PLA parts printed in linear architecture with 100% filling ratio has the best fracture toughness. But overall, all the architectures printed at 100% filling ratio have the best fracture toughness results in pure parts. This is an expected situation for pure parts, since they have no reinforcement, the fewer gaps in the parts will achieve better results in fracture properties. Fracture toughness values have resulted in different situations for 0.5 wt% and 1 wt% reinforced parts, overall, while the amount of reinforcement increases, the lower filling ratios have achieved better results in the Mode-II fracture toughness values. In order to see and better understand the dispersion of nanoparticles and the gaps and molten filaments in the

parts, data from SEM examinations would help. As can be seen from Figure 4.48, pure PLA parts showed brittle behavior under mode-II and mode I-II loadings. The voids between printed layers can be seen clearly, even the layers had time to bond with previous layer, this situation is inevitable in FDM 3D printing. Increasing the filling ratio from 50% to 100% will reduce the gaps between layers. In shear loading, linear architecture showed more brittle behavior as can be seen from Figure 4.48 (b) in x1000 magnification. The layers of cracked area are more straight and smoother.



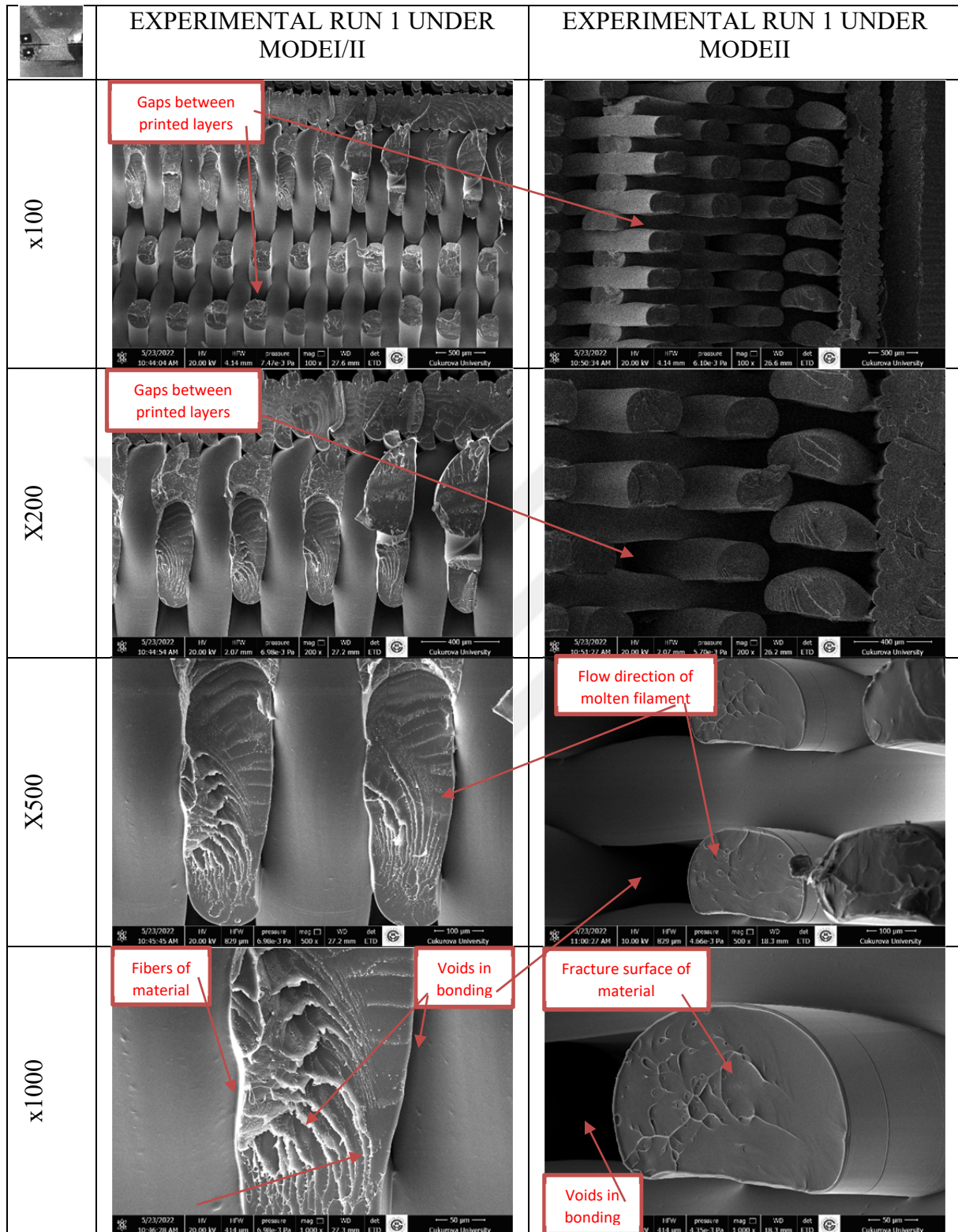


Figure 4.48. SEM images in different magnifications of internal layers of a) pure linear PLA parts printed at 20 mm/s printing speed, 0.09 mm layer thickness and 50% filling ratio (Taguchi Experimental Run 1), under Mode-I/II loading, b) under Mode-II loading.

4.2.8.1. ANOVA of K_{II} fracture toughness in the Mode-II loading for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the mode-II fracture toughness (K_{II}) values. Figure 4.49 shows the best sequence of parameters in order to obtain the highest mode-II fracture toughness (K_{II}) in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the mode-II fracture toughness (K_{II}) values was found as, with a slight difference, 1 wt% CaCO₃ reinforced triangular internal architected parts printed at 40 mm/s printing speed, 0.09 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest toughness in the mode-II loading, resulted in highest strain energy release rate in this study.

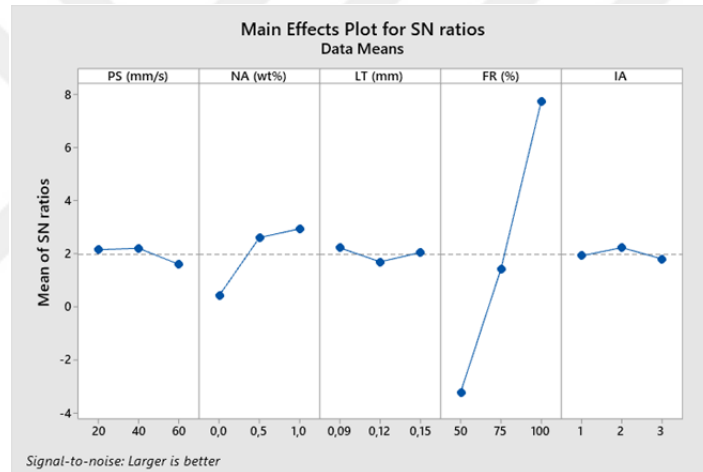


Figure 4.49. S/N ratios from Taguchi analysis for K_{II} fracture toughness in the Mode-II.

Table 4.12. ANOVA for modified quadratic model of K_{II} fracture toughness in the Mode-II of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	16.46	9	1.83	40.61	< 0.0001	significant
A-PS (mm/s)	0.1176	1	0.1176	2.61	0.1246	
B-NA (%)	0.8278	1	0.8278	18.38	0.0005	
C-LT (mm)	0.0013	1	0.0013	0.0278	0.8696	
D-FR (%)	14.28	1	14.28	316.99	< 0.0001	
E-IA	0.0540	2	0.0270	0.5990	0.5605	
BC	0.8841	1	0.8841	19.63	0.0004	
DE	0.3290	2	0.1645	3.65	0.0479	
Residual	0.7656	17	0.0450			
Cor Total	17.22	26				
R ² , 0.9556; adjusted R ² , 0.9320; predicted R ² , 0.8954; adequate precision, 20.2779						

Table 4.12 represents the ANOVA for modified quadratic model of mode-II fracture toughness (K_{II}) in the Mode-I/II of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. However, E (internal architecture) is an input variable that has p-value greater than 0.05. In order to keep the hierarchy of the models and to increase the overall significance and predictability of the model, E (internal architecture) is kept as a variable in the quadratic models in this study. The Model F-value of 40.61 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case B, D, BC, DE are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the K_{II} fracture toughness in the Mode-II of PLA and PLA-based nanocomposites. The most important factors influencing K_{II} fracture toughness in the Mode-II of PLA based nanocomposites were found as nanoparticle addition (%), and filling ratio (%) with probability values of $p = 0.0005$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC), and filling ratio $\times$ internal architecture (DE) were also found to be significant with probability values of $p = 0.0004$, and $p = 0.0479$, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is close to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9556 suggested that 95.56% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.8954 is in reasonable agreement with the Adjusted R^2 of 0.9320; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the K_{II} fracture toughness in the Mode-II are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 20.278 indicates an adequate signal. This model can be used to navigate the design space.

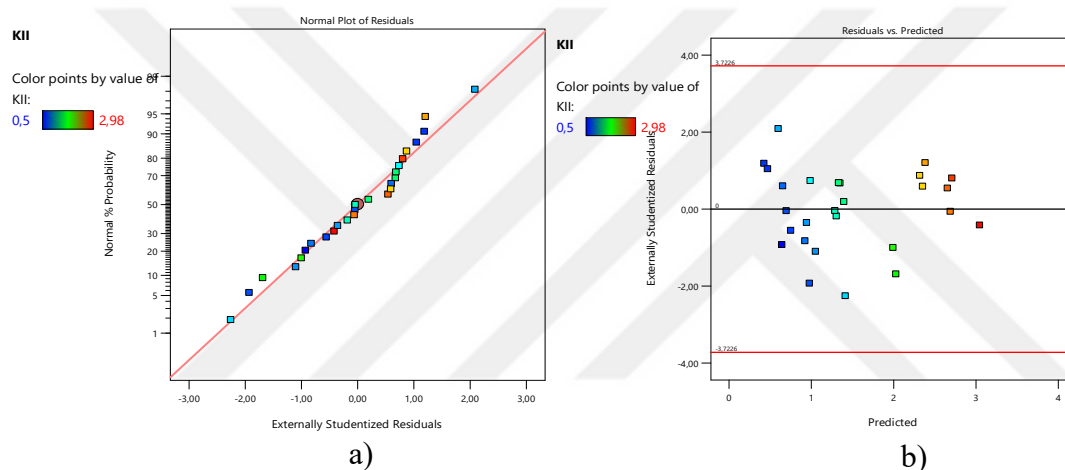


Figure 4.50. a) Normal plot of residuals b) residuals vs predicted plot of K_{II} fracture toughness in the Mode-II of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.50 indicates the normal of residuals and residuals vs. predicted plots for K_{II} fracture toughness of PLA and PLA-based nanocomposites in the Mode-II loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of K_{II} fracture toughness in the Mode-II loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy. Design of experiments (DOE) and response surface methodology (RSM) with an orthogonal array of the Taguchi method have been conducted to obtain optimum input parameters for the best fracture characteristics of parts in the Mode-II loading. 3D surface response diagrams help to better understand to how input parameters affect each other.

According to Table 4.12, the interactions between BC and DE were found significant. To better understand the interaction between these parameters, 3D response surface graphs have been plotted.

