

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**CONDUCTIVE POLYAMIDE /CARBON BLACK, CARBON FIBER AND
CARBON NANOTUBES COMPOSITES FOR ELECTROSTATIC PAINTING**

M.Sc. THESIS

Amirhossein NASRI

Polymer Science and Technology

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Amirhossein NASRI

(515131002)

Department: Polymer Science and Technology

Programme: Polymer Science and Technology

Thesis Advisor: Prof. Dr. Esma SEZER

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**ELEKTROSTATİK BOYAMAYA UYGUN İLETKEN POLİAMİD/ KARBON
SİYAHİ, KARBON LİF VE KARBON NANO TÜP KOMPOZİTLERİ**

YÜKSEK LİSANS TEZİ

Amirhossein NASRI

(515131002)

Polimer Bilimi ve Teknolojisi

Polimer Bilimi ve Teknolojisi

Tez Danışmanı: Prof. Dr. Esma SEZER

MAYIS 2015

Amirhossein NASRI, a **M.Sc.** student of **ITU Graduate School of Polymer Science and Technology** student ID **515131002**, successfully defended the **thesis** entitled “**CONDUCTIVE POLYAMIDE /CARBON BLACK, CARBON FIBER AND CARBON NANOTUBES COMPOSITES FOR ELECTROSTATIC PAINTING**” which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Esma Sezer**

Istanbul Technical University

Jury Members : **Prof. Dr. Yücel Şahin**

Yildiz Technical University

Prof. Dr. Ayşen Onen

Istanbul Technical University

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FOREWORD

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ABBREVIATIONS

ABS	: Acrylonitrile Butadiene Styrene
CB	: Carbon Black
CF	: Carbon Fiber
CNTs	: Carbon Nanotubes
DSC	: Differential Scanning Calorimeter
EP	: Electrostatic Painting
EM	: Extrusion Method
ATR-FTIR	: Attenuated Total Reflection- Fourier Transform Infrared
HRTEM	: High Resolution Transmission Electron Microscopy
ICPs	: Intrinsically Conductive Polymers
MWNT	: Multi Walled Nanotubes
PA	: Polyamide
PAH	: Polycyclic Aromatic Hydrocarbons
SEM	: Scanning Electron Microscope
SWNT	: Single Walled Nanotubes
SSWNT	: Synthesized Single-Walled Carbon Nanotubes
TGA	: Thermogravimetric Analysis

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CONDUCTIVE POLYAMIDE/CARBON BLACK, CARBON FIBER AND CARBON NANOTUBES COMPOSITES FOR ELECTROSTATIC PAINTING

SUMMARY

Conductive polymer composites (CPCs) coming out from the combination of an insulating polymer matrix with conductive fillers exhibit several interesting features and many applications. In automotive industry metal parts can be replaced by CPCs which means a vehicle with the lower weight and lower fuel consumption. The motivation behind this study was to produce an engineering plastic in order to use in the automotive industry with cost reduction, to improve mechanical properties and production efficiency. For this purpose, this study was aimed to find a conductive polyamide compound (CPAC) formula in order to use as raw material to produce hubcap (wheel cover) which is suitable for electrostatic painting (EP) system. The CPAC was prepared by extrusion methods by using commercial polyamide (Minlon) and carbon based conductive materials such as carbon black (CB), carbon fiber (CF), and carbon nano-tube (CNT). Compatibilizer was also added to the formula to obtain the suitable CPAC, which covers the requirements for the resulting composite. Formulations with different carbon filler contents were prepared and then produced and tested. They were compared with commercial product of Noryl, which have been used for EP applications. The disadvantage of Noryl is poor mechanical properties for some applications such as wheel cover. There are types of method to produce the conductive polymer composites (CPCs) such as; solution, melt mixing etc. In this study, the extrusion, which is one of the melt mixing method, was used. After compounding materials, electrical conductivity of composites was measured by a 4-point probe method. ATR-FTIR, DSC, SEM and mechanical properties tests were also performed on the samples. Wheel cover was produced from the samples that have the desired properties and after electrostatic painting the basic tests such as cross cut, hardness, drop weight impact were carried out on the final product. The results of all these tests suggested that, the suitable composites for EP were prepared and these composites fit the requirements of the wheel cover.

ELEKTROSTATİK BOYAMAYA UYGUN İLETKEN POLİAMİD / KARBON

SİYAHİ, KARBON LİF VE KARBON NANO TÜP KOMPOZİTLERİ

ÖZET

Son yıllarda plastiklere iletken özellik kazandırmak üzerine çalışmalar önem kazanmıştır. İletkenlik özelliğinin yanında mekanik, optik, termal ve fiziksel özelliklerinde elde edilmesi için nano katkılar kullanılmaktadır. Örneğin karbon nanotüp (CNT) bu özellikleri kompozite kazandırmak için kullanılan katkılardan biridir ve iletkenlik ve sertliği artırırken elastiklik özelliğini azalttığı yönünde bulgular elde edilmiştir. Birden fazla iletken katkı kullanılarak sinerjetik etki yaratılması üzerine yapılan çalışmalar da mevcuttur. Karbon yapıli bileşiklerin birlikte kullanıldığı matrislerde sinerjetik etki ile iletken ağı yapısının daha iyi oluştuğı görülmüştür. Endüstride de bu amaçla karbon bazlı katkılar kullanılmaktadır.

İletken kompozitlerin eldesinde düşük miktarlardaki katkılarla iletken ağı yapısının oluşumunun sağlanması ve perkolasyon limit değeri düşürülmesi önemlidir. Karbon katkılarının tek başına ve birlikte kullanılmasıyla ilgili çok sayıda çalışma yapılmış olmasına rağmen poliamid (PA) için hepsinin ayrı ayrı ve birlikte kullanıldığı bir çalışmaya rastlanmamıştır. Bu tez çalışmasında da literatürdeki bu eksikliğe katkı sağlanması amaçlanmıştır.

İletken dolgu malzemesinin, yalıtkan polimer matrisi ile birleştirilerek elde iletken polimer kompozitler (CPCs) birçok ilginç özelliğe sahip olduklarından çok sayıda uygulama alanında kullanılabilir. Örneğin araç ağırlık azaltma çalışmaları sonucunda metal parçaların yerini alan mühendislik plastiklerinin ürüne dönüştürülmesi aşamalarının iyileştirilmesi gerekmektedir. Parça kalitesi ile direkt ilgili üretim aşaması olan boyama operasyonunda son teknolojik gelişme olan elektrostatik boyama (EP) sisteminin metal malzemelerde olduğu gibi mühendislik plastiklerine de uygulanabilir hale getirilebilmesi birçok avantaj sağlayacaktır. Otomobil parçalarından biri olan jant kapağının, sadece bir firmada yıllık üretim yaklaşık adedi 560 bin ve yıllık cirosu 1,8 M€'dur. Geleneksel ıslak boyama işlemi malzeme sarfiyatı, uygulama alanı gereklilikleri, çevreye olan olumsuz etkileri ve enerji tüketimi açısından yüksek maliyetli bir operasyondur. Mühendislik plastikleri ile üretilen jant kapağı parçasının boya uygulama işleminde EP sistemine geçilmesi ile %50 boya tasarrufu sağlanacaktır. EB sisteminde kullanılan boyada kimyasal çözücü geleneksel ıslak boyanın içerdiğinden daha az olduğu için üretim sırasında tehlikeli kimyasal salınımı en düşük seviyeye inmiş olacaktır. Malzemenin yüzey enerjisi, boyanın homojen dağılımı ve tutunması ile doğrudan etkilidir. Yüzeyin temizlenmesi ve yüzey enerjisinin artırılması için kimyasal temizlik ve flamaj gibi ön işlemler boya atımı öncesi parçalara uygulanır. Metal parçaların yağdan arındırılması için kimyasal temizlik, plastik parçaların yüzey enerjilerinin artırılması için flamaj işlemi maliyetin artırılmasına ve verimliliğinin düşmesine sebep olmaktadır. Mühendislik plastiklerinde EP sistemine başarılı bir şekilde geçilmesi yüzeyin tozdan arındırılması için daha düşük maliyetli bir yıkama işlemi olacaktır. Islak boya atım sisteminde kabin yüzeyinde kürlenmiş boyalar düzenli aralıklarla kabinlerin bakım ve onarımına alınmasını gerektirmektedir. Bakım, onarım sırasında kabinin kullanıma kapanması ve işçilik maliyetinin artması üretim verimliliğini düşürmektedir. EP sistemine geçilmesi ile üretim verimliliğinde %50 artış öngörülmektedir. Bu

çalışmanın asıl amacı, otomotiv sektöründe maliyet azaltıcı, iyi mekanik özelliklere ve üretim verimliliğine sahip bir mühendislik plastiği üretmektir. Bu amaçla iletken metal yüzeylerde başarılı sonuç sağlayan EP sisteminin plastik malzemeler için de kullanımını yaygınlaştırmak üzere plastik malzemelere iletken özellik kazandırılması ve EP uygulaması için uygun hale getirilmesi plânlanmıştır.

Poliamide iletken özellik kazandırılması ve EP uygulaması için uygun hale getirilmesi amacı ile karbon siyahı (CB), karbon fiber (CF) ve CNT ile kompozitleri oluşturularak gerekli iletkenlik değerlerine ulaşılmasına çalışılmıştır. PA matrisi olarak Dupont firması tarafından üretilen ve %15 katkı içeren Minlon isimli ticari ürün kullanılmıştır. Dolgu olarak ise, ABCR firmasından temin edilen CB (Acetylene, 50% compressed), Grafen firmasından temin edilen, çok duvarlı CNT, (Çap:9.5 nm, Uzunluk: 1.5 µm Yüzey alanı:250-300m²/g) ve Dost Kimya çapı 7.2 µm uzunluğu 3-12 mm olan kırılmış CF kullanılmıştır. Her bir bileşen ekstruderde kullanılmadan önce 80°C’ de 2 saat kurutulmuştur.

Deneylerde çift burgulu Scientific marka ekstruder kullanılmıştır. Vida hızı, ön denemeler sonucunda 30 rpm olarak belirlenmiştir.

Ekstrüzyon yapmadan önce başlangıç maddesinin (Minlon), ve nihai ürünün termal özellikleri TA Q10 Model DSC cihazında 50 ml/ dak akış hızı ile 0-400 °C aralığında incelenmiştir. Erime sıcaklığı yaklaşık 260°C’de gözlemlenmiştir. Bu sonuca göre ekstruderde çalışmak için uygun aralık 260-280°C olarak belirlenmiştir.

Piyasada ticari olarak Noryl (N1) adıyla satılan ve EP boyama için uygun, ancak mekanik özellikleri Minlona göre zayıf olan malzeme, elde edilen kompozitlerin iletkenliklerini kıyaslamak için referans olarak kullanılmıştır. 4. Nokta probe tekniği ile ölçülen iletkenliği 2.310⁻⁸ S/cm olarak elde edilmiştir. Bu projede Minlondan hareketle elde edilecek kompozitlerin iletkenliği karbon katkıları ile bu derece eşit yada yüksek hale getirilmiştir.

SEM ölçümleri ile karbon katkıların poliamid matrisi içinde dağılımı ve uyumlaştırıcının kompozitin homojenliği üzerindeki etkisi incelenmiştir. Sonuçlar, karbon dolguların yapıya katıldığı ve homojen olarak dağılabildiği uyumlaştırıcının karbon içeriğinin homojen dağılmasına katkısı olduğunu göstermektedir.

Kompozitlerin mekanik test sonuçlarına göre üretilen kompozitin elastik modülü ve 23°C ve -30°C’lerdeki darbe dayanımlarında artışlar gözlenmiştir. Diğer özellikleri ise kullanım amacına uygun sınırlar içerisinde ve Minlon’un özellikleriyle yakın değerlerde bulunmuştur. Bu çalışmada elde edilen kompozitlerin mekanik özellikleri amaca uygun olacak şekilde korunurken, iletkenlik kazandırılarak elektrostatik boyamaya uygun hale getirilmiştir.

Bu çalışmada prototip malzeme olarak jant kapağı seçilmiş ve üretimi için hammadde olarak kullanılacak iletken poliamid kompozitleri, ticari Minlon ve CB,CF ve CNT olmak üzere karbon esaslı iletken dolgular kullanılarak ekstrüzyon metodu ile hazırlanmıştır. Kompozitleri daha homojen hale getirmek amacıyla kompozit formülasyonlarına ayrıca uyumlaştırıcı da ilave edilmiştir. Farklı karbon dolgular içeren formüller hazırlanmış, kompozitler üretilip ve test edilmiştir. Elde edilen kompozitlerin iletkenlik ve mekanik özellikleri EP uygulamaları için kullanılan ticari ürün olan Noryl ile karşılaştırılmıştır. Noryl’in dezavantajı jant kapağı gibi EP uygulamaları için gerekli olan mekanik özelliklere sahip olmamasıdır. Bu çalışmada Noryl’e göre mekanik özelliklerinin amaca uygun olarak iyileştirilmesi hedeflenmiştir.

CPC üretmek için çözelti, eriyik karışımı etc. gibi metodlar kullanılmaktadır. Bu çalışmada, ekstrüzyon metodu kullanılmıştır. Ekstrüzyondan sonra, kompozitlerin elektriksel iletkenlikleri 4 nokta probe metodu ile ölçülmüştür. Ayrıca ürünler ATR-FTIR, DSC, SEM ve mekanik özellik testleri ile karakterize edilerek jant kapağı için istenen özelliklere sahip kompozit formülasyonları belirlenmiştir. Mekanik, elektrik ve maliyet açısından optimum özelliğe sahip kompozit formülasyonu ile enjeksiyon yöntemi kullanılarak jant kapağı elde edilmiştir. Jant kapakları elektrostatik olarak boyanmış ve daha sonra çapraz kesim, sertlik, ağırlık düşmesi darbe direnci gibi temel testlere tabii tutulmuştur. Tüm bu test sonuçları, mevcut ürüne göre yaklaşık aynı maliyette mekanik özellikleri iyileştirilmiş, EP için uygun bir kompozit hazırlandığını ve jant kapağı üretimi için gerekli özelliklere sahip olduğunu ve ön denemelere göre ticari olarak kullanıma uygun olduğunu göstermektedir.

Geri kazanım EP sisteminin en büyük ekonomik avantajlarından biridir. Diğer avantajları ise aşağıdaki şekilde özetlenebilir;

- Islak boya uygulama kabinlerinde, boyanın kabine tutunmasını önlemek amacı ile kabin duvarlarından akan çözücü kimyasal içeren su çevrim ünitesi, EP kabinleri için gerekli değildir.
- Atık kimyasal miktarı EB sisteminde ıslak boyamaya göre oldukça düşüktür.
- Islak boya sistemi daha sık bakım, temizlik ve onarım gerektirdiği için personel maliyeti %38 daha yüksektir.
- EP sisteminde boya sarfiyatında %60-70 arasında kazanç sağlanmıştır.
- Kabinlerin temizlik ve bakım masrafları EP sisteminde, geleneksel boya yöntemine göre %50 daha azdır.

Bu avantajlar sayesinde bu endüstride EP sistemine geçilmesi ile sistemin 6 ay içinde kendini amorti edebileceği öngörülmektedir.

Bundan sonraki otomobil parçası üretimlerinde mevcut ithal malzemeye ihtiyaç duyulmadan ülkemizde üretilecek iletken kompozit kullanılması mümkün olabilecektir. Bunun da önemli bir yaygın etki olduğu düşünülmektedir.

1. INTRODUCTION

Nowadays technical applications of conductive polymer composites are growing so fast. Conductive polymer composites (CPCs) coming out from the combination of an insulating polymer matrix with conductive fillers exhibit several interesting features. However, this important sensitivity of CPC toward its environment also means that a good control of final properties is impossible if the numerous influent factors involved during the formulation and processing are not identified. The main significant factor is the filler distribution within the matrix, which can result from processing conditions (temperature, shearing, viscosity, and orientation), formulation (filler content, molecular weight and crystallinity of the polymer (Meyer, 1973; Feller et al., 2002), solubility parameters, particle/particle and particle/macro-molecule interactions (Gubbels et al., 1998; Zhang et al., 1998)) and spatial parameters (shape factor of the conducting particles (Vilčáková et al., 2000), exclusion domains in which particles cannot go (Gubbels et al., 1998; Zhang et al., 1998; Narkis et al., 2000; Feller et al., 2002)). Whatever the application, the percolation threshold, i.e., the volume fraction (ϕ_c) over which the CPC becomes conductive, is very sensitive to variations of any of the previously mentioned parameters. For many applications, it is useful to decrease the percolation threshold to both reduce the CPC cost and make the processing easier. This can be achieved with multiphase CPC matrices (Gubbels et al., 1998; Zhang et al., 1998; Feller et al., 2002) which usually can be done with two conventional methods: solution and extrusion. Many studies have been carried out on conductive polymer composites due to the increasing industrial demands. Different types of polyamide were investigated to see the influence of carbon black, carbon fiber and, CNTs with different portion on electrical conductivity of the polyamides (Finegan and Tibbetts, 2001; Leer et al., 2006; Dasari et al., 2009; Leboeuf et al., 2010; Kim et al., 2011; Socher et al., 2011; Socher et al., 2011; Caamaño et al., 2012). Also, other polymers and blends have been studied to see the electrical conductivity tolerance with different portion of conductive fillers (McNally et al., 2005; Alig et al., 2007; Wang et

al., 2008; Deng et al., 2009; Etika et al., 2009; Zhang et al., 2009; Farimani and Ebrahimi, 2012; Shen et al., 2012).

In this study, compounding runs followed by injection molding of carbon filled Minlon were conducted. Volume resistivity, surface resistivity, DSC, and scanning electron microscope were used to determine electrical conductivity, aspect ratio and homogeneity of distribution of conductive fillers. The investigated carbon fillers include carbon fiber (CF) (diameter: 7.2 μm , length of fibers: 3-12 mm), Carbon black (CB) (Acetylene, 50% compressed) and Multi wall Carbon nano tubes (MWNTs) (diameter: 9.5 nm, length: 1.5 μm , Surface area: 250-300 m^2/g). In total, seven nylon 6,6 (minlon) based formulations with different carbon filler contents were produced and tested. These formulations included increasing amounts of single carbon filler. The goal of this study was to determine the effect of fillers, both individually and in combined form, on the electrical conductivity of the Minlon.

2. CONDUCTIVE POLYMERS

Polymers are normally used in electrical and electronic applications as insulators, where advantage is taken of their high resistivities and good dielectric performances. Typical examples of this type of application include cable sheathing, capacitor films, printed circuit substrates, and various encapsulants and conformal protective coatings. However, polymers are also widely exploited because of their other advantageous properties, including mechanical strength, flexibility, stability, low cost and ease of processing, and it is the promise of combining these properties with electrical conductivity that has prompted the now great interest in conductive polymers. There are two major categories for conductive polymers. First, intrinsically conductive polymers (CPs) in which polymers can be made electrically conducting via their own structures and second one is method of introducing conductivity to a polymer. In this method, conductivity is achieved via the incorporation of conductive fillers. Although in this case, the conductivity is not related to the chemistry of the polymer, but rather to the nature of the filler, these materials have been widely exploited commercially to sum up, the categories of conductive can be divided in two; intrinsically conductive polymers and conductive polymer composites (Cooper, 1996).

2.1 Conductive Polymer Composites

An alternative method of inducing electrical conductivity in polymers is to make polymer composite materials with conductive additives or fillers, which results in conductive polymer composites (CPCs). Typical examples of conductive components used to prepare this type of conducting polymer include conducting solids (carbon black, carbon fibers, carbon nanotubes, aluminum flake, stainless steel fibers, metal-coated fillers, metal particles, etc.) and conjugated conducting polymers. Because the conductivity is introduced through the addition of the conducting components, various polymer materials including both amorphous polymers (polystyrene, PVC, PMMA, polycarbonate, acrylonitrile butadiene styrene (ABS), polyethersulphone, polyetherimides, etc.) and crystalline polymers (nylons, polyethylene, polypropylene, polyphenylene sulphide, etc.) can be made electrically conducting. Various processing techniques such as extrusion, hot compression, etc. have been used to prepare the CPCs (Dai, 2004).

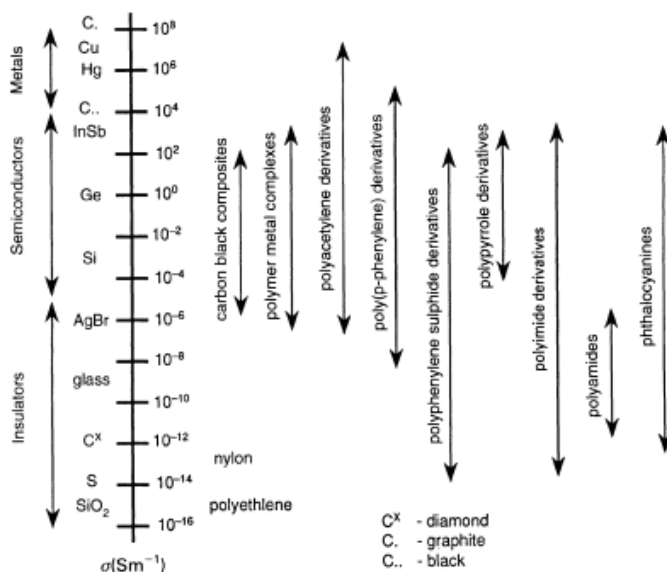


Figure 2.1: Conductivities of various elements, compounds and polymers (Cooper, 1996).

2.1.1 History and properties

Since early work in the 1950s (Frydman, 1948), electrically conductive polymer composites (CPCs) have interested many research groups (Kohler, 1966; Bueche, 1973; Meyer, 1973; Narkis et al., 1978; Carmona and Mouney, 1992; Gubbels et al., 1994; Tchoudakov et al., 1996; Yi et al., 1998). CPCs are obtained by blending insulating polymers with conductive particles such as carbon black, carbon fibers, carbon nanotubes, metal particles or conducting polymers such as polyaniline (Narkis et al., 1997) and lead to several applications such as shielding, switching or heating. More recently CPCs were also used as sensors (Chen and Tsubokawa, 2000; Srivastava et al., 2000).

2.1.2 Application

The main applications of CPCs are being replaced with metals in electromagnetic interference-shielding applications, electrostatic discharge or dissipative properties, and electrostatic painting.

2.1.3 Components of CPCs

Polymer composites are combinations of materials differing in composition, where the individual constituents retain their separate identities. These separate constituents act

together to give the necessary mechanical strength or stiffness to the composite part. Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different from those of any of the constituents. Matrix phase is the primary phase having a continuous character. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. Dispersed (reinforcing) phase is embedded in the matrix in a discontinuous form. This secondary phase is called the dispersed phase. Dispersed phase is usually stronger than the matrix, therefore, it is sometimes called reinforcing phase (Jose and Joseph, 2012). CPCs have the similar constituents that discussed earlier. So the components of CPCs can be divided in two main categories; Polymer (matrix) and additives.

2.1.3.1 Polyamide

If wood is the world's most versatile natural material, polyamide (PA) is probably the most useful synthetic one. PA is a thermoplastic, silky material, which can be molded into everyday products or drawn into fibers for making fabrics (Trossarelli, 2003).

History

Wallace Carothers and his colleague invented PA in DuPont Company (Hermes, 1996). First, it was called nylon, since the nylon family contains characteristic amide groups in the backbone chain, later it was named as polyamide (PA). Ever since it first came on the market, nylon's many uses have greatly influenced most facets of our daily lives, including automotive industry, mountaineering, clothes fabrics, package paper, pipes, and etcetera (Hermes, 1996). At the beginning it was used for toothbrushes and later women's stockings ("nylons"; 1940) after being introduced as a fabric at the 1939 New York World's Fair.

PA was the first commercially successful synthetic thermoplastic polymer. It was intended to be a synthetic replacement for silk and substituted for it in many different products. After silk became scarce during World War II, it replaced silk in military applications such as parachutes and flak vests, and was used in many types of vehicle tires. Solid PA is used in hair combs and mechanical parts such as machine screws, gears and other low to medium-stress components previously cast in metal. Engineering-grade PA is processed by extrusion, casting, and injection molding (Hounshell and Smith, 1988).

Synthesis method

This polymer obtained by the condensation of diamines with bicarboxylic organic acids, or from omega-amino acids. In more specific terms, it is a polyamide, i.e. one of a class of polymers whose molecular chains are formed by regularly spaced -CONH- amide groups. Since Carothers and his group invented nylon (Hermes, 1996), PA has been conventionally accompanied by some figures indicating the number of carbon atoms in structural unit(s). PA6, PA4/6, PA6/6, PA6/10, PA6/12, PA11 and PA12 are examples of PA category. The first figure shows the carbon atoms of the diamine, the second those of the bicarboxylic acid. The PA invented by Carothers and known as PA 6/6, or poly(hexamethylenedipamide), therefore, is read as six-six, not sixty-six, which means that it is composed of two structural units, each with six carbon atoms, namely the residues of hexamethylenediamine ($\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$) and adipic acid ($\text{HOOC}(\text{CH}_2)_4\text{COOH}$). The reason for choosing the PA 6/6 for our purpose is its unique mechanical and physical properties on the other hand it is less expensive than other types of polyamide (Trossarelli, 2003).

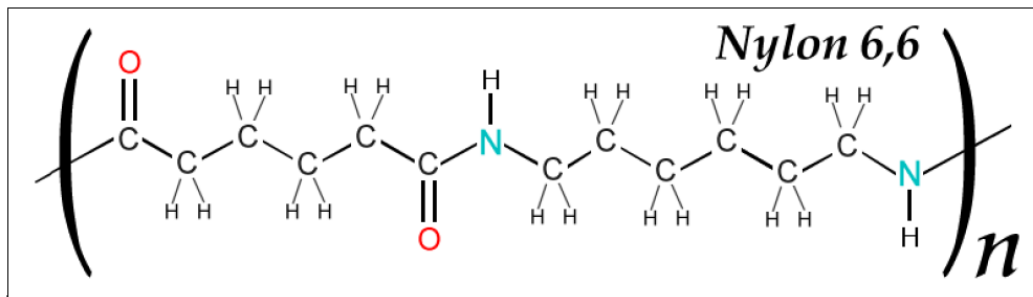


Figure 2.2: Nylon 6,6 closed formula.

PA 6/6 is one of the most versatile engineering thermoplastics. It is popular in every major market using thermoplastic materials. Because of its excellent balance of strength, ductility and heat resistance, PA 6/6 is an outstanding candidate for metal replacement applications. PA6/6 is very easy to process with a very wide process window. This allows it to be used for everything from complex, thin walled components to large thick walled housings.

PA 6/6 is very easy to modify with fillers, fibers, internal lubricants, and impact modifiers. With the use of fiber reinforcements, the physical strength of PA 6/6 can be improved five times that of the base resin. The stiffness of PA 6/6 can be improved up to 10 times. With impact modifiers, the ductility of PA 6/6 is comparable to

polycarbonate. The use of internal lubricants improves on the already excellent wear resistance and friction properties on PA 6/6. Its versatility allows it to be used in almost any application that requires high physical strength, ductility, heat resistance and chemical resistance (Margolis, 1985).

Properties

PA 6/6 has a melting point of 265°C, high for a synthetic fiber, though not a match for polyesters or aramids such as Kevlar. This fact makes it the most resistant to heat and friction and enables it to withstand heat setting for twist retention. Its long molecular chain results in more sites for hydrogen bonds, creating chemical “springs” and making it very resilient. It has a dense structure with small, evenly spaced pores. This means that PA6/6 is difficult to dye, but once dyed it has superior colorfastness and is less susceptible to fading from sunlight and ozone and to yellowing from nitrous oxide (Palmer, 2002).

The high melting point of PA6/6 is a function of both the strong hydrogen bonding between the chains and the crystal structure. This also allows the materials to retain significant stiffness above the glass-transition temperature, which is 50°C for PA 66 and almost up to the melting point (Mark, 1999; Charles et al., 2009).

Nowadays PAs are used in electrical applications mainly for their combination of mechanical, thermal, chemical, and electrical properties. They are reasonably good insulators at low temperatures and humidity and are generally suitable for low frequency, moderate voltage applications. The relatively high dissipation factor of PA causes problems under conditions of high electrical stress, particularly when moist, because of the likelihood of overheating. Dry PA has volume resistivity in the $10^{14} - 10^{15} \Omega \cdot \text{cm}$ region, but this decreases with increasing moisture and temperature (Mark, 1999; Charles et al., 2009).

Commercial PAs contain semicrystalline structure which play role as a high strength (tensile, flexural, compressive, and shear) due to crystallinity and good toughness (impact strength) as a result of the amorphous region. There are kinds of matters, which affect the PA properties like copolymerization, molecular weight, moisture content, temperature and additives. Increasing density of amide groups and crystallinity in aliphatic nylons will increase the modulus (stiffness) and strength of PA but on the

other hand reduces the impact strength and elongation. PA 6/6 has higher stiffness and strength compared to PA6, which makes it special for us. See

PA has the ability to be very lustrous, semilustrous or dull. Its high tenacity fibers are used for seatbelts, tire cords, ballistic cloth and other uses. Properties such as high elongation, excellent abrasion resistance, highly resilient (PA fabrics are heat-set), paved the way for easy-care garments, high resistance to insects, fungi, animals, as well as molds, mildew, rot and many chemicals, used in carpets and PA stockings, melts instead of burning can be mentioned (Mark, 1999). Like every materials PA 6/6 has in own disadvantages such as high water absorption, poor chemical resistance to strong acids and bases (Palmer, 2002).