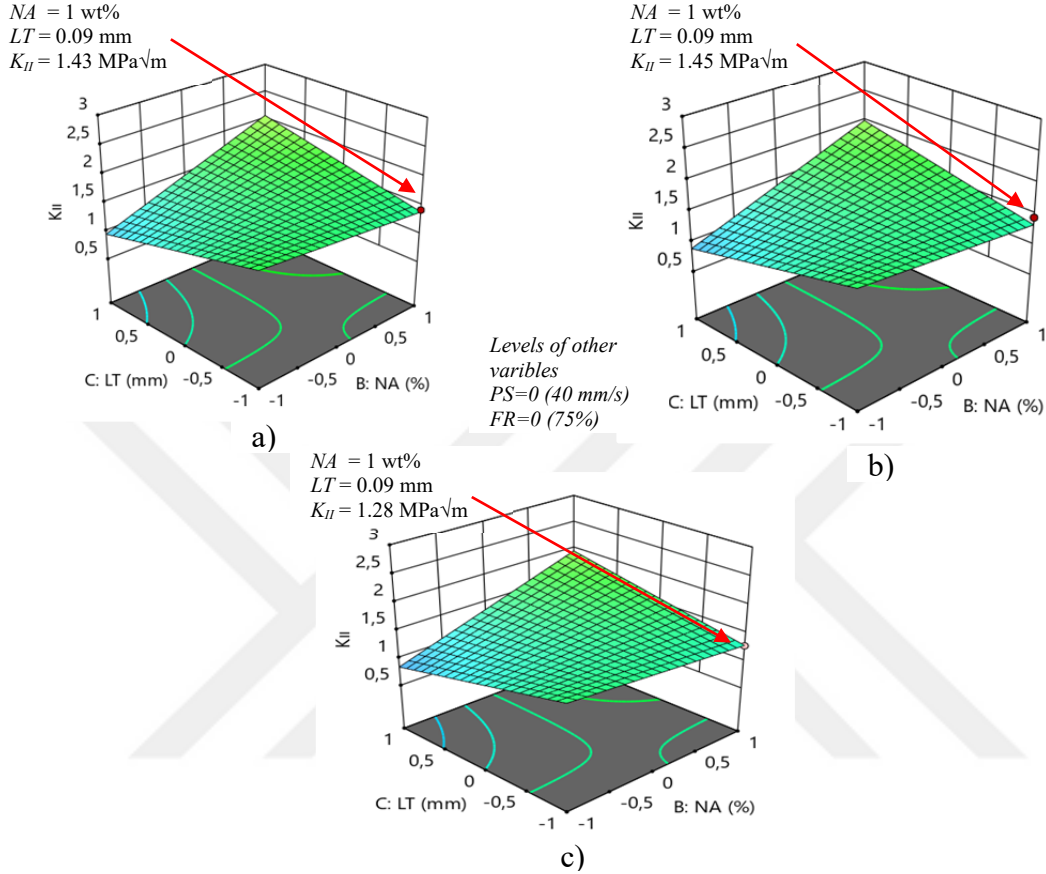


Figure 4.51. 3D response surface plot for NA (%) and LT (mm) of K_{II} fracture toughness in the Mode-II of PLA and PLA-based nanocomposites printed in a) linear b) triangular c) hexagonal internal architecture.

Figure 4.51 represents the interaction between the layer thickness (mm) and nanoparticle addition (%) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_{II} fracture toughness in the Mode-II loading. From this figure, it can be concluded that parts printed with the three architectures yield almost approximated K_{II} fracture toughness values with each other. This figure shows the layer thickness change according to nanoparticle addition at different internal architectures in the Mode-II loading. As can be seen from this figure, the thickness of printed layers should be decreased with increasing the nanoparticle concentration in the matrix for the linear, triangular and hexagonal architectures to realize the maximum enhancement of fracture

toughness of fabricated samples under mode-II loading. It can be said that the fracture properties of parts increases with the increment of nanoparticle concentration in the matrix.

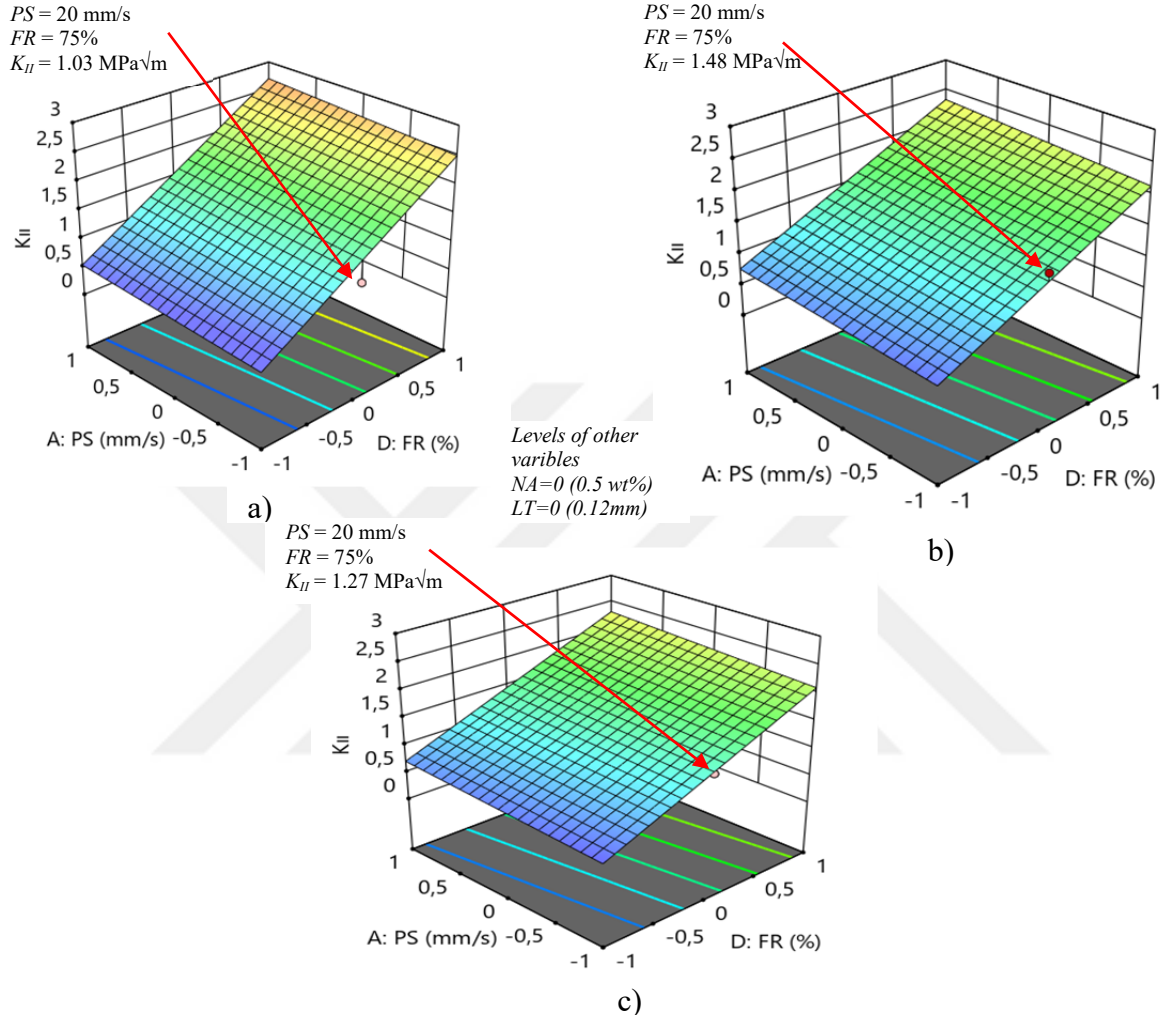


Figure 4.52. 3D response surface plot for PS (mm/s) and FR (%) of K_{II} fracture toughness in the Mode-II of PLA and PLA-based nanocomposites printed in linear internal architecture.

Figure 4.52 represents the interaction between the printing speed (mm/s) and filling ratio (%) of PLA and PLA-based nanocomposites printed in linear, triangular and hexagonal internal architectures for K_{II} fracture toughness in the Mode-II loading. From this figure, it can be concluded that parts printed with the triangular yields almost approximated K_{II} fracture toughness value, which is higher than hexagonal with a slight difference. This figure shows the filling ratio change according to printing speed at different internal architectures in the Mode-II loading. As can be seen from this figure, the printing speed should be reduced with the increase of filling ratio in linear, triangular and hexagonal architectures in order to obtain

the maximum fracture toughness of 3D printed samples under mode-II loading. It can be said that the fracture properties of parts increases with the increment of filling ratio.

4.2.9. ANOVA of P_C critical load in the Mode-II loading for printed PLA/CaCO₃ nanocomposites

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the critical load (P_C) values in the Mode-II. Figure 4.53 shows the best sequence of parameters in order to obtain the highest critical load in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the critical load (P_C) values in the Mode-II found as, 0.5 wt% CaCO₃ reinforced triangular internal architected parts printed at 40 mm/s printing speed, 0.09 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest critical load in mixed mode in this study.

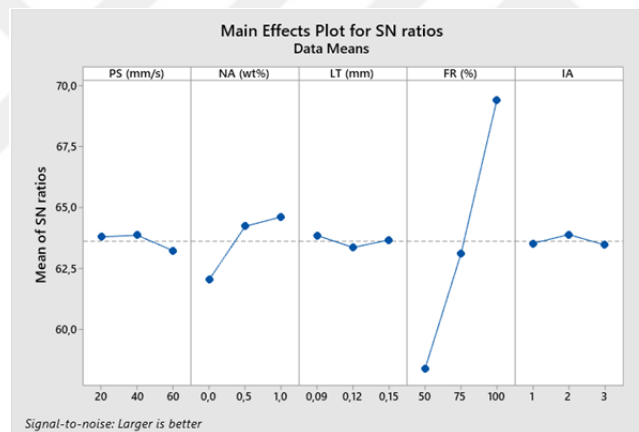


Figure 4.53. S/N ratios from Taguchi analysis for critical load (P_C) in the Mode-II.

Table 4.13. ANOVA for modified quadratic model of critical load (P_C) in the Mode-II of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.433E+07	10	2.433E+06	42.37	< 0.0001	significant
A-PS (mm/s)	1.513E+05	1	1.513E+05	2.63	0.1241	
B-NA (%)	10472.94	1	10472.94	0.1824	0.6750	
C-LT (mm)	1530.89	1	1530.89	0.0267	0.8724	
D-FR (%)	4.337E+06	1	4.337E+06	75.52	< 0.0001	
E-IA	71217.85	2	35608.93	0.6200	0.5504	
AC	1.858E+05	1	1.858E+05	3.24	0.0910	
BC	3.542E+05	1	3.542E+05	6.17	0.0245	
DE	4.812E+05	2	2.406E+05	4.19	0.0344	
Residual	9.189E+05	16	57430.05			
Cor Total	2.525E+07	26				
R ² , 0.9636; adjusted R ² , 0.9409; predicted R ² , 0.9090; adequate precision, 20.4459						

Table 4.13 represents the ANOVA for modified quadratic model of critical load (P_C) in the Mode-II of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. However, E (internal architecture) is an input variable that has p-value greater than 0.05. In order to keep the hierarchy of the models and to increase the overall significance and predictability of the model, E (internal architecture) is kept as a variable in the quadratic models in this study. The Model F-value of 42,37 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise. P-values less than 0,0500 indicate model terms are significant. In this case D, BC, DE are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the critical load (P_C) in the Mode-II of PLA and PLA-based nanocomposites. The most important factor influencing critical load (P_C) in the Mode-II of PLA based nanocomposites was found as filling ratio (%) with probability values of $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC) and filling ratio $\times$ internal architecture (DE) were also found to be significant with probability values of $p = 0.0245$, and $p = 0.0344$, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is near to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9636 suggested that 96.36% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0,9090 is in reasonable agreement with the Adjusted R^2 of 0,9409; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the critical load (P_C) in the Mode-II are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 20,446 indicates an adequate signal. This model can be used to navigate the design space.

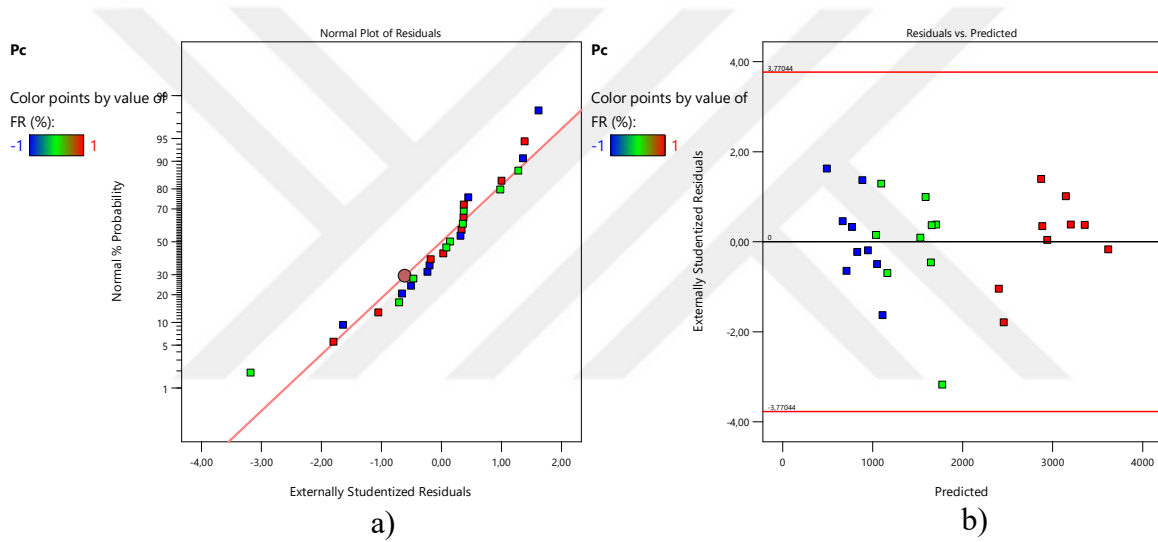


Figure 4.54. a) Normal plot of residuals b) residuals vs predicted plot of critical load (P_C) in the Mode-II of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.54 shows the normal of residuals and residuals vs. predicted plots for critical load P_C of PLA and PLA-based nanocomposites in the Mode-II loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of critical load P_C in the Mode-II loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy.

4.2.10. J_{II} critical strain energy release rate in the Mode-II loading

After the input and output variables specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the total strain energy release rate (J_{II}) values in the Mode-II. Figure 4.55 shows the best sequence of parameters in order to obtain the highest strain energy release rate in this study. As shown in this figure, the S/N ratios after the Taguchi analysis, the best sequence of factors for the strain energy release rate (J_{II}) values in the Mode-II found as, 1 wt% CaCO_3 reinforced linear internal architected parts printed at 20 mm/s printing speed, 0.09 mm layer thickness, and 100% filling ratio. The printed parts with this sequence will have the highest total strain energy release rate in the Mode-II loading in this study.

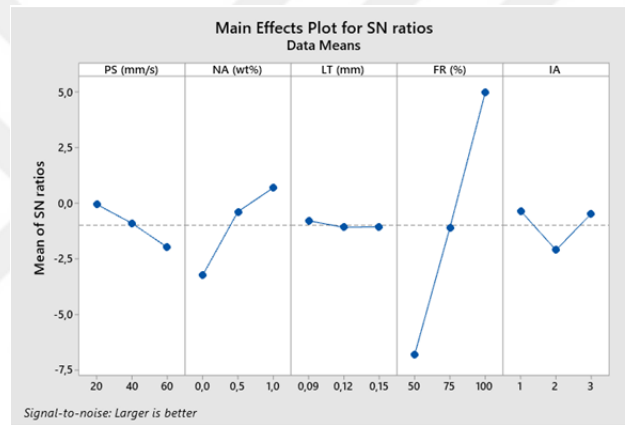


Figure 4.55. Taguchi analysis for strain energy release rate J_{II} in the Mode-II.

Table 4.14. ANOVA for modified quadratic model of critical strain energy release rate J_{II} in the Mode-II of PLA and PLA-based nanocomposites produced at different printing parameters.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	11.65	9	1.29	23.53	< 0.0001	significant
A-PS (mm/s)	0.0240	1	0.0240	0.4370	0.5174	
B-NA (%)	1.17	1	1.17	21.31	0.0002	
C-LT (mm)	0.0244	1	0.0244	0.4440	0.5141	
D-FR (%)	8.69	1	8.69	157.93	< 0.0001	
E-IA	0.2910	2	0.1455	2.65	0.0999	
BC	0.4118	1	0.4118	7.49	0.0141	
DE	0.5834	2	0.2917	5.30	0.0162	
Residual	0.9350	17	0.0550			
Cor Total	12.58	26				
R^2 , 0.9257; adjusted R^2 , 0.8864; predicted R^2 , 0.8149; adequate precision, 17.1312						

Table 4.14 represents the ANOVA for modified quadratic model of critical strain energy release rate J_{II} in the Mode-II of PLA and PLA-based nanocomposites produced at different printing parameters. The models are quadratic models with removed insignificant input variables, which their p-values are greater than 0.05. However, E (internal architecture) is an input variable that has p-value greater than 0.05. In order to keep the hierarchy of the models and to increase the overall significance and predictability of the model, E (internal architecture) is kept as a variable in the quadratic models in this study. The model F-value of 23.53 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case B, D, BC, DE are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The factors with a confidence level greater than 95% were considered significant. Thus, the process factors with $P < 0.05$ and confidence level $> 95\%$ were judged to have a significant effect on the strain energy release rate (J_{II}) in the Mode-II of PLA and PLA-based nanocomposites. The most important factors influencing strain energy release rate (J_{II}) in the Mode-II of PLA based nanocomposites were found as nanoparticle addition (%), and filling ratio (%) with probability values of $p = 0.0002$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC) and filling ratio $\times$ internal architecture (DE) were also found to be significant with probability values of $p = 0.0141$ and $p = 0.0162$, respectively.

The determination coefficient (R^2) values indicate how much the experimental variables and their interactions may be responsible for the variability of the observed response values. The R^2 value is always between 0 and 1. When the R^2 value is near to 1, the model is more reliable and capable of making accurate predictions of the response. In this case, a R^2 of 0.9257 suggested that 92.57% of the total data variance is attributable to the tested variables. The Predicted R^2 of 0.8149 is in reasonable agreement with the Adjusted R^2 of 0.8864; i.e. the difference is less than 0.2. This indicates that the predicted and measured values of the total strain energy release rate (J_{II}) in the Mode-II are highly consistent. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 17.131 indicates an adequate signal. This model can be used to navigate the design space.

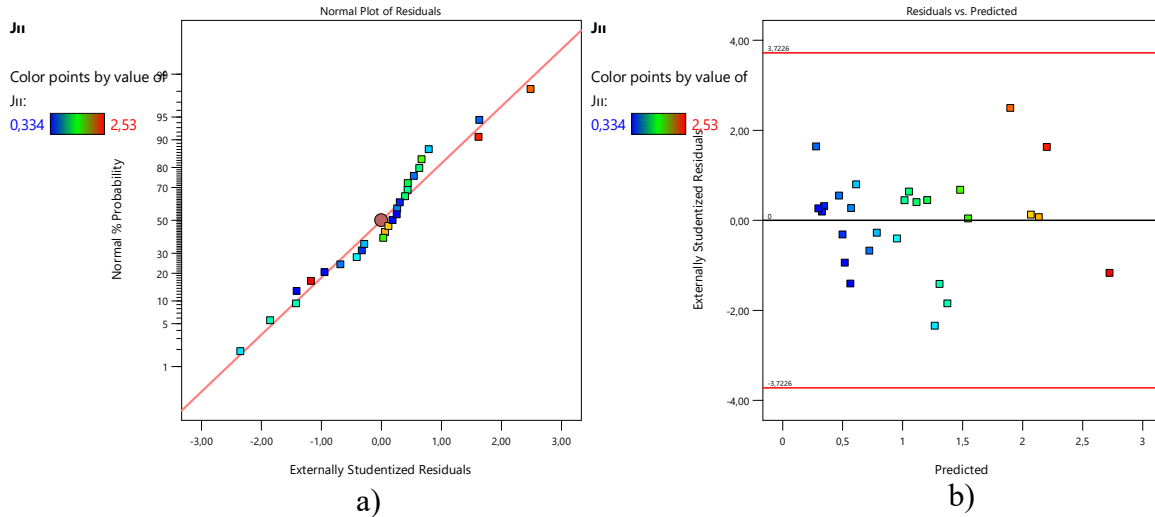


Figure 4.56. a) Normal plot of residuals b) residuals vs predicted plot of critical strain energy release rate J_{II} in the Mode-II of PLA and PLA-based nanocomposites produced at different printing parameters.

Figure 4.56 shows the normal of residuals and residuals vs. predicted plots for total critical strain energy release rate J_{II} of PLA and PLA-based nanocomposites in the Mode-II loading. The residuals are regularly distributed and near to the diagonal line, it shows the model is well-fitted the data. Utilizing the normal probability plot is important to investigation of whether the residuals have a normal distribution and in which situations the points will follow a straight line. The plot of predicted values vs. residuals of total critical strain energy release rate J_{II} in the Mode-II loading shows the residuals scattered uniformly and randomly parallel to the diagonal line, confirming the model's adequacy.

4.3. Differential scanning calorimetry (DSC) results

In order to the examination of transition temperatures such as glass transition temperatures, melting temperatures, and cold crystallization temperatures as well as the enthalpies of transitions, DSC analyses have been conducted. Furthermore, the percent crystallinity of PLA and PLA-based nanocomposites was calculated from DSC results using Eq. (43). The melting enthalpy of 100% crystalline PLA is calculated as 93.7 J/g (Akarsu, 2011). Three different DSC results have been discussed in order to compare and examine the effects of nanoparticle addition in different weight fractions on the transitions and crystallization behavior of parts.

Solid states of polymers appear in the form of amorphous and crystalline structures. The molecular chains in the amorphous structure resemble woolen balls that have been randomly twisted in relation to one another. All of the polymer chains are in a certain order or have crystallized in the crystal structure. Below the T_g temperature, amorphous materials become rigid and brittle. The structure turns rubbery when the T_g temperature is surpassed. Amorphous polymers are common in the industry, including PPE and PVC (Saçak, 1998). Instead of having a completely crystalline structure when solid, polymers typically have a blend of amorphous and crystalline structure. They are polymers with the same chemical make-up, but their molecular chains are linear and branched. The PLA exhibits a semi-crystalline, amorphous, and crystalline structures. The amount of crystalline phase present in the structure affects the characteristics of these polymers (Kodal, 2018). That is, the material tends to grow more brittle as the crystallinity rises (Callister Jr & Rethwisch, 2020). As a result, it is represented by the factor X_C (Degree of Crystallization). The melting enthalpy estimates also rely on the crystallinity of the materials.

4.56 – 4.58 and Table 4.15 represent the thermograms and results of PLA and PLA-based nanocomposites provided from DSC analyses. First of all, it was realized that the melting temperature (T_m) of the samples had increased first, then remained almost the same in 0.5 wt% CaCO_3 and 1 wt% CaCO_3 nanocomposite parts. The increase in T_m demonstrates that strong interface interactions have been created between CaCO_3 nanoparticles and the PLA matrix. The change in the glass transition temperature (T_g) provided a better understanding of the toughness characteristics of PLA and PLA-based nanocomposites. According to the figures, it was realized that the T_g of the samples increased first by with the increment of the weight fraction of CaCO_3 from pure to 0.5 wt%. This small enhancement may be caused by the physical cross-linking brought on by the interactions between the CaCO_3 and PLA, which might be responsible for the reduction in free volume in the polymer matrix. Then, an increment of the weight fraction of CaCO_3 from 0.5 wt% to 1 wt% decreases T_g . It can be caused by the increase of nanoparticles over a certain amount, which may weaken the interfacial interactions between the polymer matrix and CaCO_3 nanoparticles, or the decreased mobility of macromolecular chains in the vicinity of the nanoparticles may be a result of that situation. This situation consists of the experimental results.

Secondly, cold crystallization peaks can be observed in Figures 4.57 – 4.59. This indicates that the crystalline region of the polymer matrix is totally crystallized. Furthermore, pure PLA

and PLA-based nanocomposites showed high crystallinity as expected. The degree of crystallinity sheds light on the molecular chain arrangement of the nanoparticles under the processing conditions used to produce the final part. The percent crystallinity of pure PLA has been calculated as 31.6% and enhanced with the addition of 0.5 wt% CaCO_3 up to 36.1%. The percent crystallinity results are consistent with the experimental results and the dispersion characteristics of nanoparticles. Besides, it is a fact that the addition of nanoparticles enhances the crystallinity of pure polymers. But also, the decrement of X_C in 1 wt% CaCO_3 parts may be the result of the extrusion process of PLA filament processing, extrusion process may cause PLA to deteriorate with chain scissions, which produces shorter PLA chains and increased chain mobility.