Table 2.1: Mechanical properties of PA 6/6 (Mark, 1999; Charles et al., 2009).

Mechanical Properties	ASTM Test Method	Units	PA 6/6
Tensile Strength 73°F	D638	psi	12,400
Elongation 73° F	D638	%	90
Flexural Strength, 73° F	D790	psi	17,000
Flexural Modulus, 73°F	D790	psi	4.1 X 10 ⁵
Izod Impact Strength, Notched, 73°F	D256	----	R120 - M79
Rockwell Hardness	D785	ft-lbs/in.	1.2

Characterization methods

Attenuated Total Reflection- Fourier Transform InfraRed (ATR-FTIR), Differential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA), and scanning electron microscope (SEM) are commonly used methods for characterization of PA.

FTIR is a simple and reliable technique used in different field of study. It can be used to study and identify chemicals.

The aim of using Differential Scanning Calorimeter (DSC) is to observe thermal transitions in different materials like polymers.

Thermogravimetric analysis (TGA) is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatile (such as moisture). It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, and composites.

Samples were cryogenically fractured in liquid nitrogen then observed with a scanning electron microscope (SEM). In this method, a piece of sample placed between pliers was immersed into a vessel containing a liquid nitrogen. After a couple of minutes, the sample was fractured inside vessel and left to dry heat to room temperature. Afterwards, exposed surfaces of samples were coated with a fine gold(Or platinum) layer (about 20 nm) by ion sputtering and examined with SEM in a high vacuum mode at the accelerating voltage of 10 and 20 kV.

Polyamide application

Polyamide has a wide range of uses such as : Hosiery, Weaving and wrap knitting, tires and conveyor belts, Coated fabrics, Carpeting, Furnishing/ floor coverings, Textiles(Apparel, tooth brushes, Tyre cord), Automotive (Bearings, slides, door handles, hubcaps, door and window stops), Furniture (Locks, hangers, chairs etc.). Since our target is related to automotive industry, we will investigate PA6/6 usage in this industry. If the automotive industry had its own periodic table, PA66 would be a key element. Thanks to its versatility, mold ability and resistance to high temperatures and harsh chemicals, PA 66 PA is the most used engineering thermoplastic in the automotive industry today. Descriptions of uses for polyamides split into the principal application areas that are given below.

Under the hood

In the engine compartment, PA 66nylon's performance properties make it a rising star. PA 66 reinforced with glass fiber can be used in engine-cooling flex fans; transmission thrust washers and spring guides; and air cleaner support brackets. Even valve stem oil deflectors, which are required to resist oil and temperatures as high as 320°F are converted to nylon. Tapped PA 66 can be used as mechanical, pneumatic and electrical control systems, many of which have to withstand temperatures reaching 300°F. Applications included throttle control cable end fittings, lever retainers and “umbrellas;” downshift cables and hood release cable jackets. An exhaust gas recirculation (EGR) interface adapter was brought to U.S. marketing by DuPont and General Motors Companies. The innovative EGR valve interface joint reduced EGR temperatures to levels manageable by PA air intake manifolds. Fuel rails, fans, fan shrouds, thermostat housings, and valve and engine covers water tubes or water rails to replace rubber hoses in the coolant circuit are some other examples of PA66 under the hood applications (Mark, 1999; Charles et al., 2009; Qiu et al., 2013).

Interior

Today, the latest research on potential airbag materials including polyester fiber, continues to point the industry towards PA66 (due its higher seam strength and low air permeability compared to polyester). Polyamides have been used for switches, handles, seat belt components, etc. (Mark and Seidel, 2014).

Exterior

The most usage of area for PA 66 in this part is in hubcaps (wheel cover), which imparts decorative part for wheels. External mirror bracket, hood release, front cover, front-end module, fuel filler cap, fuel filler door, headlight bezel, etc., Are the other examples of PA 66's applications (Mark and Seidel, 2014).

2.1.3.2 Additives

An additive is usually a minor component of the mixture formed and usually modifies the properties of the polymer. Examples of additives are antioxidants, plasticizers, flame-retardants, processing aids, other polymers, colorants, UV absorbers, extender, compatibilizer and fillers.

Carbon materials

Nowadays, additives such carbon materials play an important part in human life, they can be used in many different fields like automobile industry and so on. There are types of carbon with different subcategory. The main three carbon categories are carbon nanotubes (CNTs), carbon fiber (CF), and carbon black (CB).

Carbon nanotubes

Carbon nanotubes (CNTs) are remarkable objects that look set to revolutionize the technological landscape in the near future. Tomorrow's society will be shaped by nanotube applications, just as silicon-based technologies dominate society today. Space elevators tethered by the strongest of cables; hydrogen-powered vehicles; artificial muscles: these are just a few of the technological marvels that may be made possible by the emerging science of carbon nanotubes (Narkis and Tobolsky, 1969).

CNTs are mainly classified in two types: single walled nanotubes (SWNT) and multi walled nanotubes (MWNT). Single walled nanotubes diameter are about 1nm and their electrical conductivity can show metallic or semiconducting behaviour. In multi walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphene, the interlayer distance is about 3-4 Å. There are two models that can describe the multi walled nanotubes; 1- Russian doll model, 2- Parchment model. Carbon nanotubes have the strongest tensile strength of any material known. It also has the highest modulus of elasticity. Nanotubes were first observed in 1991 in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 amps that was intended to produce fullerenes (Meyer, 1973; Gubbels et al., 1998; Zhang et al., 1998; Feller et al., 2002).

History

Carbon nanotubes having nanoscale dimension (1-D) have been well-known over the past 15 years. The molecules were first discovered by Iijima in 1991 (Feller et al., 2002) when he was studying the synthesis of fullerenes by using electric arc discharge technique. The high-resolution transmission electron microscopy (HRTEM) was employed for observation of that phenomenon. Carbon nanotubes that Iijima observed were so called multi-walled carbon nanotubes (MWNTs) as shown in Fig. 1a, nested as Russian dolls, containing at least two graphitic layers, and generally have inner

diameters of around 4 nm. Two years later, Iijima and Ichihashi of NEC (Feller et al., 2003) , Bethune, and colleagues of the IBM Almaden Research Center in California (Boiteux et al., 1999) synthesized single-walled carbon nanotubes (SWNTs) as shown in Fig. 1b. The SWNTs were synthesized by the same route of producing MWNTs but adding some metal particles to the carbon electrodes.

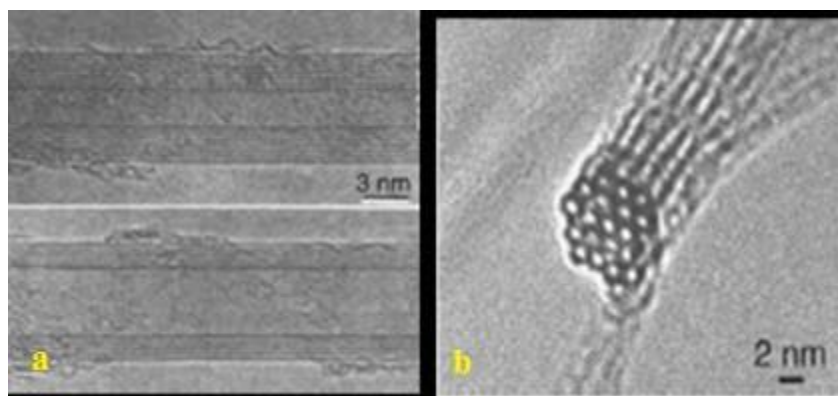


Figure 2.3: (a) HRTEM images of two MWNTs (b) and SWNTs rope: each black circle is the image of one SWNT of the rope.

Manufacture of CNTs

There are various methods of production of carbon nanotubes such as production of nanotubes by arc discharge, chemical vapor deposition, laser ablation, flame synthesis, high-pressure carbon monoxide (HiPco), electrolysis, pyrolysis etc. However, they can be mainly classified into following groups.

- 1) Physical Processes
- 2) Chemical Processes
- 3) Miscellaneous Processes

Physical processes

These are the processes, which make use of physical principles of carbon conversion into nanotubes. These include popular process of carbon nanotubes production such as arc discharge and laser ablation. Due to their wide spread popularity they are by far the most widely used processes for nanotubes production for experimental purposes.

Arc discharge

This is one of the oldest methods of carbon nanotube production. First utilized by Iijima (Feller et al., 2002) in 1991 at NEC's Fundamental Research Laboratory to produce new type of finite carbon structures consisting of needle-like tubes. The tubes were

produced using an arc discharge evaporation method similar to that used for the fullerene synthesis. The carbon needles, ranging from 4 to 30 nm in diameter and up to 1 mm in length, were grown on the negative end of the carbon electrode used for the direct current (DC) arc-discharge evaporation of carbon. During the process Iijima used a pressurized chamber filled with a gas mixture of 10 Torr methane and 40 Torr argon. Two vertical thin electrodes were installed in the center of the chamber (Figure 2.4). The lower electrode (cathode) contained a small piece of iron in a shallow dip made purposefully to hold iron.

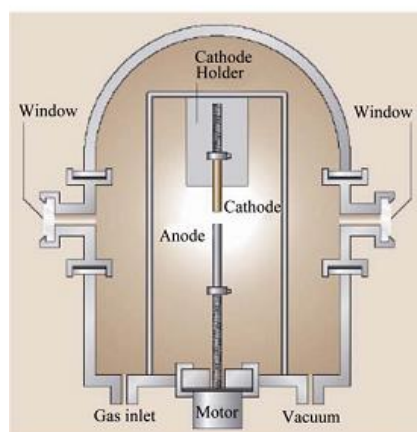


Figure 2.4: Arc discharge method for CNT.

The arc was generated by running a DC current of 200 A at 20 V between the electrodes. The use of the three components, namely argon, iron and methane, was critical for the synthesis of SWNT. Carbon soot produced as result of arc-discharge settled and nanotubes grew on the iron catalysts contained in negative cathode. The nanotubes had diameters of 1 nm with a broad diameter distribution between 0.7 and 1.65 nm. In a similar process Bethune *et al.* used thin electrodes with bored holes as anodes, which were filled with a mixture of pure powdered metals (Fe, Ni or Co) (catalysts) and graphite. The electrodes were vaporized with a current of 95 - 105 A in 100 - 500 Torr of Helium. SWNT were also produced by the variant of arcechnique by Journet *et al.* (Qin et al., 2003) as well. In his variant, the arc was generated between two graphite electrodes in a reaction chamber under helium atmosphere (660 mbar). This method also gave large yield of carbon nanotubes. Ebbesen and Ajayan, (Cheah et al., 1999) however, reported large-scale synthesis of MWNT by a variant of the standard arc discharge technique as well.

Laser ablation process

In the laser ablation process, a pulsed laser is made to strike at graphite target in a high temperature reactor in the presence of inert gas such as helium, which vaporizes a graphite target. The nanotubes develop on the cooler surfaces of the reactor, as the vaporized carbon condenses. A water-cooled surface is also included in the most practical systems to collect the nanotubes (Figure 2.5). This method was first discovered by Smalley and Co-workers at Rive University in 1995 “Polyamides, Plastics,” in Encyclopedia Of Polymer Science and Technology, 1 ed., vol. 10, pp. 460-482.. At the time of discovery, they were studying the effect of laser impingement on metals. They produced high yields (>70%) of Single walled Carbon Nanotubes by laser ablation of graphite rods containing small amounts of Ni and Co at 1200°C. In this method two-step, laser ablation was used. Initial laser vaporization pulse was followed by second pulse to vaporize target more rapidly. The two-step process minimizes the amount of carbon deposited as soot. Tubes grow in this method on catalyst atoms and continued to grow until too many catalyst atoms aggregate at the end of the tube. The tubes produced by this method are in the form of mat of ropes 10 - 20 nm in diameter and up to 100 micron or more in length. By varying temperature, catalyst composition and other process parameters average diameter and length of carbon nanotube could be varied.

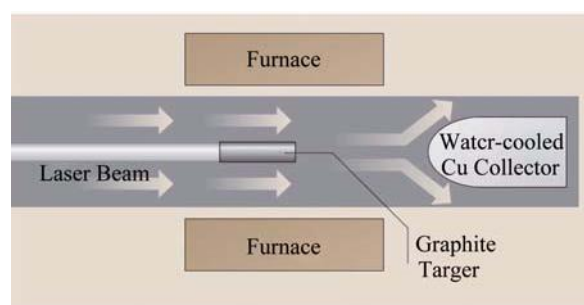


Figure 2.5: Schematic view of laser ablation method for carbon nanotube production.

Chemical processes

Chemical vapor deposition

In 1996, Chemical vapor deposition emerged as potential method for large-scale production and synthesis of carbon nanotubes. This method is capable of controlling growth directions on a substrate and synthesizing a large quantity of carbon nanotubes.

In this process a mixture of hydrocarbon gas (ethylene, methane or acetylene) and a process gas (ammonia, nitrogen, hydrogen) is made to react in a reaction chamber on heated metal substrate at temperature of around 700°C - 900°C, at atmospheric pressures. CNTs formed as a result of decomposition of hydrocarbon gas and deposit and grow on metal catalyst (substrate). The catalysts particle can stay at the bottom or top of growing carbon nanotube. The use of the catalyst and preparation of the substrate is one of the most important factors in CVD, as this substrate will define the nature and type of carbon nanotubes formed. The usually substrate material is silicon, but glass and alumina are also used. The catalysts are metal nanoparticles, like Fe, Co and Ni, which can be deposited on substrates by means of electron beam evaporation, physical sputtering or solution deposition. Porous silicon is an ideal substrate for growing self-oriented nanotubes on large surfaces. The nanotube diameter depends on the catalyst particle size, therefore, the catalyst deposition technique should be chosen carefully to yield desired results.

High pressure carbon monoxide reaction (HiPco®)

This is a unique method developed at Rice University in 1999 for the production of carbon nanotubes Introduction to Fourier Transform Infrared Spectroscopy, Thermo Nicolet Corporation, 2001. . Unlike other methods in which the metal catalysts are deposited or embedded on the substrate before the deposition of the carbon begins, in this method catalyst is introduced in gas phase. Both the catalyst and the hydrocarbon gas are fed into a furnace, followed by catalytic reaction in the gas phase. This method is suitable for large-scale synthesis, because the nanotubes are free from catalytic supports and the reaction can be operated continuously. Usually CO gas is used as hydrocarbon gas which reacts with iron pentacarbonyl, $\text{Fe}(\text{CO})_5$ to form SWNT. This process is called HiPco process. SWNT have also been synthesized in a variant of HiPco process in which a mixture of benzene and ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$ reacts in a hydrogen gas flow to form SWNT H. W. F. H.-J. D. S. C. Hohne G, An Introduction for Practitioners, Berlin, Germany: Springer-Verlag, 1996. . In both methods, catalyst nanoparticles are formed through thermal decomposition of organometallic compounds, such as iron pentacarbonyl and ferrocene.

CoMoCAT® process

Recently an effort has been made at University of Oklahoma (Haines et al., 1998), to develop a process using Cobalt and Molybdenum catalysts and CO gases. In this method, SWNT are grown by CO disproportionation (decomposition into C and CO₂) in the presence of CoMo Catalyst (specifically developed for the purpose) at 700°C - 950°C in flow of pure CO at a total pressure that typically ranges from 1 to 10 atm. This process is able to grow a significant amount of SWNT (about 0.25 g SWNT/g catalyst) in a couple of hours, keeping selectivity towards SWNT better than 80%. The secret of the process is in synergistic effect of Co and Mo. Catalyst is most effective when both metals Co and Mo are present at a time on silica substrate with low Co:Mo ratio. The material produced by the HiPco process yields a much larger number of bands, which indicate a greater variety of diameters than the material produced by CoMoCAT Process. The distribution of diameters produced by the HiPco process reported in the literature is also significantly broader than that of the product obtained from the CoMoCAT process. This process carries strong prospects in it to be scaled up as large-scale production process for the production of SWNT.

Miscellaneous processes

Some miscellaneous and relatively less used processes of carbon nanotube production are given below.

Helium arc discharge method

It was reported in 2006 by scientists of NASA's Goddard Space Flight Center that they have developed a simple, safe, and very economical process of Single walled carbon nanotubes production (Danley, 2002). In this method, scientists used a helium arc welding process to vaporize an amorphous carbon rod and then form nanotubes by depositing the vapor onto a water-cooled carbon cathode. This process yields bundles, or "ropes," of single-walled nanotubes at a rate of 2 grams per hour using a single setup. It was claimed that process would produce SWCNT with yield of 70% at a much lower cost as compared to previously achieved yield of 30% - 50% at a cost of approximately \$100 per gram. Further, it was claimed, as process does not require any metal catalyst no metal particles need to be removed from the final product. Eliminating the presence of metallic impurities results in the SWCNTs exhibiting higher degradation temperatures (650°C rather than 500°C) and eliminates damage to

the SWCNTs by the purification process. This process is under discussion for potential use as commercial scale process.

Electrolysis

In this method carbon nanotubes were produced at University of Miskolc by G. Kaptay & J. Sytchev (Zucca et al., 2004) by depositing alkali metals on a graphite cathode from a high-temperature molten salt system. The deposited metallic atoms intercalate into the space between the graphitic sheets and diffuse towards the bulk of the graphite cathode, causing some mechanical stress inside graphite. This stress induces the ablation of separate graphitic sheets, which will turn into carbon nanotubes due to interfacial forces, trying to recombine broken carbon-carbon bonds. Though this method has been reported to yield good quality of carbon nanotubes. It is not scalable to large-scale production method to produce carbon nanotubes.

Flame synthesis

This method is based on the synthesis of SWNT in a controlled flame environment, that produces the temperature, forms the carbon atoms from the inexpensive hydrocarbon fuels and forms small aerosol metal catalyst islands (Chen and Tsubokawa, 2000; Feller and Grohens, 2004). SWNT are grown on these metal islands in the same manner as in laser ablation and arc discharge. These metal catalyst islands can be made in three ways. The metal catalyst (cobalt) can either be coated on a mesh (Qiu et al., 2013), on which metal islands resembling droplets were formed by physical vapor deposition. These small islands become aerosol after exposure to a flame. The second way is to create aerosol small metal particles by burning a filter paper that is rinsed with a metal-ion (e.g. iron nitrate) solution. The third way is the thermal evaporating technique in which metal powder (e.g. Fe or Ni) is inserted in a trough and heated (Postek, 1980). In a controlled way a fuel gas is partially burned to gain the right temperature of $\sim 800^{\circ}\text{C}$ and the carbon atoms for SWNT production. On the small metal particles the SWNT are then formed. As optimization parameters the fuel gas composition, catalyst, catalyst carrier surface and temperature can be controlled (Qiu et al., 2013). In the literature found, the yield, typical length and diameters are not stated.

Application of CNTs

A carbon nanotube is inert, has a high aspect ratio and a high tensile strength, has low mass density, high heat conductivity, a large surface area, and a versatile electronic behavior, including high electron conductivity. However, while these are the main characteristics of individual nanotubes, many of them can form secondary structures such as ropes, fibers, papers and thin films with aligned tubes, all with their own specific properties. These properties make them ideal candidates for a large number of applications provided their cost is sufficiently low. The cost of carbon nanotubes depends strongly on both the quality and the production process. High-quality single-shell carbon nanotubes can cost 50 – 100 times more than gold. However, carbon nanotube synthesis is constantly improving, and sale prices are falling rapidly. The application of carbon nanotubes is therefore a very fast moving field, with new potential applications found every year, even several times per year. Therefore, creating an exhaustive list of these applications is not the aim of this section. Other application of CNTs are chemical sensors, catalyst support, gas storage, gas separation, adsorbents, biosensors, metal matrix composite, polymer matrix composite etc. (Narkis and Tobolsky, 1969).

Carbon fiber

A carbon fiber (CF) is a long, thin strand of material about 0.0002-0.0004 in (0.005-0.010 mm) in diameter, which constitute more than 90 % carbon atoms. The carbon atoms are bonded together in microscopic crystals that are more or less aligned parallel to the long axis of the fiber (Carlson et al., 1996).

History

The earliest commercial use of carbon fibers is often attributed to Thomas Edison's carbonization of cotton and bamboo fibers for incandescent lamp filaments (Leboeuf et al., 2010). However, practical commercial use of carbon fibers for reinforcement applications began in the late 1950s with the pursuit of improved ablative materials for rockets (Dasari et al., 2009). Union Carbide marketed a carbonized rayon based fabric in the early 1960s (Socher et al., 2011). DuPont's work with "black Orlon" in the late 1950s showed that acrylics could be thermally stabilized, while Shindo in Japan and Watt et al. in the United Kingdom demonstrated that, by using tension through the carbonization process, high mechanical properties could be realized (Kim et al.,

2011). Activity increased rapidly during the 1960s and 1970s to improve the performance/price ratio of carbon fibers. Much of this effort focused on evaluation of various precursors, since carbon fiber can be made from almost anything that yields a quality char upon pyrolysis. Donnet and Bansal (Caamaño et al., 2012) present a good overview of various researchers' efforts to evaluate different precursors, including PAN (polyacrylonitrile), pitch, rayon, phenol, lignin, imides, amides, vinyl polymers, and various naturally occurring cellulosic materials. Overall carbon fiber demand grew to approximately 1000 metric tons by 1980, fueled primarily by the aerospace industry, with the sporting goods industry taking some excess capacity and off-specification fiber. Polyacrylonitrile-based carbon fiber usage had exceeded all other precursors at that time. This was a surprise to some, since the anticipation in the late 1970s had been that the significantly lower raw material price and higher char yield of pitch would result in the winning combination. However, higher processing costs are required to make a spinnable pitch, so better overall properties for PAN fibers resulted in their dominance. Rayon was relegated to third place, despite having a lower raw material cost, because inferior properties and a low char yield (20 to 25%) after carbonization made for a higher overall cost. Properties can be improved by stress graphitization at high temperatures, but this increases cost further, making the fiber even less desirable. Rayon is still used today for insulating and ablative applications but not for structural applications. By the mid-1990s, a new cost-effective, PAN- based carbon fiber made from a modified textile precursor was being aggressively promoted by companies like Zoltek and Fortafil for commercial applications. In 1995, one manufacturer announced the goal of reaching a price level of \$5/ lb (\$11/kg) by the year 2000, which brought a lot of attention to and greatly accelerated application development (Finegan and Tibbetts, 2001).

Manufacture of carbon fibers

Precursor sources used, in order of volume, are PAN, pitch, and rayon. Although the specific processing details for each precursor is different, all follow a basic sequence involving spinning, stabilization, carbonization, and application of a finish or sizing to facilitate handling, as shown in Fig. 1. Discontinuous carbon fiber whiskers are also now produced in a batch process from hydrocarbon gases using a vapor-liquid-solid growth mechanism (Leer et al., 2006).

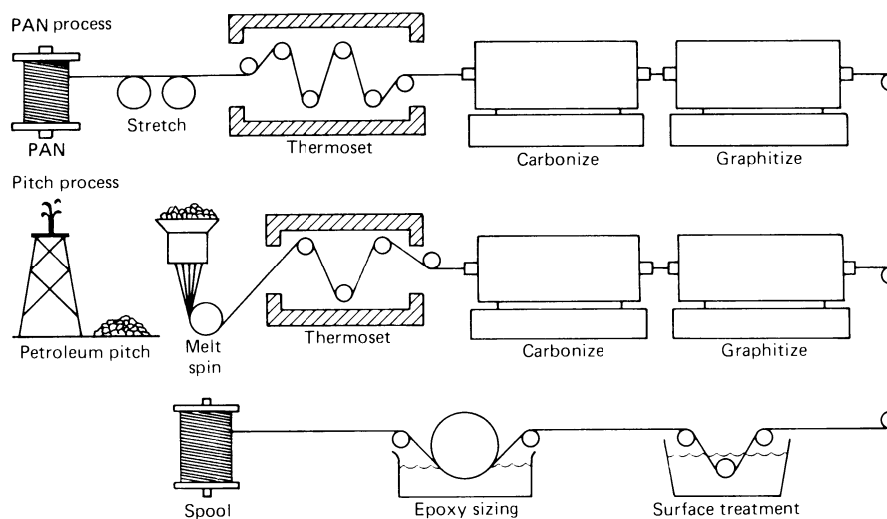


Figure 2.6: The processing sequence for polyacrylonitrile (PAN) and mesophase-pitch-based precursor fibers shows the similarities for the two processes.

PAN-based carbon fibers

The majority of all carbon fibers used today are made from PAN precursor, which is a form of acrylic fiber. Precursor manufacture is accomplished by spinning the PAN polymer into filaments using variants of standard textile fiber manufacturing processes. The PAN fibers are white in color, with a density of approximately 1.17 g/cm^3 (0.042 lb/in^3) and a molecular structure comprised of oriented, long chain molecules. Stabilization involves stretching and heating the PAN fibers to approximately 200 to 300 °C (390 to 570 °F) in an oxygen-containing atmosphere to further orient and then crosslink the molecules, such that they can survive higher-temperature pyrolysis without decomposing. Stretching after spinning and during stabilization helps develop the highly oriented molecular structure that allows development of a high tensile modulus and improved tensile strength upon subsequent heat treatment. Carbonization of standard and intermediate modulus fiber typically involves pyrolyzing the fibers to temperatures ranging from 1000 to 1500 °C (1800 to 2700 °F) in an inert atmosphere, typically to 95% carbon content. An additional high heat treatment step is included just after carbonization for some very high-modulus fibers. During carbonization, the fibers shrink in diameter and lose approximately 50% in weight. Restraint on longitudinal shrinkage helps develop additional molecular orientation, further increasing mechanical properties. After carbonization, the fibers may be run through a surface

treatment step designed to clean and attach functional groups to the fiber surface, which increases bond strength with matrix resins. Most manufacturers use an electrolytic oxidation process that creates carboxyl, carbonyl, and hydroxyl groups on the surface for enhanced bonding. A sizing or finish is then applied to minimize handling damage during spooling and enhance bonding with matrix resins. The fiber is then spooled. Today, there is differentiation among manufacturers between those who use a modified textile-type PAN precursor and those who use an aerospace-type precursor. The textile-type precursor is made on a very large scale in modified- acrylic textile fiber plants in tows or rovings consisting of >200,000 filaments. The tows are then split down into smaller bundles (approximately 48,000 filaments) after carbonization for spooling. Aerospace precursor is made in smaller specialty plants and processed in 3000 (3K) to 12K filament tows that can be assembled into 24K or larger tows after carbonization. Manufacturing cost is lower for the textile-type precursor, due to higher line throughputs, larger economies-of- scale, and less handling of small tow bundles. This type fiber is more targeted for industrial applications. The aerospace-type precursor, because it is processed in smaller tow sizes, is less fuzzy and available in the smaller tow sizes favored by the aerospace industry, for whom it was originally developed. Physical properties can be similar for both types (Leer et al., 2006).

Pitch-based fibers

Pitch is a complex mixture of aromatic hydrocarbons and can be made from petroleum, coal tar, asphalt, or PVC (Socher et al., 2011). Starting raw material selection is important to the final fiber properties. Pitches must be processed through a pre-treatment step to obtain the desired viscosity and molecular weight in preparation for making high-performance carbon fibers. The pre-processed pitch contains “mesophase”, a term for a disk-like liquid crystal phase (Farimani and Ebrahimi, 2012) that develops regions of long-term ordered molecules favorable to manufacture of high-performance fibers. Without this step, the result is an isotropic carbon fiber with low strength and low modulus of less than 50 GPa (7×10^6 psi) (Shen et al., 2012). Process details of the final composition and method of spinning mesophase pitch are generally held secret by the manufacturers. Once spun, the stabilization, carbonization, surface treatment, application of sizing, and spooling of pitch-based fibers follows a sequence similar to the manufacture of PAN-based fibers, as shown in Fig. 1. Actual process parameters, such as temperatures, ramp rates, and time at temperature for stretch and

stabilization, are different for pitch than for PAN. Gas species evolved during pyrolysis and their onset of evolution are very different for PAN and pitch. The response to heat treatment is also greater for mesophase-pitch-based fibers at higher temperatures, a consequence of their more ordered starting molecular structure. For example, a mesophase-pitch-derived fiber processed to the same temperature as a PAN fiber will exhibit higher density and thermal and electrical conductivity, all else being equal.

Other precursors

Rayon is processed in similar fashion to PAN, as shown in Fig. 1; the difference is the actual process parameters used. Carbon fiber “whiskers” can be formed from gas-phase pyrolysis via catalyzed cracking of hydrocarbon gases like methane. One process involves growth of a thin carbon tube of 10 to 50 nm from a submicron iron particle in a hydrocarbon-rich atmosphere, followed by a secondary process of thickening the tube by chemical vapor deposition of carbon on the surface (Zhang et al., 2009). Others have discussed similar processes, some capable of longer length fibers (Alig et al., 2007). Although only discontinuous fibers are fabricated, they have unique properties approaching those of single crystal graphite in some cases.

Available formats for fibers

Commercially available carbon fibers are produced by a multitude of manufacturers with a wide range of properties and two sizes. Carbon fibers are available in many of the same formats as glass fiber. These formats include continuous filament- spooled fiber, milled fiber, chopped fiber, woven fabrics, felts, veils, and chopped fiber mattes. Most fiber today is spooled, and then processed into other formats in secondary operations. The size of the carbon fiber tow bundle can range from 1000 filaments (1K) to more than 200K. Generally, aerospace carbon fibers are available in bundles of 3K, 6K, 12K, and 24K filaments, while most commercial-grade fibers are available in 48K or larger filament counts. Composite fabrication equipment, such as filament winders and weaving machines, must be adapted to handle the larger cross section of commercial grade fiber (Leer et al., 2006).