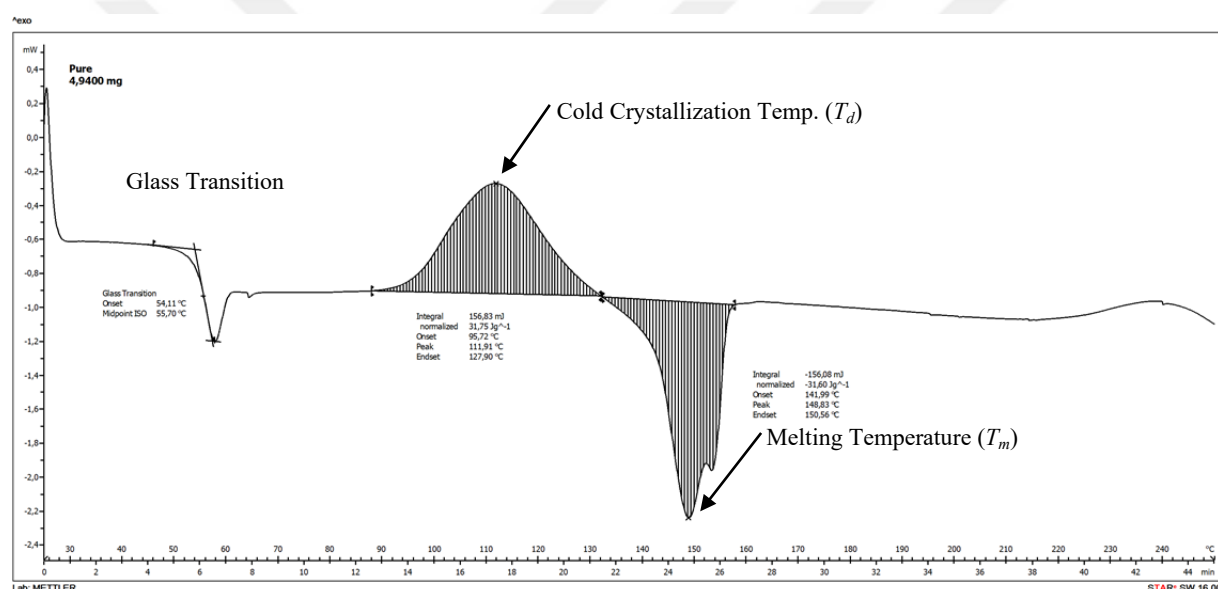


Figure 4.57. DSC results of pure PLA parts.

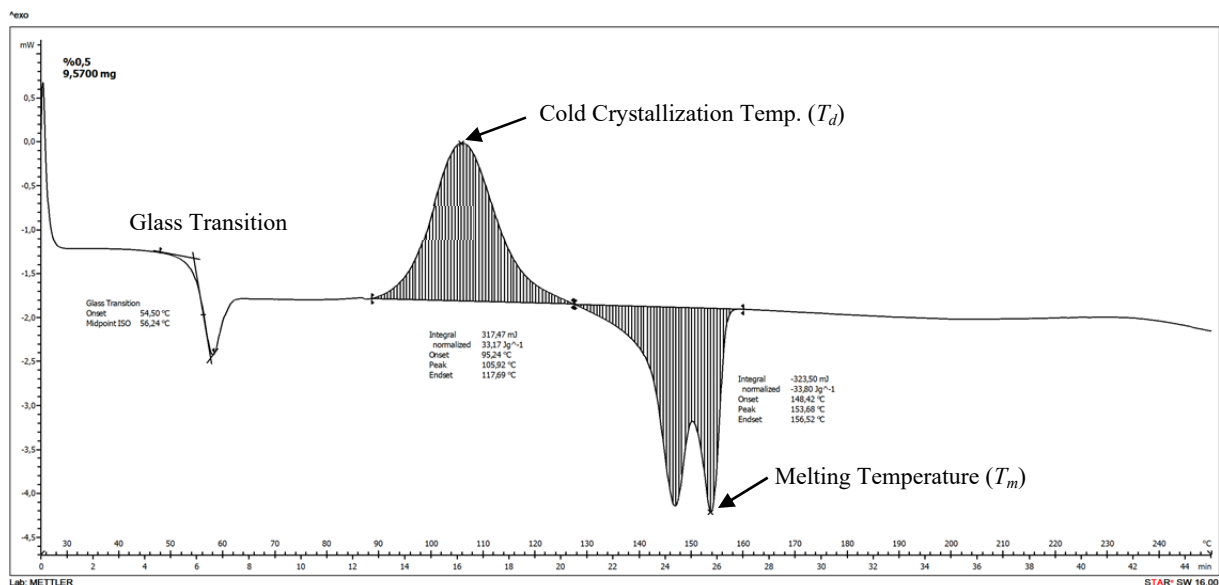


Figure 4.58. DSC results of 0.5 wt% CaCO₃/PLA parts.

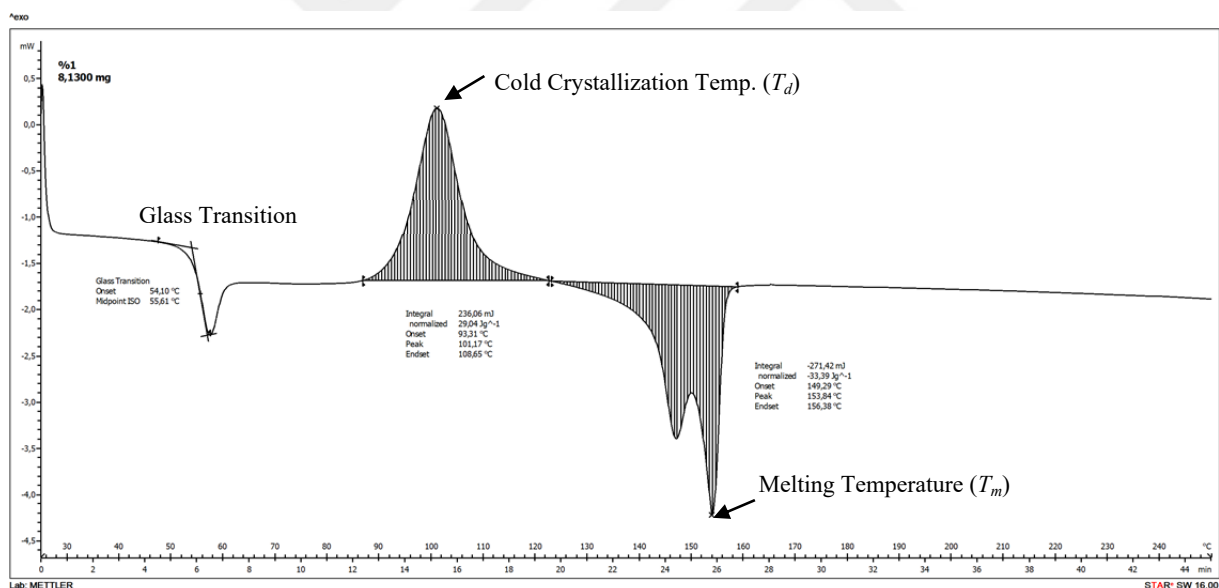


Figure 4.59. DSC results of 1 wt% CaCO₃/PLA parts.

Table 4.15. Results of DSC experiments of pure and PLA/CaCO₃ nanocomposite samples produced in FDM process at parameters of $PS = 20$ mm/s, $FR = 100\%$, and $PP =$ linear.

Material	Glass transition		Crystallization				Melting				Degree of crystallinity X_c (%)
	T_{go}	T_{mid}	T_{co}	T_{cp}	T_{ce}	ΔH_c	T_{mo}	T_{mp}	T_{me}	ΔH_m	
Pure PLA	54.1	55.7	95.7	111.9	127.9	31.75	142	148.8	150.6	31.6	33.7
PLA/0.5 wt% CaCO ₃	54.5	56.3	95.5	105.9	117.7	33.17	148.4	153.7	156.5	33.8	36.1
PLA/1 wt% CaCO ₃	54.1	55.6	93.3	101.2	108.7	29.04	149.3	153.8	156.4	33.4	35.6
T_o is the onset, T_{mid} indicates the mid, and T_e is the ending temperature in Celsius. In the subscript of the T indicates indicate g as glass transition, c as crystallization and m as melting.											

4.4. Molecular dynamics results

In order to investigate the thermo-mechanical properties of PLA and PLA-based nanocomposites on an atomic scale, Biovia Materials Studio software has been conducted to perform molecular dynamics simulations. The calculation method and theoretical procedure have explained in Chapter 3. Table 4.16 represents the specifics of the RVEs of PLA/CaCO₃ and PLA/GR nanocomposites after packing process, NPT, and NVT ensembles.

Table 4.16. Details of RVEs of PLA/CaCO₃ and PLA/GR nanocomposites.

Weight fraction of nanoparticles (wt%)		0	1	3	5
Initial size of the unit cell (Å°)	CaCO ₃	159	186	166	143
	GR	159	179	161	135
Final size of the unit cell (Å°)	CaCO ₃	66	100	68	57.2
	GR	66	91	64	54
Number of PLA molecular chains	CaCO ₃	149	458	159	93
	GR	149	372	126	72

The mechanical characteristics of the CaCO₃/PLA nanocomposites are greatly influenced by the distribution of PLA molecules surrounding the nanoparticles. The radial distribution function is a local measurement of the spatial distribution of a system of particles and a method for describing amorphous materials. The situation of $g(r) = 1$ reveals that the particles are distributed uniformly in the subvolume dV at a distance r . The distribution of polymer

layers surrounding the nanoparticle is depicted in the radial distribution function (RDF) of RVE for 5wt% GR and CaCO_3 , which is shown in Figures 4.60 and 4.61. Increasing the distance from the CaCO_3 nanoparticle's surface results in a larger density and concentration of molecules near the nanoparticle, which corresponds to the general density of the RVE. As can be seen from figures, $g(r) \approx 7.5$ for 5 wt%PLA/GR, and $g(r) \approx 8$ for 5 wt% CaCO_3 nanocomposites. Since the distribution of GR nanoparticles is nearly uniform, the GR nanoparticle moves a bit more freely and interacts rarely with another particle in the system (Younge, Christenson, Bohara, Crnkovic, & Saulnier, 2004). Hence, the distribution of nanoparticles is a bit more close to uniform.

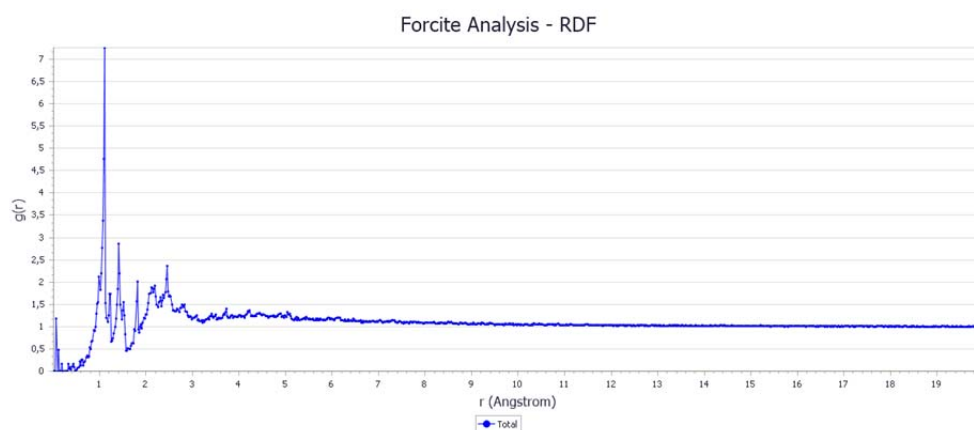


Figure 4.60. Radial distribution function of RVE of 5 wt% GR/PLA nanocomposite.

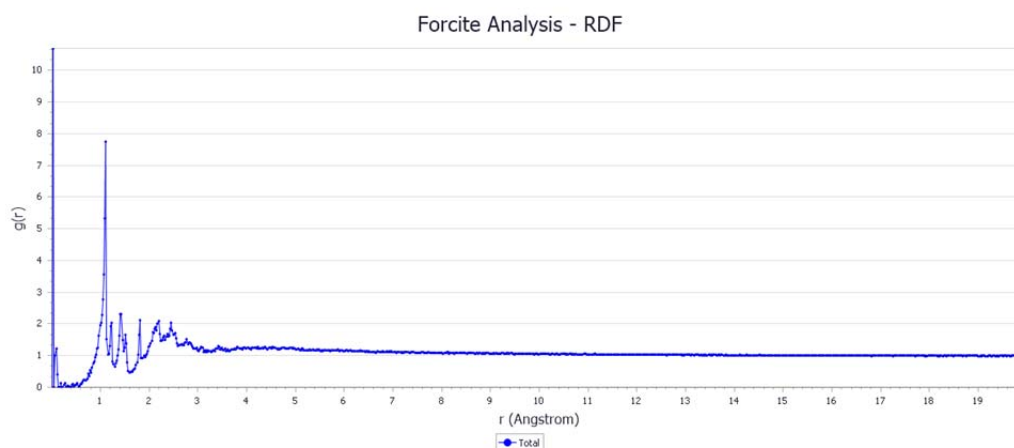


Figure 4.61. Radial distribution function of RVE of 5 wt% CaCO_3 /PLA nanocomposite.

Figures 4.62 and 4.63 represents the energy and temperature changes that occurred during NPT and NVT ensembles PLA nanocomposites that contains 5wt% of CaCO_3 and GR.

These figures show that the duration of the dynamic runs is adequate for the system of both nanocomposites to reach the equilibrium state because the RVE achieves the energy balance in the NPT run below 20 ps and the temperature of the nanocomposite fluctuates only slightly in the NVT run between 294 and 304 K.

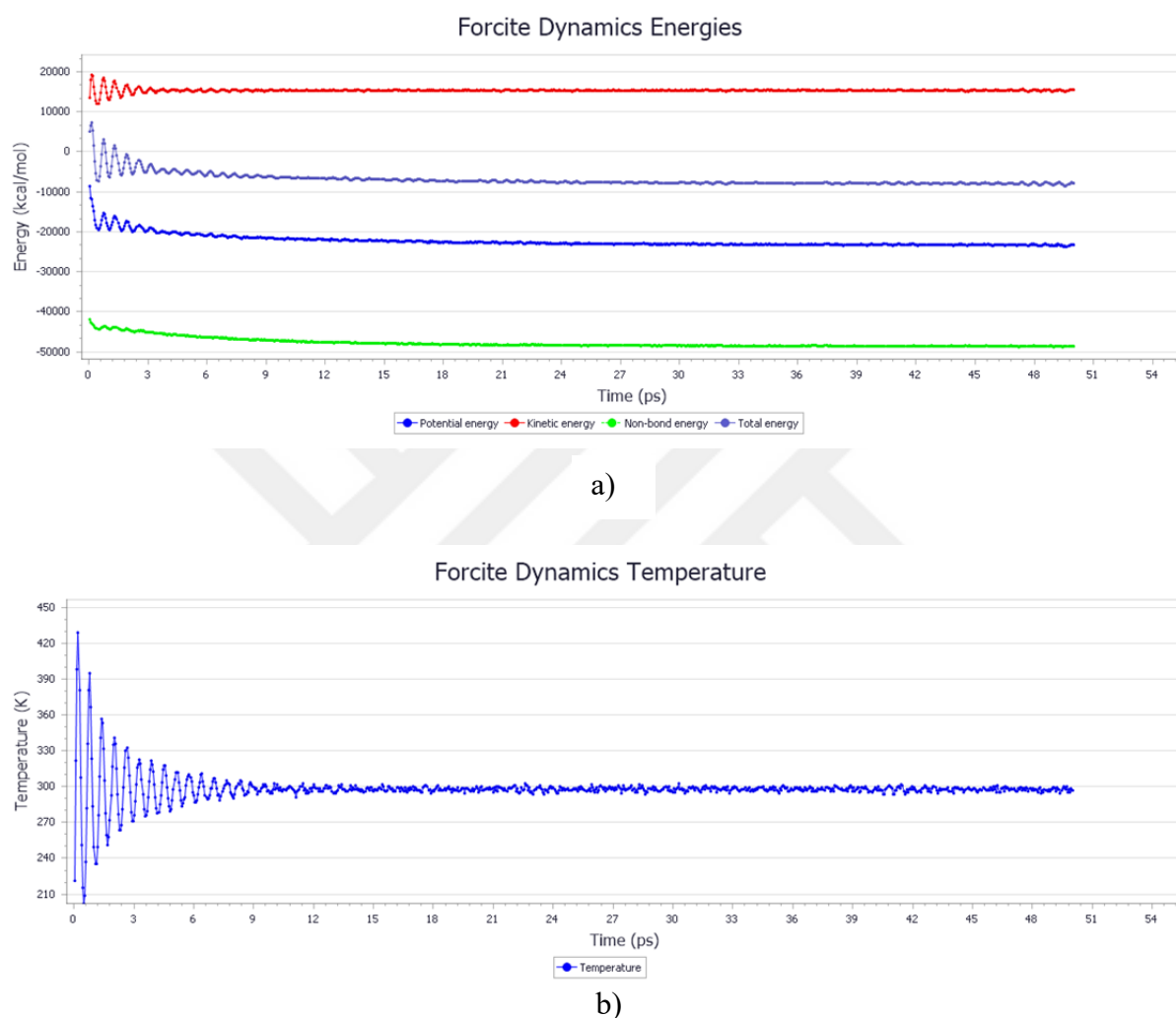
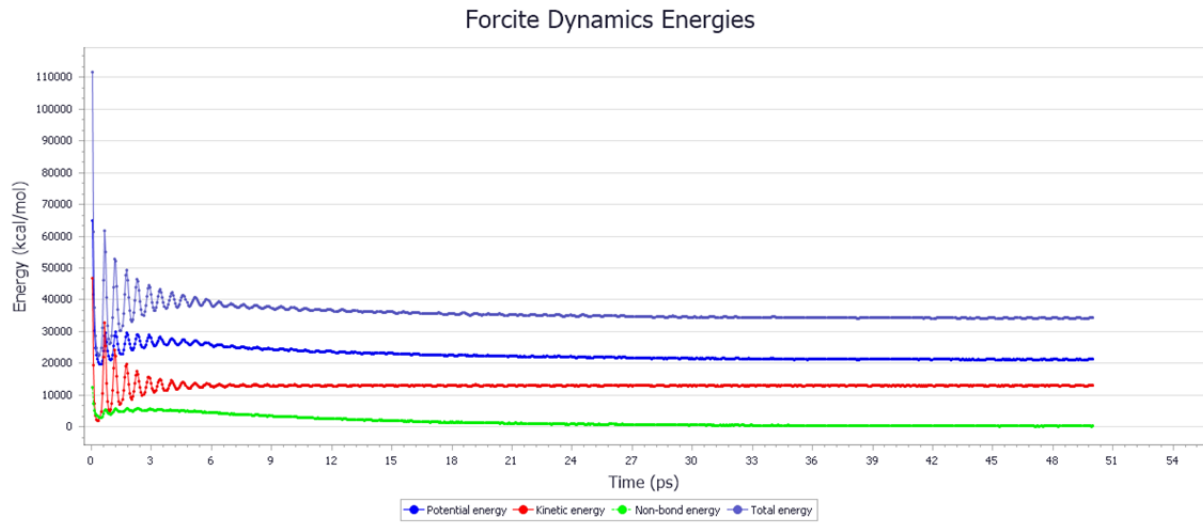
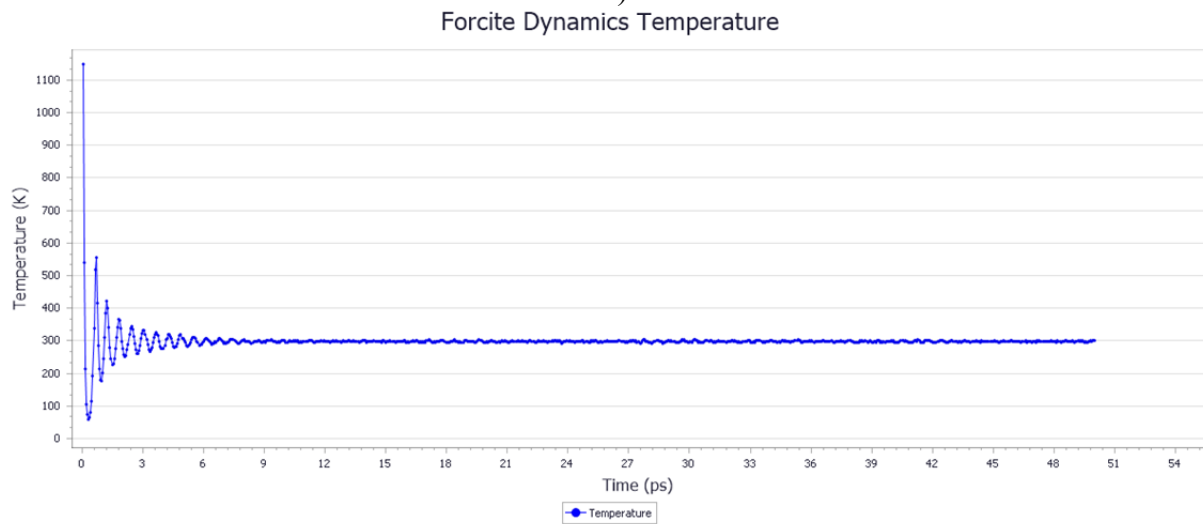


Figure 4.62. Variables of 5 wt% CaCO_3 /PLA nanocomposite RVE in forcite dynamics; a) energy evolution during NPT, and b) temperature evolution during NVT ensembles.



a)



b)

Figure 4.63. Variables of 5 wt% GR/PLA nanocomposite RVE in forcite dynamics; a) energy evolution during NPT, and b) temperature evolution during NVT ensembles.

4.4.1. Mechanical properties of PLA and PLA-based nanocomposites

Mechanical properties of PLA and PLA-based nanocomposites have calculated using the elastic stiffness constants and the Eqs. (62) and (63) in Chapter 3. Table 4.17 represents the calculated values of mechanical properties of PLA nanocomposites in different weight fractions of CaCO_3 and GR with the summary of the relative errors between the experimentally determined mechanical characteristics of PLA/ CaCO_3 nanocomposites and the values predicted by MD simulations.

Table 4.17. Mechanical properties of PLA and PLA-based nanocomposites in different weight fractions.

Weight fraction of GR nanoparticles (wt%)		0	1	3	5
Modulus of elasticity (GPa)	^a MD	4.03	4.18	4.89	4.58
	^b Exp.	3.79	4.22	4.81	4.50
	^c Error (%)	5.95%	0.94%	1.63%	1.74%
Shear Modulus (GPa)	MD	1.91	2.01	2.27	1.76
	Exp.	1.84	1.94	2.23	1.82
	Error (%)	3.66%	3.48%	1.76%	3.29%
Poisson's ratio	MD	0.460	0.421	0.471	0.239
	Exp.	0.429	0.416	0.51	0.24
	Error (%)	6.73%	1.18%	7.64%	0.41%
Weight fraction of CaCO ₃ nanoparticles (wt%)		0	1	3	5
Modulus of elasticity (Gpa)	^a MD	4.03	4.12	4.51	4.48
	^b Exp.	3.79	4.13	4.62	4.55
	^c Error (%)	5.95%	0.24%	2.38%	1.53%
Shear Modulus (Gpa)	MD	1.91	2.01	2.09	2.08
	Exp.	1.84	1.95	2.18	2.17
	Error (%)	3.66%	2.98%	4.12%	4.14%
Poisson's ratio	MD	0.460	0.443	0.453	0.430
	Exp.	0.429	0.412	0.465	0.415
	Error (%)	6.73%	6.99%	2.58%	3.48%
1. The values obtained by MD simulations. 2. The experimental values. 3. The error of the simulation results with respect to the experimental values.					