Typical applications of carbon fibers

Carbon fiber usage is growing in a variety of applications, including aerospace, sporting goods, and a variety of commercial/industrial applications. Growth is fastest in the

commercial/ industrial applications. In many instances, carbon composites have displaced metal parts, despite being more expensive on a direct replacement purchased cost basis. Where successful, carbon composites have lowered total system costs through reduced maintenance, faster processing speeds, and improved reliability. Many new uses under development are enabling, meaning applications that were not practical with metal or other materials are now possible with carbon composites (Leer et al., 2006).

Aerospace

Perhaps nowhere is the need to save weight greater than in the aerospace industry. Early growth of the carbon fiber industry was driven almost exclusively by the desire for higher performance aircraft made possible with carbon fiber composites. Today, carbon fiber is used on aircraft for primary and secondary structures. Use is growing, having already established a strong track record in primary structures on military aircraft. All of these applications use carbon fiber for its high specific strength and specific stiffness. Fiber formats used include prepreg for layup processes and fabrics for resin transfer molding and similar processes. Satellites incorporate very high modulus pitch-based carbon fibers, partly for the high stiffness-to-weight ratios and partly for their negative axial coefficient of thermal expansion (Leer et al., 2006).

Sporting goods

Golf club shafts are presently the largest sporting goods application for carbon fibers. Lighter weight and higher stiffness shafts, made possible with carbon fiber, allow club manufacturers to place more weight in the club head, which increases club head speed for improved distance. Most golf shaft manufacturing today is done with unidirectional prepregged sheets of carbon fiber in a roll wrapping operation. Some shafts are filament wound. Carbon fiber fishing rods are favored by fisherman for their lightweight and sensitive touch. The rods are manufactured via a roll wrapping process similar to golf shafts, using unidirectional prepreg. Most racquets for tennis, racquetball, and squash are made from prepregged carbon fiber that is sheeted, wrapped around a bladder, and cured. Carbon composite arrows are fabricated by either of two processes: pultrusion or roll wrapping. Skis and bicycle components tend to use fabrics made from carbon fiber etc. (Leer et al., 2006).

Carbon black

Carbon black (CB) is a high purity colloidal carbon produced in large quantities worldwide for myriad industrial and consumer application. Commercial carbon black differs in important respects from soots and other environmental carbonaceous particles but it is useful as an idealized model for investigating the adsorption properties, atmospheric reactions, and to a lesser extent, the environmental effects of these materials (Deng et al., 2009).

History

Carbon black was first produced commercially in China by burning purified animal or vegetable oil in porcelain pots. For two thousand years this lampblack process underwent only minor evolutionary change until the advent of the modern Carbon Black Industry in 1872. In that year, a small plant was built in Pennsylvania to produce channel black from natural gas. As the supply of by-product gas from the oil fields in Pennsylvania diminished, the industry moved to new gas fields in West Virginia and then to Louisiana, Oklahoma, and Texas. About 500,000 pounds of channel black and lampblack were produced in 1881, increasing to 3 million pounds per year (mainly channel black) by 1895. (Wang et al., 2008). Carbon black was used primarily as a pigment in printing inks, paints, and lacquers until the early 1900's when its use as a reinforcing filler for rubber became important following the discovery in England of carbon black's ability to strengthen and toughen rubber. The rubber industry soon became the major market for carbon black. Its requirements led to the development of more efficient, lower cost, high-volume furnace processes for the production of carbon black. In the first of these, a limited range of carbon blacks was obtained from natural gas. The gas furnace process was developed in the USA in 1922 and employed for about 40 years. A method for producing carbon black from heavy aromatic liquids was introduced in the USA in 1943. Today, the oil furnace process accounts for over 95% of world production (Deng et al., 2009).

Technology of manufacture

Mechanism of formation

In all carbon, black processes except that for acetylene black, a liquid or gaseous hydrocarbon feedstock is pyrolyzed at 1200-1700 °C. The resultant molecular

fragments polymerize in the vapor phase to polycyclic aromatic species, which condense to form liquid nuclei. Small amounts of stable polycyclic aromatic hydrocarbons (PAH) are formed also as a minor by-product. Subsequent coalescence and carbon deposition yields spherical particles with diameters of 5-20 nm in the furnace and channel processes and up to 500 nm in the thermal process. Progressive dehydrogenation leads to an increase in viscosity and "stickiness" so that further collisions cause the particles to cohere and partially fuse but not to coalesce into spherical form. Continued dehydrogenation and carbon deposition yields carbon aggregates of characteristic morphology made up of fused particles having turbostratically oriented graphite-like carbon layers. When solid aggregates are present the temperature must be decreased to retard oxidation of the carbon in the presence of the high concentration of water vapor in the flue gas. This process appears to proceed via hydroxyl radical attack to produce porosity and loss of surface carbon (Etika et al., 2009).

Channel process

The original process employed a sheet metal building containing thousands of natural gas flames quenched by overhead reciprocating iron channels. A limited air supply was admitted at the base of the building with combustion products vented to the atmosphere. Most of the carbon deposited on the channel and was scraped off and collected in hoppers. The product from many hot houses was converged to a central processing unit where coke and foreign materials were removed. Yields were very low, usually < 5% of the theoretical carbon, with up to 20% of the carbon black lost as smoke through the vents (Deng et al., 2009).

Acetylene black process

Flowing acetylene gas is decomposed exothermically to carbon and hydrogen at 1000 °C in a water-cooled refractory lined metal reactor. Almost all input carbon is converted to product since no oxygen or other oxidant is present (Deng et al., 2009).

Thermal process

Gas or vaporized oil is pyrolysed in a preheated refractory brick retort at 1300-1500 °C to produce carbon suspended in an off-gas composed of > 85% hydrogen plus methane and heavier hydrocarbons. After cooling with a water spray, the carbon is

removed by cyclone separators followed by bag filters or wet scrubbers. Two reactors are operated in tandem; one being heated by combustion of recycled off-gas in air while the other is producing carbon (Deng et al., 2009).

Gas furnace process

Natural gas is injected into a gas-air flame at 1400 °C in a refractory lined furnace with the combined pyrolysis and combustion products subsequently cooled to 200-300 °C by water sprays. In the original process, carbon black was collected using electrostatic precipitators in series with cyclone separators but process modifications led to the use of more efficient bag filters (Deng et al., 2009).

Oil furnace process

In this modern successor to the gas furnace process, a highly aromatic liquid feedstock derived from coal or petroleum is sprayed into a flame at 1300-1700 °C in a refractory lined or water-cooled reactor. The carbon laden gas is cooled to 300 °C by water sprays then filtered through coated glass fiber or teflon fabric filter bags to remove and collect fluffy carbon black (Deng et al., 2009).

Application

Carbon black is an essential ingredient in thousands of industrial products, however, over 90% of the carbon black produced is used as a reinforcing filler in elastomers, mainly in the manufacture of rubber tires. Some other important applications are: pigment in inks, paints, plastics, and paper; conductive filler; radio-frequency insulator; dry cell batteries; magnetic tapes; UV stabilizer and antioxidant in plastics; and photocopy toners. A few of the grades used in inks, enamels, and toners are after treated with ozone, nitric acid or nitrogen oxides to yield an acidic, oxidized product. These grades account for < 1% of total furnace black production (Deng et al., 2009).

2.2 Intrinsically Conductive Polymer

Intrinsically conductive polymers (ICPs) are organic polymers that conduct electricity. They can be used like the metallic conductors or semiconductors (iPolycond).

2.2.1 History and properties

Typically conventional polymers such as plastics, rubbers, etc., offer significant resistance to electrical conduction and are either dielectrics or insulators. With the invention of conductive polyacetylene in the 1970s, Intrinsically conductive polymers (*ICPs*) have received significant attention from both science and engineering communities. This culminated in 2000 when the Nobel Prize was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa for their discovery and development of electrically conductive polymers (Shirakawa et al., 1977). Polyacetylene, polypyrrole, polythiophene, polyaniline and their derivatives are the most common *ICPs*. All mentioned polymer has one characteristic features (scheme 1.3), they all have highly conjugated back bone.

2.2.2 Application

Much of the early research into conducting polymers was spurred on by their potential applications as replacements for existing metals and semiconductors. In particular, their low densities compared with metals and their ease of processing via typical polymer routes such as injection moulding led to conductive polymers being proposed as alternatives to existing materials in many areas. However, with almost 15 years of intensive development activity, it seems that many of the proposed applications for these materials were rather optimistic and have not yet become possible. With growing experience of these materials, a number of more realistic applications have now emerged that tend to exploit the novel features associated with conductive polymers rather than those properties that are readily obtainable in more traditional materials. Some of these applications include plastic batteries, sensors, electrochromic displays, EMI shielding, fuel cells and various biomedical devices (Stolka et al., 1995).

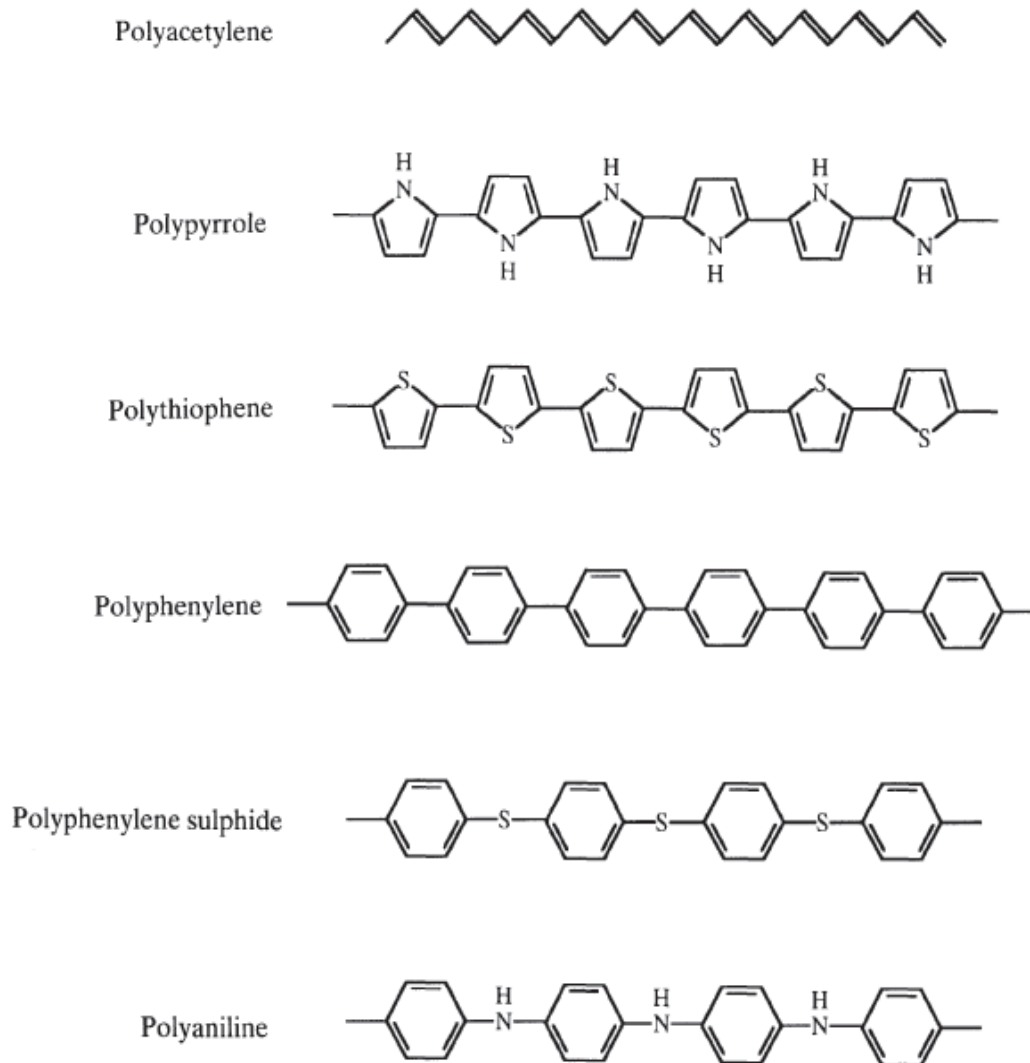


Figure 2.7: Chemical structure of some important ICPs (Stolka et al., 1995).

3. ELECTRO STATIC PAINTING

Electrostatic painting (EP) is a solvent-free method of coating objects with dry, finely grounded paint particles. The chief benefit of this process is that it avoids the environmental and economic costs of petroleum solvents used in traditional liquid coatings. ESP has been used in the United States and Europe since the 1950s.

History

In the early years, basically from its invention in the 1950s to the mid-1970s, the coating chemistry, manufacturing, and application technology had to develop. Functional applications, where coating characteristics other than appearance are important, came first, followed by decorative applications. After the mid-1970s, this basic dynamic still takes place but higher solvent costs and environmental regulations become an important driver in the substitution of liquid, solvent-based systems. The major manufacturing and application technologies had, by this time, been developed and the area of development for this relatively standardized equipment and application technology was to become computerized and automated a trend that continues today. Also by the mid-1970s, the major powder chemistries had become mature, leaving further development in the area to be increasingly specialized to narrow product segments, while powder coating as a whole becomes suitable to be used in an ever-broader array of product segments (Brun et al., 2010).

Electrostatic spray charging improves the transfer efficiency of spray finishing equipment. The transfer efficiency improvements occur because the electrostatic forces help overcome other forces, such as momentum and air flow that can cause the atomized materials to miss the intended target. Electrostatic methods save coating material, time, and labor. More of the material is attracted to and adheres to the target, and less material is lost in the spray booth and the surrounding environment. Electrostatic methods also lower solvent emissions into the air since less coating material is needed to coat each part (Graco, 1995). Electrostatic painting systems can be either automatic or manual.

3.1 Automatic Electrostatic Systems

The automatic electrostatic systems include High-speed rotational (stationary or reciprocating) atomizers, Reciprocating discs, and Automatic air spray, airless, air assisted airless, or HVLP spray guns (Figure 3.1).