The maximum error values were calculated as 5.95%, 3.66%, and 6.99% for E , G and ν values, this shows the MD simulations are effective in forecasting the mechanical performance of parts. The stress-strain curves of injection molded PLA and PLA-based nanocomposites are given in Figure 4.64. According to MD and experimental results, the addition of CaCO₃ increases the mechanical properties of PLA. With the addition of 3wt% CaCO₃, modulus of elasticity, shear modulus and Poisson's ratio values have increased by about 18%, 16%, and 8%. The addition of GR in 3wt% increased the modulus of elasticity, shear modulus, and Poisson's ratio values by about 21%, 17%, and 16%. The strong interaction between the nanoparticles and matrix as well as the enhancement in crystallinity of the polymer caused by the matrix's increased nucleation sites could both be responsible for these improvements and the decrease in 5wt%.

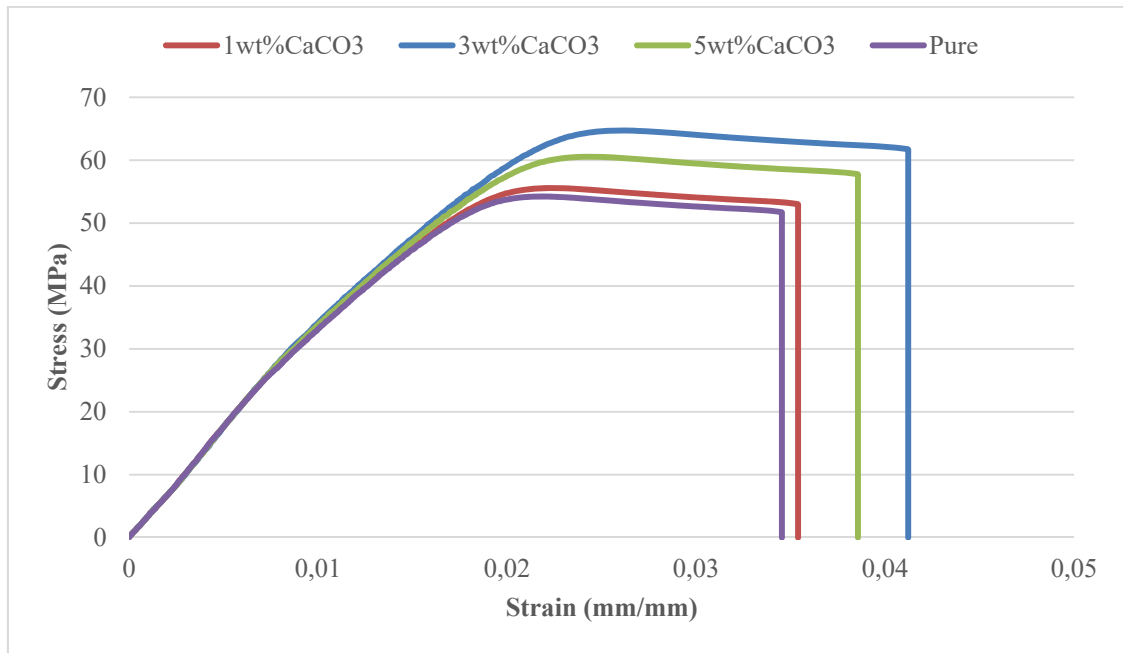


Figure 4.64. Stress-strain curve of injection molded PLA and PLA/CaCO₃ nanocomposites in different weight fractions.

5. CONCLUSIONS

This master's thesis study is aimed to (i) expand the use of polymer-based nanocomposite parts with superior thermo-mechanical properties and fracture behaviors by using a rapid and cost-effective FDM technology and (ii) produce polymer-based nanocomposite parts by utilizing the injection molding process to investigate the effectiveness of MD simulations in forecasting the mechanical performance of parts through the comparison of mechanical properties of produced parts with the results of molecular dynamics (MD) simulations.

In order to accomplish the first aim, polylactic acid (PLA), one of the foremost biodegradable polymers, was chosen as matrix material, while calcium carbonate (CaCO_3) nanoparticles were used as reinforcement materials. For this purpose, the PLA/ CaCO_3 nanocomposite filaments, containing different weight ratios (0, 0.5, and 1 wt%) of nanoparticles in the matrix, have been synthesized by melt-blending technique using a twin-screw extruder system. These filaments were used to produce samples by fused deposition technique with different printing parameters to study the effects of nanoparticles and printing parameters on the mechanical properties and fracture behavior of the PLA nanocomposites under mixed-mode fracture loadings. In this regard, this study investigates the effects and significance of these different parameters, which are called printing speed, weight fractions of nanoparticle addition, layer thickness, filling ratio, and internal architecture, on the fracture characteristics and mechanical behavior of FDM 3D printed PLA and PLA/ CaCO_3 nanocomposites. To this end, the analysis of the Taguchi design has been conducted based on the experimental results to determine the optimized levels of factors by which the maximum level of material properties could be obtained. Thus, it has been determined which combination can be used in further FDM 3D printing of PLA-based materials, or which factor level will be appropriate. A response surface methodology (RSM) was employed to model and predict the mechanical and mixed-mode fracture properties of the PLA-based nanocomposites produced in different weight ratios and different FDM printing parameters. The produced samples were subjected to uniaxial tensile tests for the mechanical characterization. Mixed-mode fracture behavior of the synthesized samples were studied by applying mixed-mode loadings on the pre-cracked samples using an in-lab developed fixture mounted on the uniaxial tensile test machine. Finite element simulations are employed to simulate the crack opening on such specimens and calculate the geometry shape functions of the fracture samples at different loading angles. Finally, after the experimental procedures, scanning electron microscopy (SEM) examinations have been

conducted on the fractured surfaces of the test samples to reveal the fracture morphology of parts and validate the presence of nanoparticles. In addition, differential scanning calorimetry (DSC) analyses are conducted to determine the variations in the glass transition and heat capacity of the PLA polymer by the incorporation of CaCO_3 nanoparticles in the PLA matrix.

Secondly, molecular dynamic (MD) simulations using Material Studio software is employed to investigate the physical behavior of injection molded PLA/ CaCO_3 nanocomposites in different weight ratios (1, 3 and 5wt%) and provide details of interactions between the molecules and nanoparticles on an atomic scale. Molecular dynamics analyses were carried out to verify the results obtained from the experimental procedures and for the reason that the molecular dynamics simulations and experimental results are consistent with each other, PLA/GR nanocomposite materials in different weight fractions were simulated to predict the mechanical properties of injection molded PLA/GR nanocomposites. It has been observed that Materials Studio software provides realistic results in estimating the mechanical properties of materials. Numerical analyses were carried out to verify the results obtained from the experimental procedures. The key findings and conclusions of this study are summarized as follows:

1. According to uniaxial tensile test results, the PLA nanocomposite parts that were fabricated according to Taguchi experimental run 23, which the parts printed with a triangular internal architecture, 0.09 mm layer thickness, 100% filling ratio at 60 mm/s and containing 0.5 wt% CaCO_3 showed the highest modulus of elasticity and yield strength values with 3868 and 43.5 MPa, which resulted in the smallest elastic strain. Then it is followed by the parts printed with linear and hexagonal internal architectures, while the other parameters are the same.
2. The PLA nanocomposite parts that were fabricated according to Taguchi experimental run 7, which the parts printed with the linear internal architecture, 0.15 mm layer thickness, 100% filling ratio at 20 mm/s and containing 1% CaCO_3 provided the best K_I fracture toughness, critical load (P_C), and strain energy release rate (J_I) values in the mode-I loading, with 3.81 $\text{MPa}\sqrt{\text{m}}$, 3710 N, and 4.136 N/mm, respectively.
3. The PLA nanocomposite parts that were fabricated according to Taguchi experimental run 7, which the parts printed with the linear internal architecture, 0.15 mm layer thickness, 100% filling ratio at 20 mm/s and containing 1% CaCO_3 provided best K_I fracture toughness, K_{II} fracture toughness, critical load (P_C), and the total strain energy

release rate (J_T) values in the mixed mode-I/II loading with $1.90 \text{ MPa}\sqrt{\text{m}}$, $2.52 \text{ MPa}\sqrt{\text{m}}$, 2800 N , and 2.873 N/mm , respectively.

4. The PLA nanocomposite parts that were fabricated according to Taguchi experimental run 7, which the parts printed with the linear internal architecture, 0.15 mm layer thickness, 100% filling ratio at 20 mm/s and containing $1\% \text{ CaCO}_3$ provided best K_{II} fracture toughness, critical load (P_C), and the strain energy release rate (J_{II}) values in the mode-II loading with $2.98 \text{ MPa}\sqrt{\text{m}}$, 3590 N , and 2.53 N/mm , respectively. According to fractographic examinations, although the more brittle behavior was observed in linear architecture in shear loading and the increase in fracture loading caused by the addition of CaCO_3 nanoparticles to the matrix due to the uniformly distributed micro-voids produced by the nanoparticles and the 3D stress state at the crack tip in samples with linear structures.
5. While the triangular internal architecture provides the best mechanical properties, linear architecture provides the best fracture characteristics in all loadings. As a consequence of its geometry, a typical loading causes tension and compression to act concurrently on the parts that have triangular internal architecture, so that the triangular internal architecture improves the reinforcing effects of nanoadditives on the mechanical response of FDM 3D printed samples. It also can be concluded that the linear internal architecture can absorb highest energy before failure due to its cross-deposition layout of $\pm 45^\circ$.
6. The addition of CaCO_3 nanoparticles enhanced the mechanical and fracture properties of parts, in overall, $0.5 \text{ wt}\%$ CaCO_3 addition into the PLA matrix provides the best characteristics for the samples printed for uniaxial tensile tests. The polymer matrix interacted with nanoparticle surfaces and intertwined around such nanoparticles. This situation could increase the tensile load-bearing capacity of polymers. For Arcan fracture samples, a $1 \text{ wt}\%$ CaCO_3 addition into the PLA matrix has resulted in the best fracture characteristics.
7. Printing speed, effects the binding between the deposited printing beads and the formation of air gap between them. Higher printing speeds, generally over 60 mm/s , would result in less stable prints and the presence of air in PLA and composite sample that significantly contributes to the creation of flaws in the printed samples. Additionally, when printing speed increased, the mechanical strength of the stacked macromolecule chains decreased. In the other hand, when the printing speed is around

to 60 mm/s, the melting material that is extruded from the nozzle has adequate time to bond with the adjacent printed component, enhancing the mechanical performance of manufactured components. According to experimental results of the fracture tests under mode-I, mode-I/II and mode-II loadings, PLA nanocomposite parts printed at 20 mm/s has the highest capacity to absorb the energy.

8. It is a fact that if the material has fewer gaps than the others, the mechanical properties of the material will be resulted in higher values. Filling ratio value of printing determines the amount of gaps into the parts. 100% filling ratio increases the reduce of cost, but also increase the properties of materials.
9. After the input and output variables have been specified, the Taguchi array has been analyzed in order to get the best sequence of factors for the mechanical and fracture properties. According to S/N ratios from Taguchi L_{27} analysis results, the best sequence of parameters have been found as:

For the modulus of elasticity,

- The best sequence of factors for modulus of elasticity (E) values was found as 0.5 wt% CaCO_3 reinforced triangular internal architected parts printed at 60 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. The printed parts with this sequence will have the highest rigidity, which resulted in the smallest elastic strain in this study. ANOVA results are consistent with the experimental results for E , in which 0.5 wt% PLA/ CaCO_3 parts have the highest E values at 60 mm/s. These observations demonstrate that the triangular pattern is the most resistant to deformation, which is also the most stiff structure.

For the yield strength,

- The best sequence of factors for yield strength values was found as, 0.5 wt% CaCO_3 reinforced triangular internal architected parts printed at 60 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest yield strength, resulting in the highest stress beyond their plastic deformation. As a consequence of its geometry, a typical loading causes tension and compression to act concurrently on the parts that have a triangular internal architecture, so that the triangular internal architecture improves

the reinforcing effects of nanoadditives on the mechanical response of 3D printed samples.

For the K_I fracture toughness in the Mode-I loading,

- The best sequence of factors for the mode-I fracture toughness (K_I) values was found as, 1 wt% CaCO_3 reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. According to the Taguchi analysis and experimental results, it can be concluded that the addition of nanoparticles by 1 wt% into the PLA matrix has resulted in better Mode-I fracture toughness characteristics. Printed parts with this sequence will have the highest toughness in the opening mode.