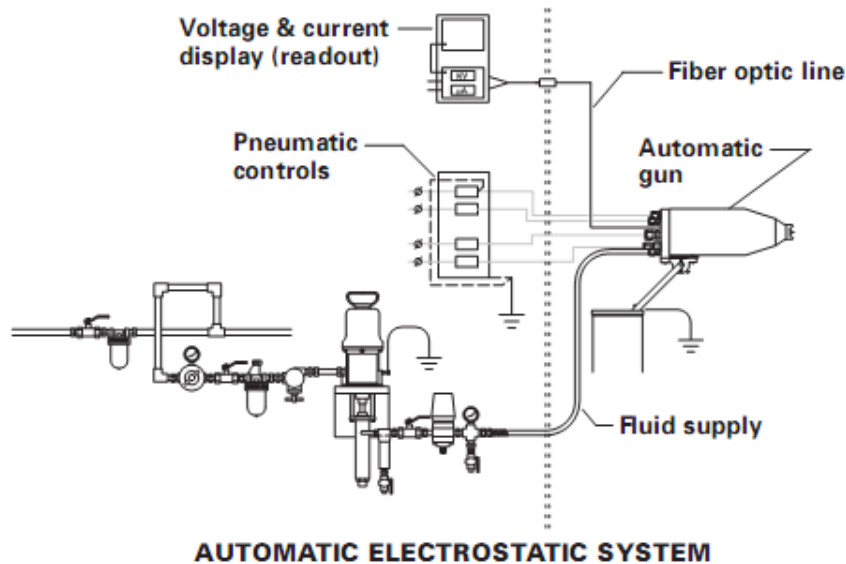


Figure 3.1: Automatic electrostatic system.

3.2 Manual Electrostatic Systems

The manual electrostatic systems include Airspray electrostatic hand-held spray guns, Air-Assisted Airless electrostatic hand-held spray guns, Airless electrostatic hand-held spray guns, HVLP electrostatic hand-held spray guns, and Hand-held rotary atomizer systems (Figure 3.2).

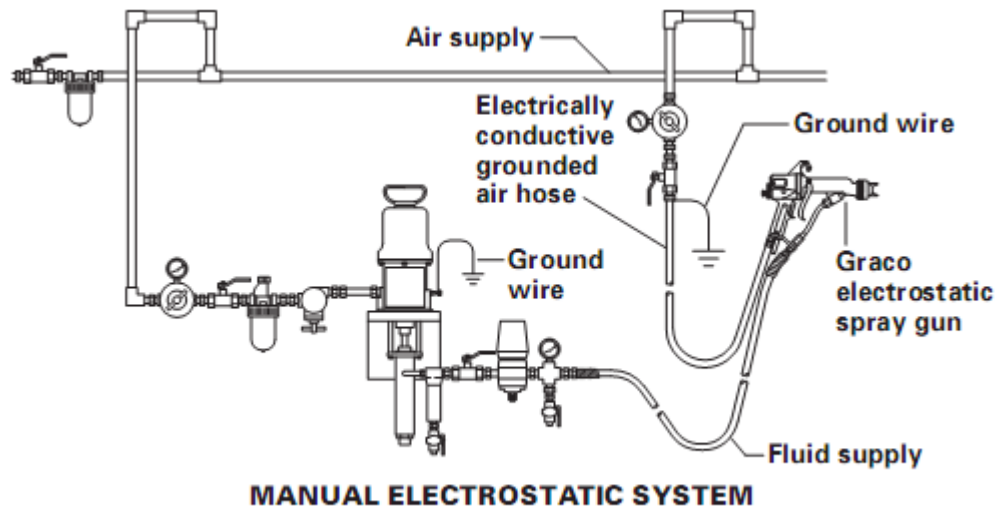


Figure 3.2: Manual electrostatic system.

3.3 The Electrostatic Spray Charging Process

Figure 3.3 shows the basic components of electrostatic spray equipment. Basic parts are a spray gun or atomizer, particles of atomized coating material, which are emerging from the gun in a spray pattern, an ionizing needle located in or near the stream of coating material and the target, or object, to be coated. In the example in Figure 3.3, the ionizing needle applies an electrical charge to the particles of material (Graco, 1995). (In an electrostatic system, the coating material may be charged either before or after it is atomized.)

As shown in Figure 3.4, the electrical field between the ionizing needle and the grounded object helps drive the charged spray particles to the grounded target. The force of the electrostatic field causes a greater percentage of the charged spray particles to reach the grounded object, rather than miss the target or be swept away by surrounding airflow. In other words, the transfer efficiency of the spray finishing process is improved through electrostatics because the electrical field draws an increased number of particles to the target (Graco, 1995).

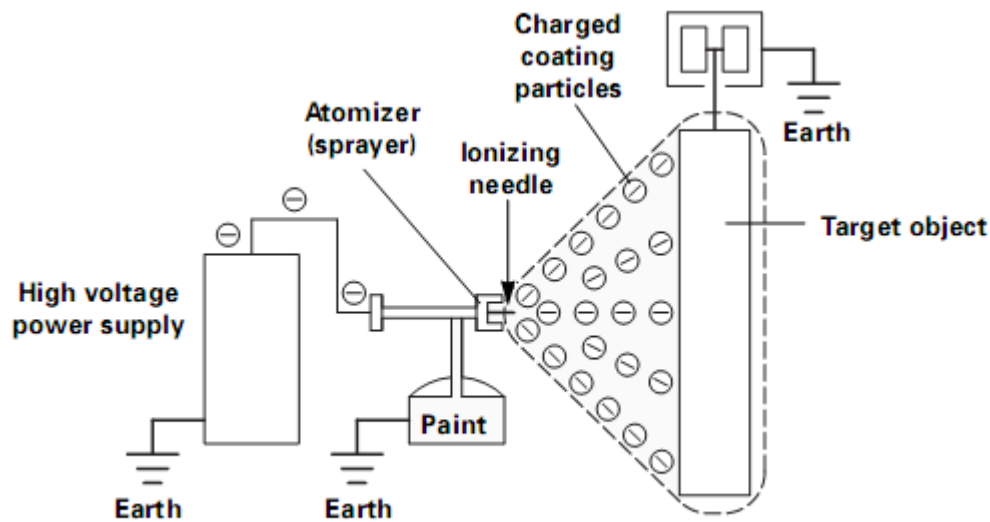


Figure 3.3: Basic components of a electrostatic painting spray equipment.

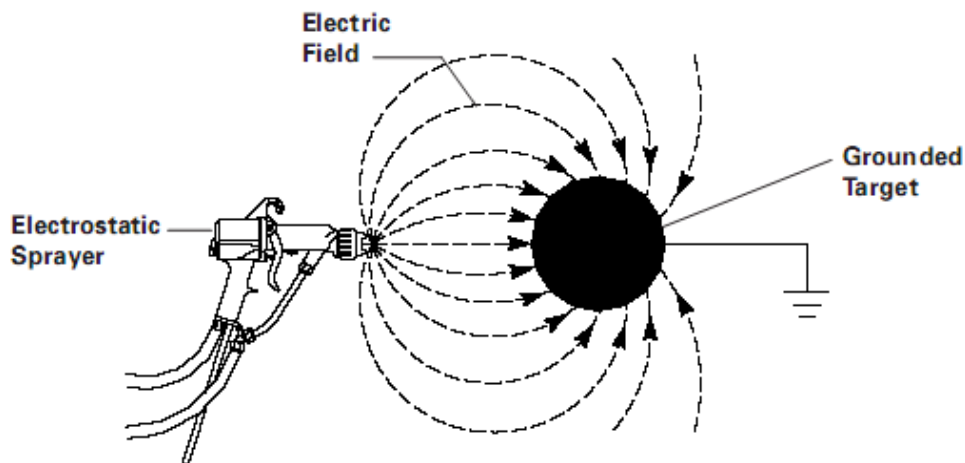


Figure 3.4: The electro field of an electrostatic system

Electrostatic Charging Methods There are four types of electrostatic charging methods. The four electrostatic charging methods that can be mentioned are corona charging, contact charging (also called conduction charging), induction charging, (also called non-contact charging) and frictional charging (also called tribo charging). Of these methods, corona and contact (conduction) charging are the two primary methods used in liquid electrostatic spray finishing which will be illustrated in the following (Graco, 1995).

3.3.1 Corona charging

The corona charging method utilizes a pointed or sharply curved electrode that is raised to a high electrical potential. The intense electric field at the electrode breaks down the

surrounding air and creates ions, which are then free to attach themselves to the atomized coating material (Graco, 1995).(See Figure 3.5)

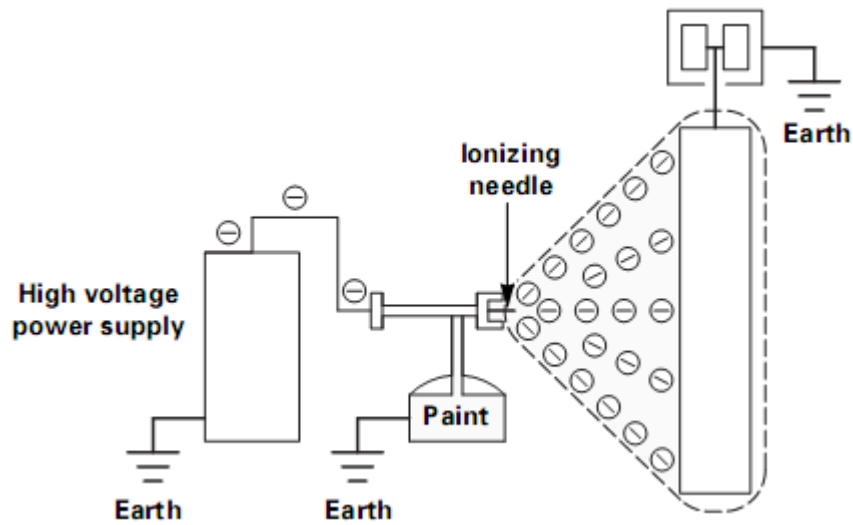


Figure 3.5: Corona charging

3.3.2 Contact charging

The contact charging (or conduction) method utilizes a direct charge transfer, rather than ionization. In this method, an electric charge flows from a source of high potential (voltage) to the coating material that has encountered the source (Graco, 1995).(See Figure 3.6)

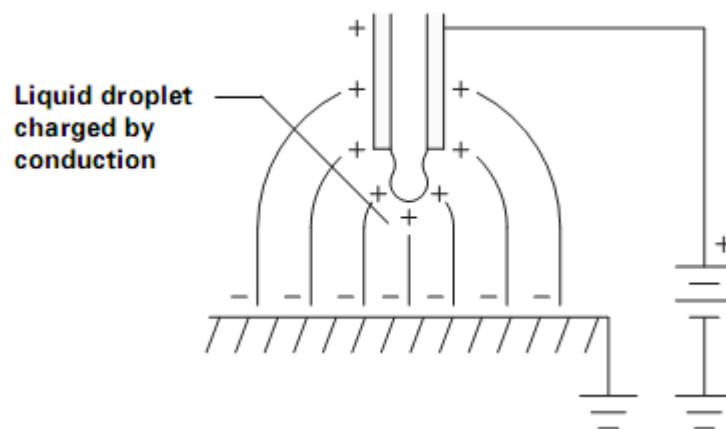


Figure 3.6: Contact charging.

Application

The market for can be divided into three main categories, general metal, appliance, and automotive market. In general metals, powder replaced porcelain enamel and liquid coating in lighting fixtures, indoor metal furnitures and tractors . In the appliances

market, powder coating replaced porcelain enamel on external surfaces in refrigerator and drier. In automotive industry, automotive components expanded to exterior applications like window frames, roof rails, wiper arm, aluminum wheels, hubcaps(wheelcover) and interior applications like seat risers and mirrors (Brun et al., 2010).

4. EXPERIMENTAL WORK

4.1 Materials And Preparation

PA 66 (Minlon) granules were supplied by DuPont Company (USA). Conductive carbon fiber (diameter: 7.2 μm , length of fibers: 3-12 mm), Carbon black (Acetylene, 50% compressed) and Multi wall Carbon nano tubes (diameter: 9.5 nm, length: 1.5 μm , Surface area: 250-300 m^2/g) were used in this study. PA66 with 15 wt. % additives (Minlon) granules and conductive fillers was dried at 80 $^{\circ}\text{C}$ for 2 to 4 h to remove residual moisture, and electrical conductive PA66 composites were prepared by the following method:

Extrusion method (EM): The PA66 granules, electrical conductive fillers (CB,CF,MWCNTs) and compatibilizer were proportionally mixed and processed in a twin-screw extruder (Scientific, south Korea) to give samples. The rotational speed of the extruder was 30 rpm, and the temperatures of its eleven sections, from the hopper to the head, were 260, 260, 265, 265, 270, 270, 270, 275, 275, 275 and 280. Then samples injected to form hubcaps (wheel covers) with a injection molding machine.

In general, the materials investigated in this study were prepared in a twin-screw extruder by compounding Minlon with various weight percentages of conductive fillers (maximum 5 wt %). and pp-g-ma (2 and 5 wt. %) as a compatibilizer. Composition and codes of the samples are listed in the Table 4.1.

Table 4.1: Composition and codes of the samples

No	PA66 (gr)	Compatibilizer(gr)	CF (gr)	CB(gr)	CNT (gr)
M1	97	-	-	-	3
M3	95	2	-	-	3
M4	90	5	5	-	-
M5	94	5	-	-	1
M6	90	5	-	5	-
M7	89	5	4	1	-
M8	89	5	4	0.5	0,5

4.2 Apparatus And Experimental Techniques

Results presented further in the study were obtained on the basis of a number of research methods and techniques. Measuring instruments used to characterize

materials, which are the subject of the study included an electrical conductivity device, scanning electron microscope (SEM), tensile testing machines, differential scanning calorimeter (DSC) and Fourier transform infrared spectroscopy (FTIR). The details were given below.

4.2.1 Electrical properties

Volume and surface resistivity were measured on Keithley connected to 4-Point Probe of Signatone and GW Instek (LCR-816).

4.2.2 Scanning electron microscope measurements

SEM of samples were taken by a JSM-7800F PRIME model.

4.2.3 Mechanical properties

Tensile test have been done on the samples. Four samples of each composite formula were used each time for measuring the mechanical properties and for increasing the accuracy of data, the average of the data has been reported. Test speed and pre-load were respectively 10mm/min and 0.5 Mpa with a Rockwell tensile device.

4.2.4 Differential scanning calorimetry (DSC) analysis

The aim of using Differential Scanning Calorimeter (DSC) is to observe thermal transitions in different materials like polymers. Composite samples were characterized by a TA Q10 Model DSC during heating to 400 °C. Heating rate of 20 °C min⁻¹ was applied. The entire thermal treatment was performed under nitrogen flow.

4.2.5 ATR-FTIR measurements

FTIR is a simple and reliable technique used in different fields of study. It can be used to study and identify chemicals. All samples ATR-FTIR measured.

4.2.5 Hardness tests

The aim of the test is to determine the hardness of the paint film based on TSH 3131G 4.5. A pencil suitable for the measurement of paint film hardness was used. At first, the wooden part of such a pencil was cut off, then the lead cylindrically to expose the tip by 3mm to 5mm was sharpened. The tip perpendicularly against sandpaper placed

on a hard flat plane was applied, and it should be sharpened gently by drawing a circle so that the tip becomes flat with an acute angle. a pencil at an angle of $45\pm 2^\circ$ should be pushed forward 10 to 20 mm to scratch the coated surface with a uniform speed (10mm/s) while pushing the pencil against the coated surface by applying load of 750g to 1250g. This test will be repeated five times using pencils of the same hardness, with their lead tips sharpened flat by an acute angle each time. The same procedure will be continued until one of the pencil scratches the paint film. In that case, the hardness of the previous pencil will be reported as its hardness.

4.2.6 Adhesive resistance (Cross-Cut) tests

This analysis method is intended to measure the strength of adhesion of paint films to substrate based on the TSH 3131G 4.8. In this test, the blade of a cutter knife was applied vertically to the test piece coated surface. Eleven equally spaced parallel cuts reaching to the interface in the selected place were made then another Eleven equally spaced parallel cuts intersecting these at right angles. A piece of adhesive tape (width: 24mm) onto the cross cut area was pressed and then uniform force to the entire area with the pad of the finger at $20\pm 2^\circ\text{C}$ and $65\pm 5\%$ RH was applied. Test pieces in which 50% or more of the crosscuts in the square frame peeled will be counted and reported. In the case, the square frame peeled was less than mentioned value material will be approved by this test.

4.2.7 Dropped weight impact tests

The purpose of this analysis is to observe the wheel cap impact behavior by throwing weights based on the TIS 01202-00N08 7. In this test, a wheel cap will be put on the disc wheel then disc wheel equipped with a cap will be placed on a plane and the disc wheel tilted at 45° . The weight will be Dropped onto the center of the cap, the spoke portion and flange portion. The test will be repeated three times or more at each location. There shall be no crack, breakage, etc., which may affect appearance and harmful flaw (confirm by visual inspection from spacing of 50cm). Otherwise, the sample will not be approved by this test.

4.2.8 Drop impact tests

The purpose of this analysis is to check the wheel cap dropping effect in terms of fracture, scratch based on the TIS 01202-00N08 8. In this test, a single unit of wheel

cap will be fallen freely in the below positions (a, b, c). The same step should be repeated for two times under the same conditions.

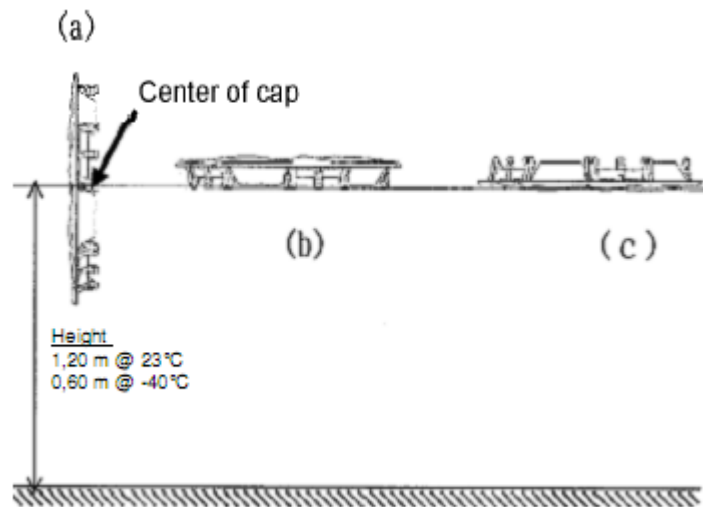


Figure 4.1 : Dropping posture in drop impact test.

There shall be no crack, breakage, etc., which may affect appearance and harmful flaw (confirm by visual inspection from spacing of 50cm). Otherwise, the sample will not be approved by this test.

5. RESULT AND DISCUSSION

5.1 Electrical Properties

The electrical conductivity of composites were obtained and summarized in Table 5.1. Noryl is a commercially available conductive composite which is suitable for electrostatic painting (EP) and has poor mechanical properties compared to the Minlon. In this thesis, it is named as (N1) and its conductivity was measured as 2.310^{-8} S/cm with the methods used in this study. This conductivity is used as a reference data for the composites conductivity obtained in this study. The conductivity of the composites should be equal or higher to Noryl's conductivity.

Table 5.1: Electrical conductivity of Noryl and samples (Minlon with different portions of CB,CNTs and CF with 2 and 5 % wt. of compatibilizer).

Sample	Minlon (gr)	compatibilizer (gr)	CF (gr)	CNT (gr)	CB (gr)	Conductivity S/cm
N1	-	-	-	-	-	2×10^{-8}
M1	97	-	-	3	-	1×10^{-7}
M3	95	2	-	3	-	1×10^{-7}
M4	90	5	5	-	-	3×10^{-8}
M5	94	5	-	1	-	4×10^{-8}
M6	90	5	-	-	5	4×10^{-8}
M7	89	5	4	-	1	2×10^{-8}
M8	89	5	4	0,5	0,5	2×10^{-8}

5.2 Scanning Electron Microscope Measurements

To have a better understanding of morphology and additives distribution in composites, the SEM is useful tools. SEM images of samples and Noryl (N1) shown in Figure 5.1 to Figure 5.9. Unfortunately, since the size of the CF, CB and CNTs are not at the same scale (mm, nm and nm respectively), it is impossible to have a good comparison between them. So each composite's SEM image has been reported with the best

magnitude. In the first image (N1) which indicates Noryl some sphere and rod shapes can be seen, which represent the CB and CF respectively. SEM images of M1, M3, M4, M5, M6, M7, and M8 composite with the presence of the carbon additives are presented. M1 and M3 respectively are without and with compatibilizer. It can be inferred from better homogeneity of additives (carbon content) in the M3. The most suitable composite that covers all of our requirements is M4; two SEM pictures with the magnification of 500 and 12000 have been presented. For sample M4, the left image shows that carbon fibers can have good distribution and the right one, with a white rod appearance, points out CF.

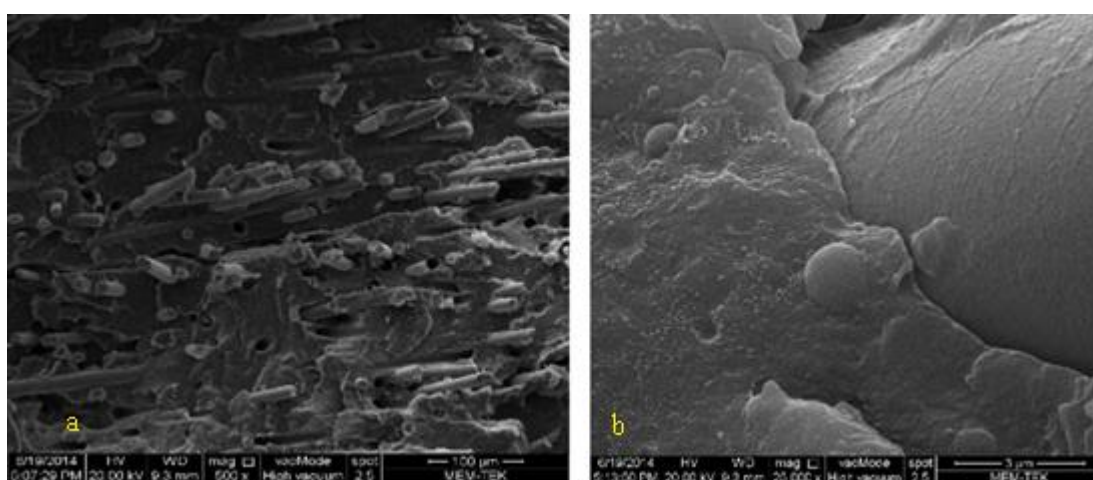


Figure 5.1: SEM images of N1 (Noryl) with different magnitudes. a) 100µm, b) 3 µm.

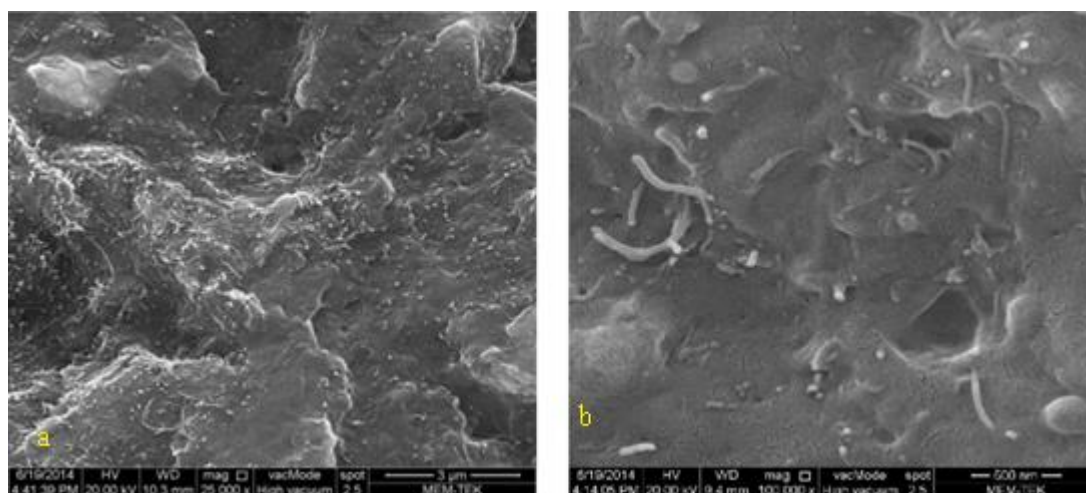


Figure 5.2 : SEM images of M1(Minlon + 3 wt. % CNT)with different magnitudes; a) 3µm, b) 500nm.

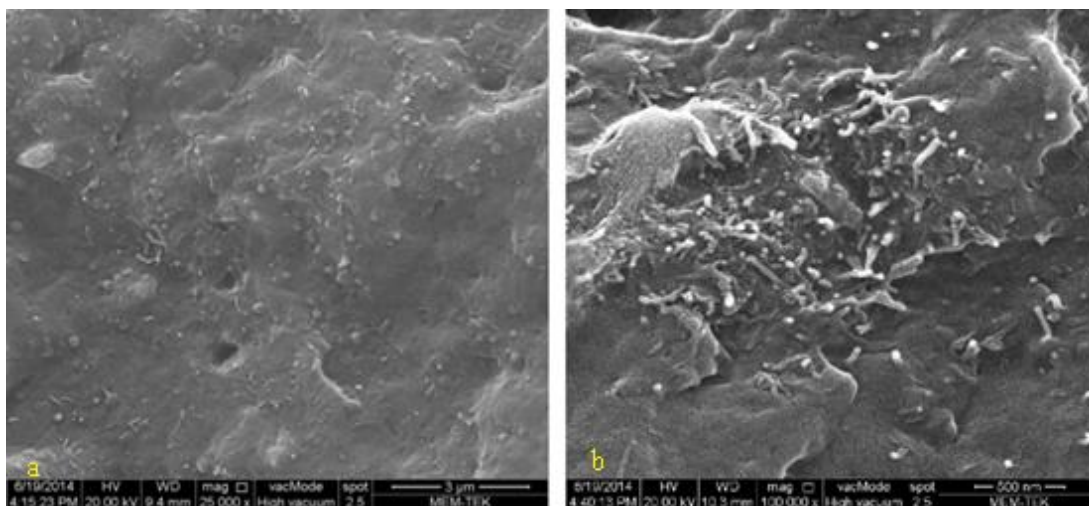


Figure 5.3 : SEM images of M3 (Minlon + 3 wt.% CNT + 2 wt.% compatibilizer) with different magnitudes; a) 3μm, b) 500nm.

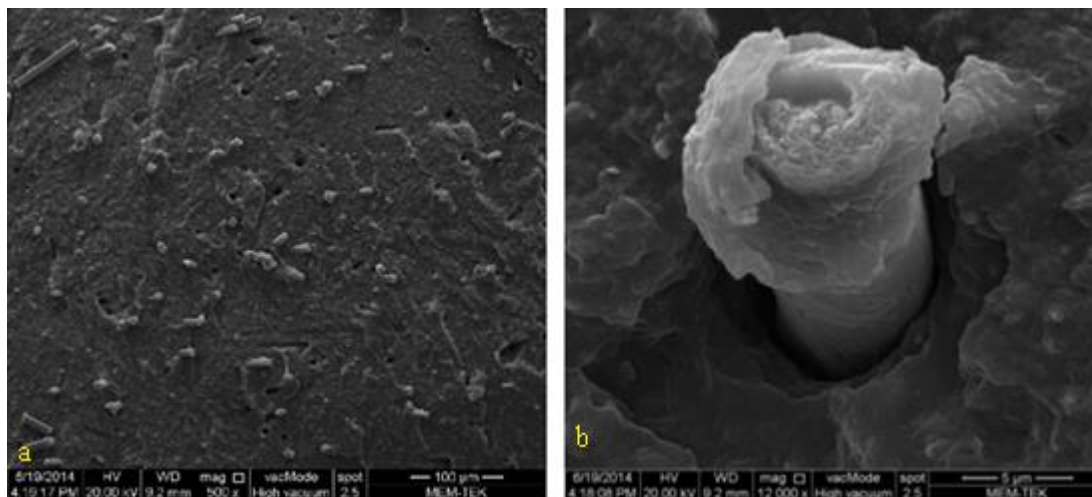


Figure 5.4 : SEM images of M4 (Minlon + 5 wt.% CF + 5wt.% Compatibilizer) with two magnitudes; a) 100µm, b) 5µm.

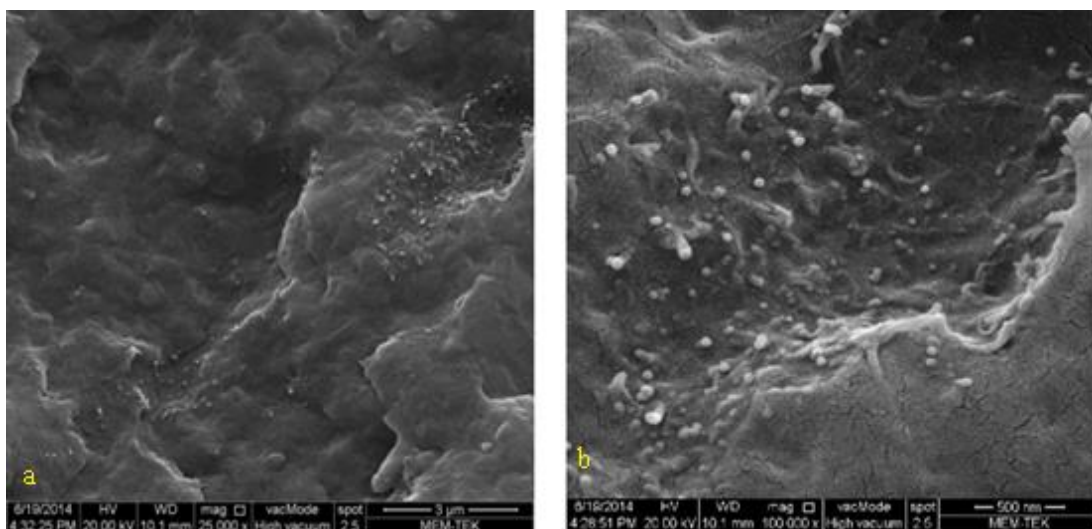


Figure 5.5 : SEM images of M5 (Minlon + 1wt.% CNT + 5wt.% Compatibilizer) with two magnitude; a) 3µm, b) 500nm.