For the critical load (P_C) in the Mode-I loading,

- The best sequence of factors for the critical load (P_C) values in the Mode-I loading was found as, 1 wt% CaCO_3 reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest critical load in the opening mode in this study.

For the strain energy release rate (J_I) in the Mode-I loading,

- The best sequence of factors for the strain energy release rate (J_I) values in the Mode-I loading was found as, 1 wt% CaCO_3 reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest strain energy release rate in the opening mode in this study.

For the $K_{I/II}$ fracture toughness in the Mode-I/II,

- The best sequence of factors for the mode-I/II fracture toughness ($K_{I/II}$) values was found as, 1 wt% CaCO_3 reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest toughness in the mixed mode loading.

For the K_{II} fracture toughness in the Mode-I/II,

- The best sequence of factors for the mode-I/II fracture toughness (K_{II}) values was found as, with a slight difference, 0.5 wt% CaCO_3 reinforced triangular internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. The reason that the 0.5 wt% reinforced parts have the better results may be due to the weak zones in the 1 wt% CaCO_3 /PLA matrix had forced to elongate along the mixed-mode loading direction. Printed parts with this sequence will have the highest toughness in the mixed mode loading.

For the critical load (P_C) in the Mode-I/II,

- The best sequence of factors for the critical load (P_C) values in the Mode-I/II found as, 0.5 wt% CaCO_3 reinforced triangular internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest critical load in the mixed mode loading in this study.

For the total strain energy release rate (J_T) in the Mode-I/II,

- The best sequence of factors for the total strain energy release rate (J_T) values in the Mode-I/II found as, 1 wt% CaCO_3 reinforced linear internal architected parts printed at 40 mm/s printing speed, 0.15 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest total strain energy release rate in mixed mode in this study.

For the K_{II} fracture toughness in the Mode-II,

- The best sequence of factors for the mode-II fracture toughness (K_{II}) values was found as, with a slight difference, 1 wt% CaCO_3 reinforced triangular internal architected parts printed at 40 mm/s printing speed, 0.09 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest toughness in the mode-II loading.

For the critical load (P_C) in the Mode-II,

- The best sequence of factors for the critical load (P_C) values in the Mode-II found as, 0.5 wt% CaCO_3 reinforced triangular internal architected parts printed at 40 mm/s printing speed, 0.09 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest critical load in mixed mode in this study.

For the strain energy release rate (J_{II}) in the Mode-II,

- The best sequence of factors for the strain energy release rate (J_{II}) values in the Mode-II found as, 1 wt% CaCO_3 reinforced linear internal architected parts printed at 20 mm/s printing speed, 0.09 mm layer thickness, and 100% filling ratio. Printed parts with this sequence will have the highest total strain energy release rate in the mode-II loading in this study.

10. Nanoparticle addition to matrix and printing parameters were found to be very effective in determining the mechanical and fracture properties of the PLA nanocomposites. According to ANOVA results, significant parameters have been found as:

For the modulus of elasticity,

- The most important factors influencing E of PLA based nanocomposites were found as printing speed, and filling ratio with probability values of $p = 0.0010$ and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition and nanoparticle addition $\times$ layer thickness were also found to be significant.

For the yield strength,

- The most important factors influencing yield strength of PLA based nanocomposites were found as printing speed, nanoparticle addition, filling ratio and internal architecture with probability values of $p < 0.0001$, $p = 0.0019$, $p = 0.0014$ and $p = 0.0198$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition, printing speed $\times$ layer thickness, and nanoparticle addition $\times$ layer thickness were also found to be significant.

For the K_I fracture toughness in the Mode-I loading,

- The most important factors influencing K_I fracture toughness in the Mode-I loading of PLA based nanocomposites were found as printing speed, nanoparticle addition, layer thickness, filling ratio, and internal architecture with probability values of $p = 0.0067$, $p = 0.0004$, $p = 0.0023$, $p < 0.0001$ and $p = 0.0198$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition, and nanoparticle addition $\times$ layer thickness were also found to be significant. The quadratic effects of the printing speed was also found to be significant with p value of 0.0002, respectively.

For the critical load (P_C) in the Mode-I loading,

- The most important factors influencing critical load (P_C) in the Mode-I of PLA based nanocomposites were found as printing speed (mm/s), nanoparticle addition (%), layer thickness (mm), filling ratio (%), and internal architecture with probability values of $p = 0.0014$, $p < 0.0001$, $p = 0.0005$, $p < 0.0001$ and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition (AB), and nanoparticle addition $\times$ layer thickness (BC) were also found to be significant. The quadratic effects of the printing speed was also found to be significant with p value of 0.0003, respectively.

For the strain energy release rate (J_I) in the Mode-I loading,

- The most important factors influencing strain energy release rate (J_I) in the Mode-I of PLA based nanocomposites were found as nanoparticle addition (%), layer thickness (mm), filling ratio (%), and internal architecture with probability values of $p = 0.0030$, $p = 0.0182$, $p < 0.0001$ and $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC) was also found to be significant.

For the K_I fracture toughness in the Mode-I/II,

- The most important factors influencing K_I fracture toughness in the Mode-I/II of PLA based nanocomposites were found as printing speed, nanoparticle addition, layer thickness, and filling ratio with probability values of $p = 0.0004$, $p = 0.0161$,

$p = 0.0141$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition, printing speed $\times$ layer thickness, and nanoparticle addition $\times$ layer thickness, and filling ratio $\times$ internal architecture (DE) were also found to be significant. The quadratic effects of the printing speed was also found to be significant with p value of 0.0229, respectively.

For the K_{II} fracture toughness in the Mode-I/II,

- The most important factors influencing K_{II} fracture toughness in the Mode-I/II of PLA based nanocomposites were found as printing speed, nanoparticle addition, and filling ratio with probability values of $p = 0.0018$, $p = 0.0456$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$ layer thickness, and nanoparticle addition $\times$ layer thickness, and filling ratio $\times$ internal architecture were also found to be significant.

For the critical load (P_C) in the Mode-I/II,

- The most important factors influencing critical load (P_C) in the Mode-I/II of PLA based nanocomposites were found as printing speed (mm/s), nanoparticle addition (%), layer thickness (mm), and filling ratio (%) with probability values of $p = 0.0015$, $p = 0.0016$, $p = 0.0358$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between printing speed $\times$ nanoparticle addition (AB), nanoparticle addition $\times$ layer thickness (BC), and filling ratio $\times$ internal architecture (DE) were also found to be significant. The quadratic effects of the printing speed was also found to be significant with p value of 0.0057, respectively.

For the total strain energy release rate (J_T) in the Mode-I/II,

- The most important factors influencing total strain energy release rate (J_T) in the Mode-I/II of PLA based nanocomposites were found as nanoparticle addition (%), and filling ratio (%) with probability values of $p = 0.0062$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC) and filling ratio $\times$ internal architecture (DE) were also found to be significant.

For the K_{II} fracture toughness in the Mode-II,

- The most important factors influencing K_{II} fracture toughness in the Mode-II of PLA based nanocomposites were found as nanoparticle addition, and filling ratio with probability values of $p = 0.0005$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness, and filling ratio $\times$ internal architecture were also found to be significant.

For the critical load (P_C) in the Mode-II,

- The most important factor influencing critical load (P_C) in the Mode-II of PLA based nanocomposites was found as filling ratio (%) with probability values of $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC) and filling ratio $\times$ internal architecture (DE) were also found to be significant.

For the strain energy release rate (J_{II}) in the Mode-II,

- The most important factors influencing strain energy release rate (J_{II}) in the Mode-II of PLA based nanocomposites were found as nanoparticle addition (%), and filling ratio (%) with probability values of $p = 0.0002$, and $p < 0.0001$, respectively. It was also noticed that the interaction effects between nanoparticle addition $\times$ layer thickness (BC) and filling ratio $\times$ internal architecture (DE) were also found to be significant.

11. Percent crystallinity of pure PLA has calculated as 31.6% and enhanced with the addition of 0.5 wt% CaCO_3 up to 36.1%. Percent crystallinity results are consistent with the experimental results and about the dispersion characteristics of nanoparticles. Besides, it is a fact that the addition of nanoparticles enhances the crystallinity of pure polymers. But also, the decrease of X_C in 1 wt% CaCO_3 parts may be the result of the extrusion process of PLA filament processing, extrusion process may cause PLA to deteriorate with chain scissions, which produces shorter PLA chains and increased chain mobility.
12. The mechanical characteristics of the CaCO_3/PLA nanocomposites are greatly influenced by the distribution of PLA molecules surrounding the nanoparticles.

According to molecular dynamics results, graphene nanoparticle moves a bit more freely and interacts rarely with another particle in the system. Hence, the distribution of nanoparticles a bit more close to uniform.

13. The maximum error values were calculated as 5.95%, 3.66%, and 6.99% for E , G and ν values, this shows the MD simulations are effective in forecasting the mechanical performance of parts. According to MD and experimental results, addition of CaCO_3 increases mechanical properties of PLA. With the addition of 3wt% CaCO_3 , modulus of elasticity, shear modulus and Poisson's ratio values have increased by about 18%, 16% and 8%. Addition of GR in 3wt% increased the modulus of elasticity, shear modulus and Poisson's ratio values by about 21%, 17%, and 16%. The strong interaction between the nanoparticles and matrix as well as the enhancement in crystallinity of the polymer caused by the matrix's increased nucleation sites could both be responsible for these improvements and the decrease in 5wt%.

6. RECOMMENDATIONS

It has been revealed that the use of polymer-based composites is widespread in the industry. Fused deposition modeling (FDM) is one of the well-known and widely used AM methods that emerges some advantages, such as low cost and high speed, and has been used in the production of polymer composite parts. However, FDM 3D printing has some limitations due to shortcomings in the thermo-mechanical properties of its building materials, known as polymeric filaments, although they have advantages such as easy processability, low cost, and good chemical resistance. Therefore, the FDM technique may be able to extend its application areas with the reinforcement of nanoparticles in building materials. This study aimed to improve the thermomechanical properties of polymers with nanoparticle reinforcement and different FDM printing parameters to find best properties with optimum sequence. Furthermore, injection molding, one of the traditional manufacturing methods, has been utilized to investigate mechanical properties of polymer nanocomposites and to compare with molecular dynamics simulations.

Within the scope of findings from this study, some further research could be carried out in order to improve the thermomechanical properties or to investigate the characteristics of polymer parts.

1. Different forms of nanofillers, for example, continuous carbon fibers can be used to produce polymer-based nanocomposites.
2. Failure criterias can be combined for elasto-plastic materials. U-notched or compact tension specimens can be produced to examine the fracture characteristics with Equivalent Material Concept (EMC) approach.
3. Nanoparticle reinforced thermoplastic blends with different compatibilizers can be produced with twin-screw extruders or injection molding processes.

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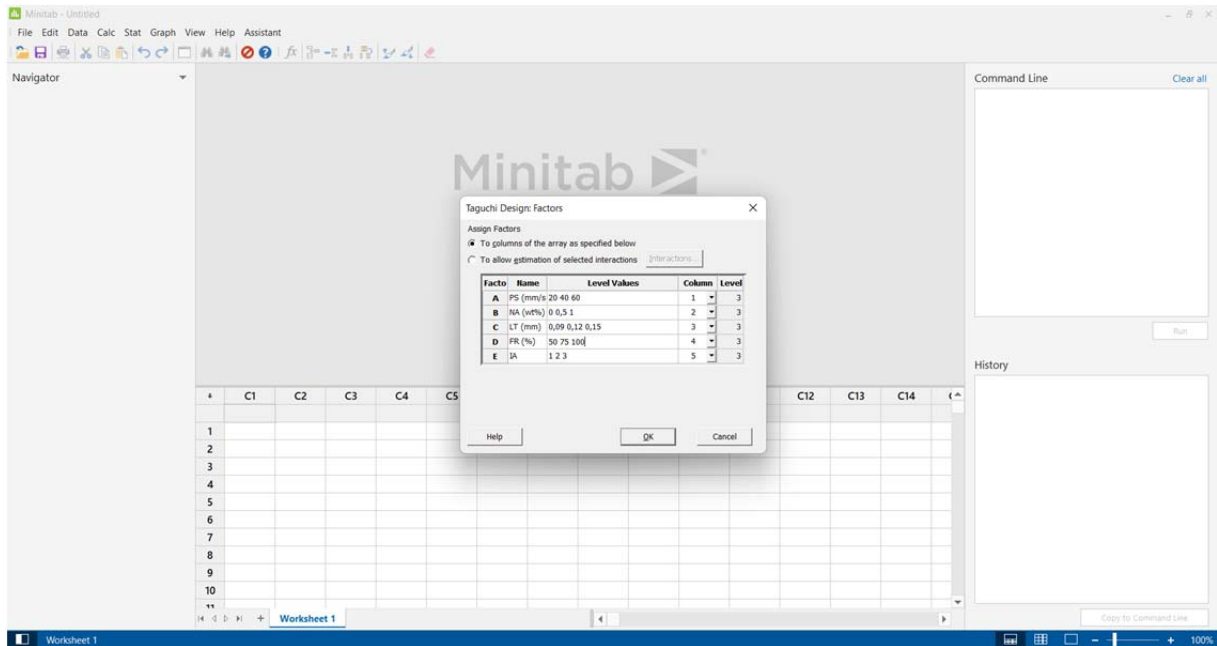


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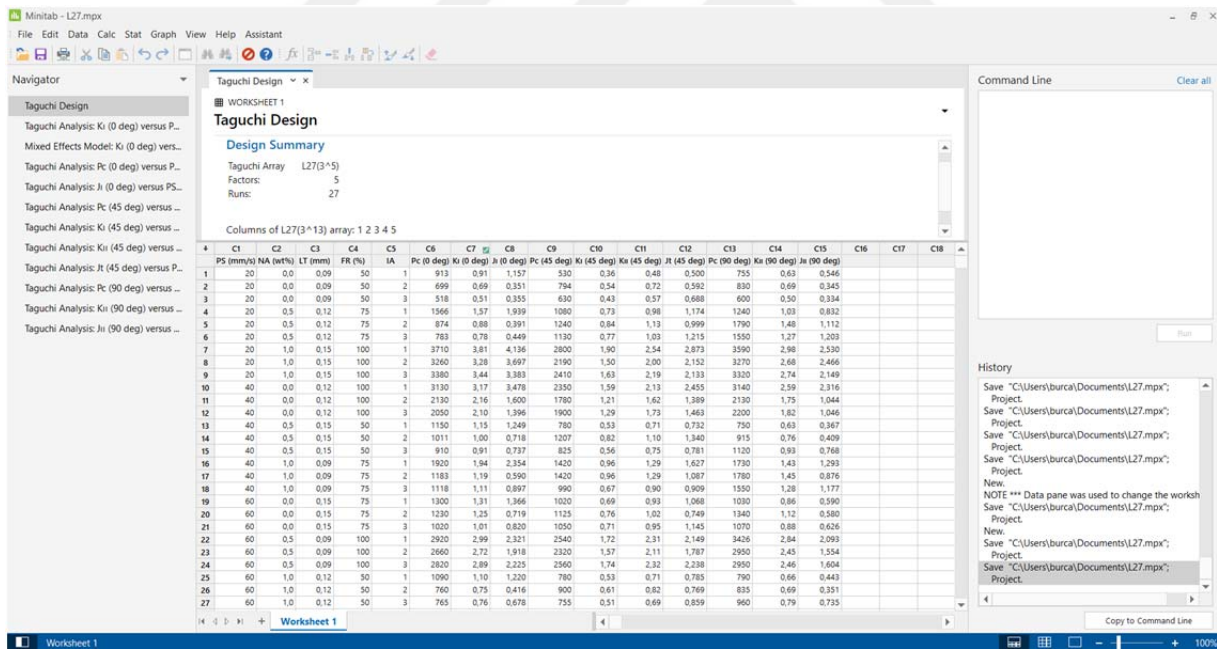




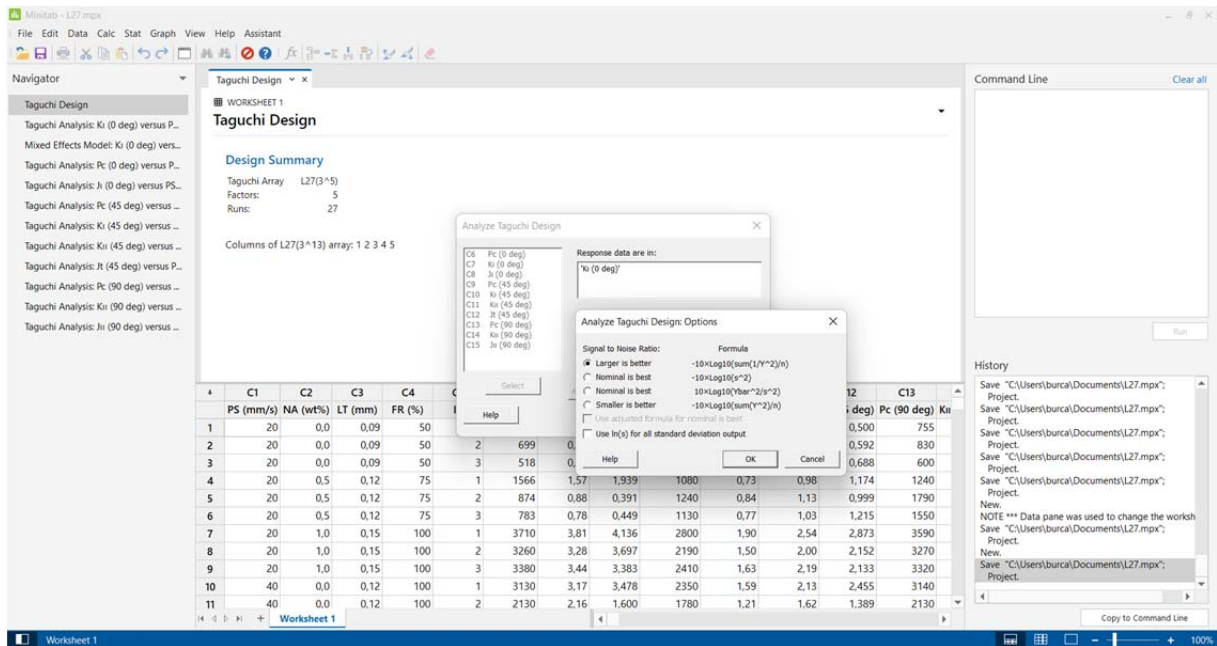
APPENDIX A



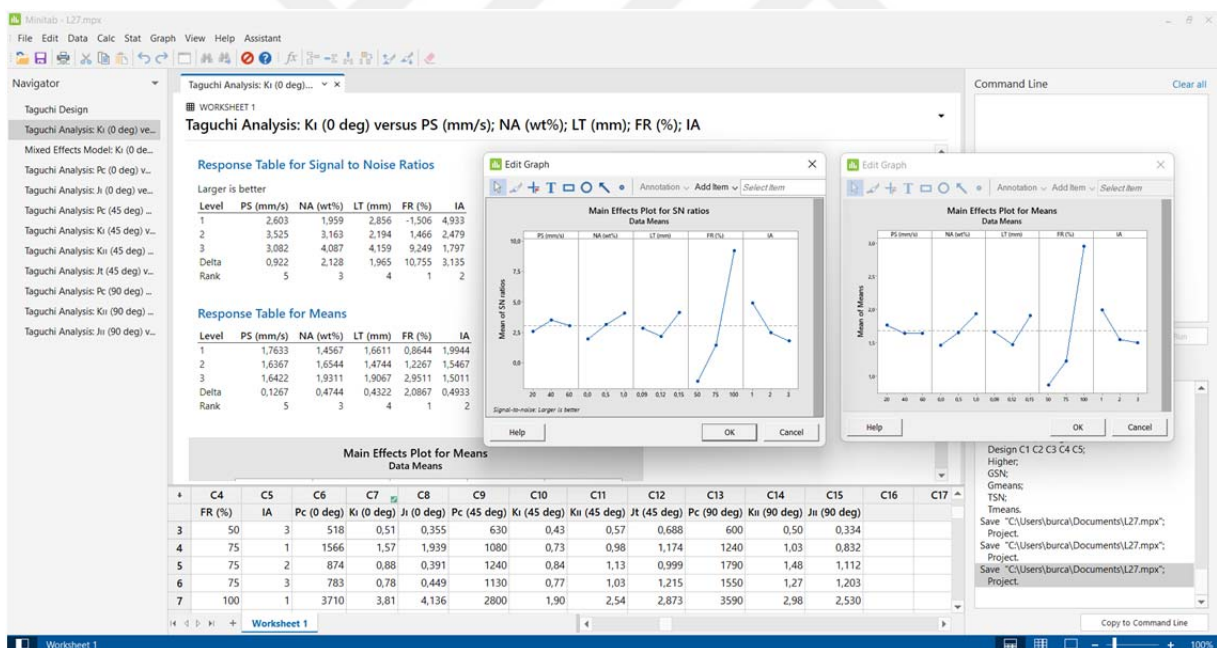
A.1. Assignment of Taguchi L_{27} design factors into MINITAB.



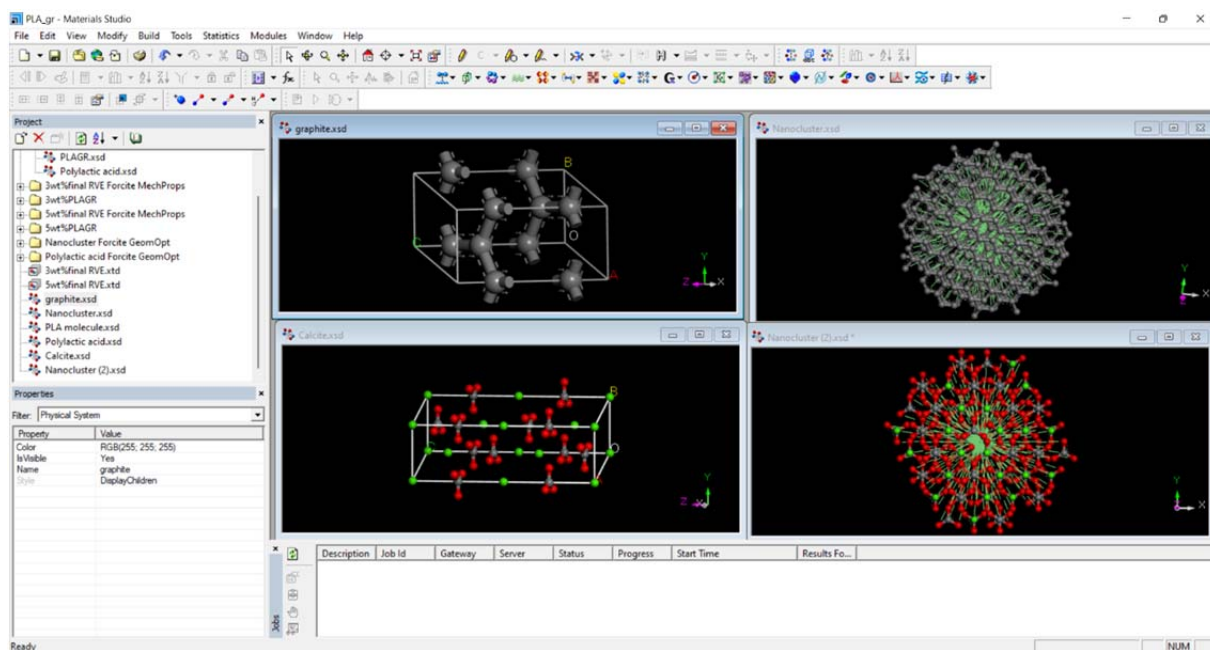
A.2. Taguchi L_{27} combination created by MINITAB with input and output variables.



A.3. Creating the analysis procedure of the Taguchi L_{27} design.



A.4. Representation of MINITAB worksheet and S/N ratios of parameters.



A.7. Creation of a) graphite unit cell, b) graphite nanocluster to be used in packing process with the PLA molecule, c) calcite unit cell, and d) calcite nanocluster to be used in packing process with the PLA molecule.