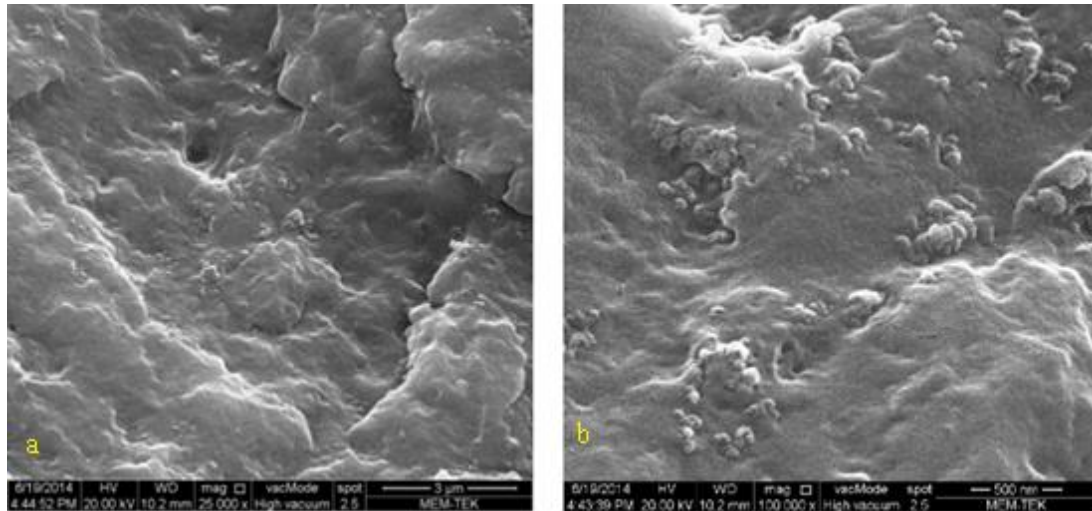


Figure 5.6 : SEM images of M6 (Minlon + 5wt.% CB + 5wt.% compatibilizer) with two different magnitudes; a)) 3µm, b) 500nm.

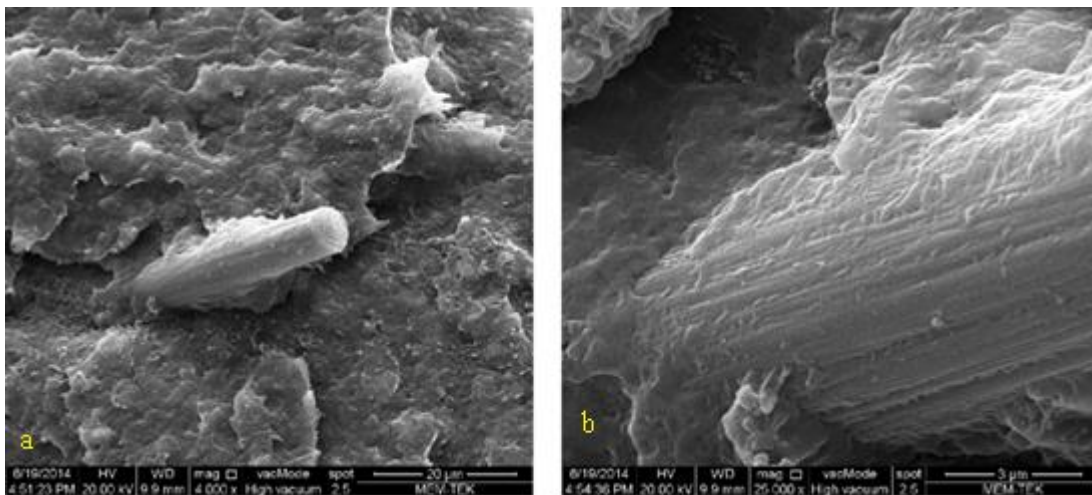


Figure 5.7 : SEM images of M7 (Minlon+4wt.% CF +1wt.% CB+ 5wt.% compatibilizer) with two different magnitudes; a)20 µm, b) 3µm.

The homogeneous dispersion of fillers (CNTs, CF, CB) in the polymer matrix is one of the most important requirements in achieving mechanical strength reinforcement because in-homogeneities can lead to structural defects in the composite material. The other issue that can be important is the type of compatibilizer. PP-g-MA used in this study .Among them MA-g-EVA, SEBS-g-MA and, PP-g-MA may be named but due to the price the PP-g-MA seems to be the best choice for this study. (HowardáEbron, 2004; Dasari et al., 2006; Pisharath et al., 2006; Lee et al., 2007) Comparing M1 and M3 which contains Minlon + 3% CNT and Minlon + 3% CNT + 2% compatibilizer respectively, it can be observed that adding compatibilizer helps to have less agglomerates and shows more uniform dispersion compared to

Minlon/MWCNTs without compatibilizer. The same result were obtained for other samples (Figure 5.4 to Figure 5.8).

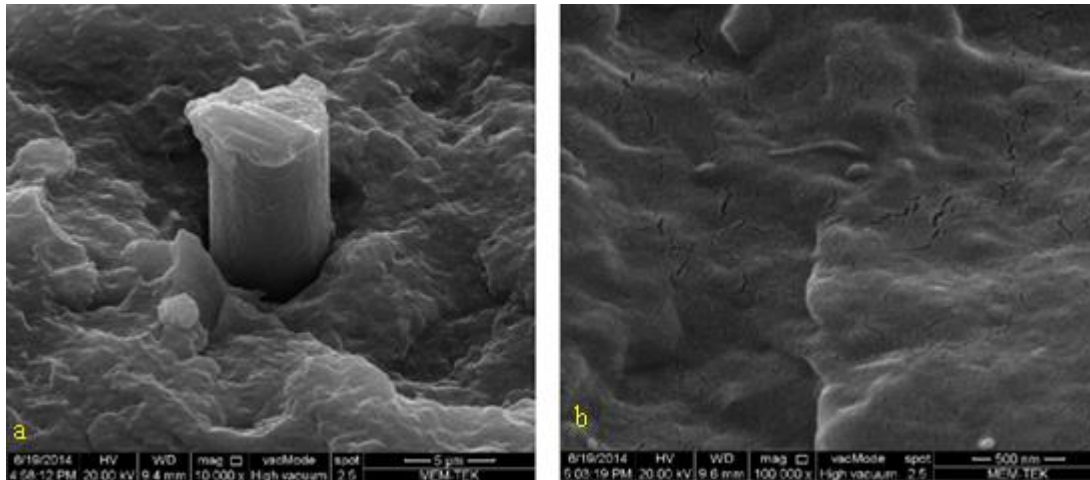


Figure 5.8 : SEM images of M8 (Minlon + 4wt.% CF + 0.5wt.% CB+ 0.5wt.% CNTs) with two different magnitudes; a) 5 μ m b)500nm.

5.3 Differential Scanning Calorimetry (DSC) Analysis

DSC graphs of PA 6,6, Minlon, Noryl and M4 shown respectively in Figure 5.9 to Figure 5.12. Before extrusion process, thermal properties of PA 6,6 without additives, PA 6,6 with additives (Minlon) and final product (M4), were investigated by a DSC (TA Q10) with the nitrogen flow rate of 50 ml/min between 0-400 °C. Melting was observed at about 260 °C(Figure 5.9) and the optimum temperature in which the extruder can work properly was determined as 260-280°C from the below measurements.

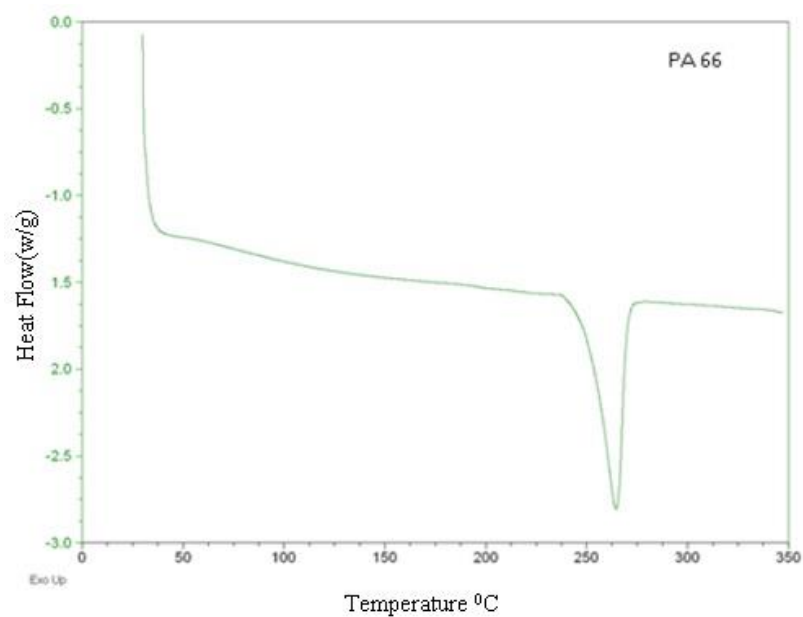


Figure 5.9: DSC curve of PA 66.

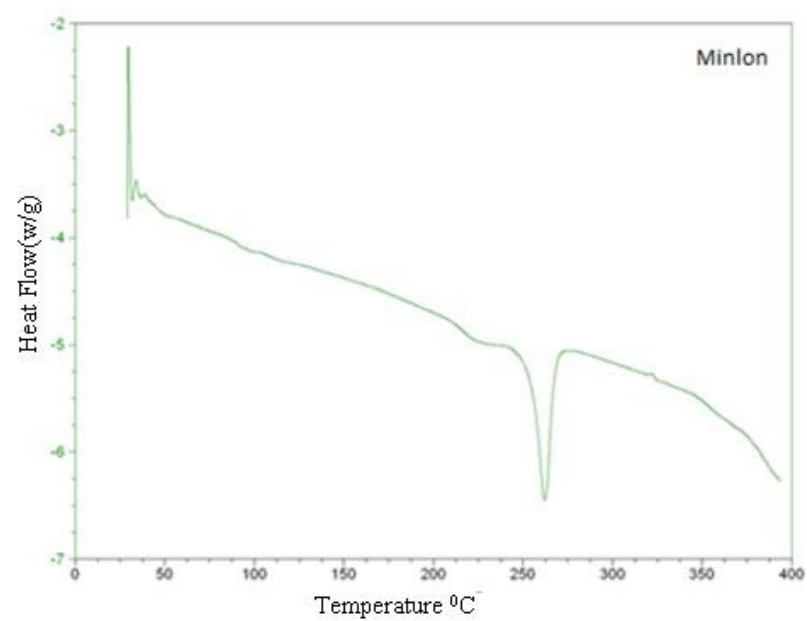


Figure 5.10: DSC curve of Minlon.

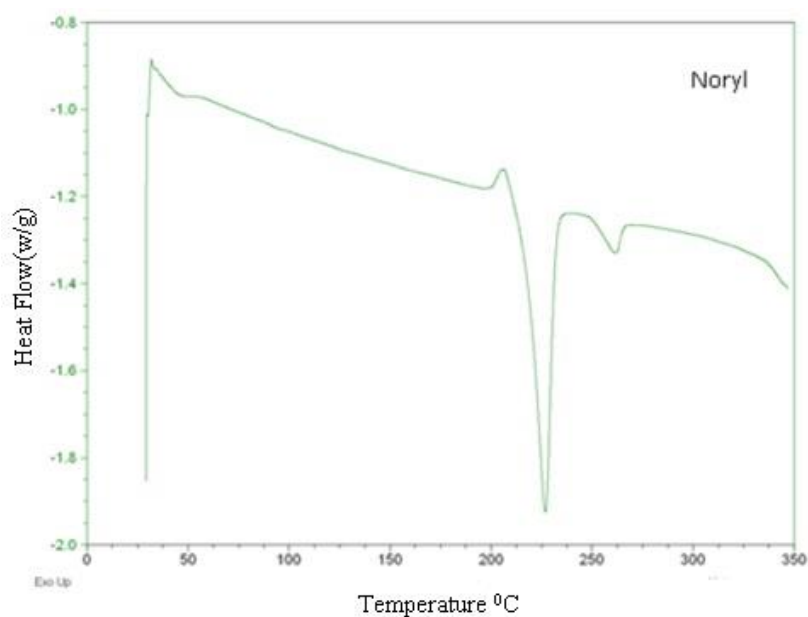


Figure 5.11: DSC curve of Noryl.

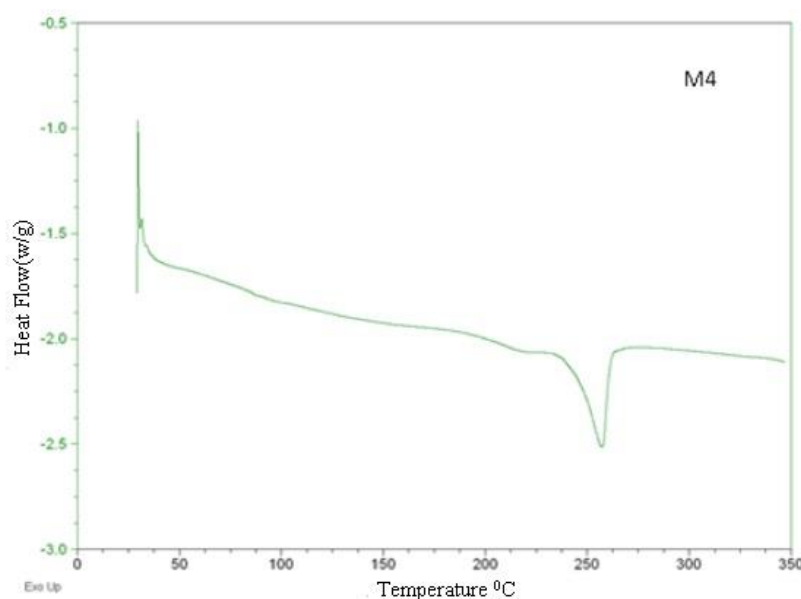


Figure 5.12: DSC curve of M4 (Minlon+5wt.%CF +5wt.% compatibilizer).

5.4 ATR-FTIR Measurements

FTIR spectra of pure PA 6,6, Minlon, Noryl, and M4, are shown in Figure 5.13. In PA 6,6, Minlon, and M4 composites 3297 , 3082 cm^{-1} peaks belong to -NH and C-N stretching. 2924 cm^{-1} shows C-H stretching and 1713 cm^{-1} is for amide group. 1634 , 1371 , and 1199 cm^{-1} show C=O , C-N-H and $\text{CH}_2\text{-NH}$ stretching respectively. Minlon and M4 ATR FTIR spectra have similar peaks, which indicate that after thermal

process, the structure of M4 has not undergone significant degradation and this shows that “temperature zones” and “screw speed” of extruder have been well adjusted.

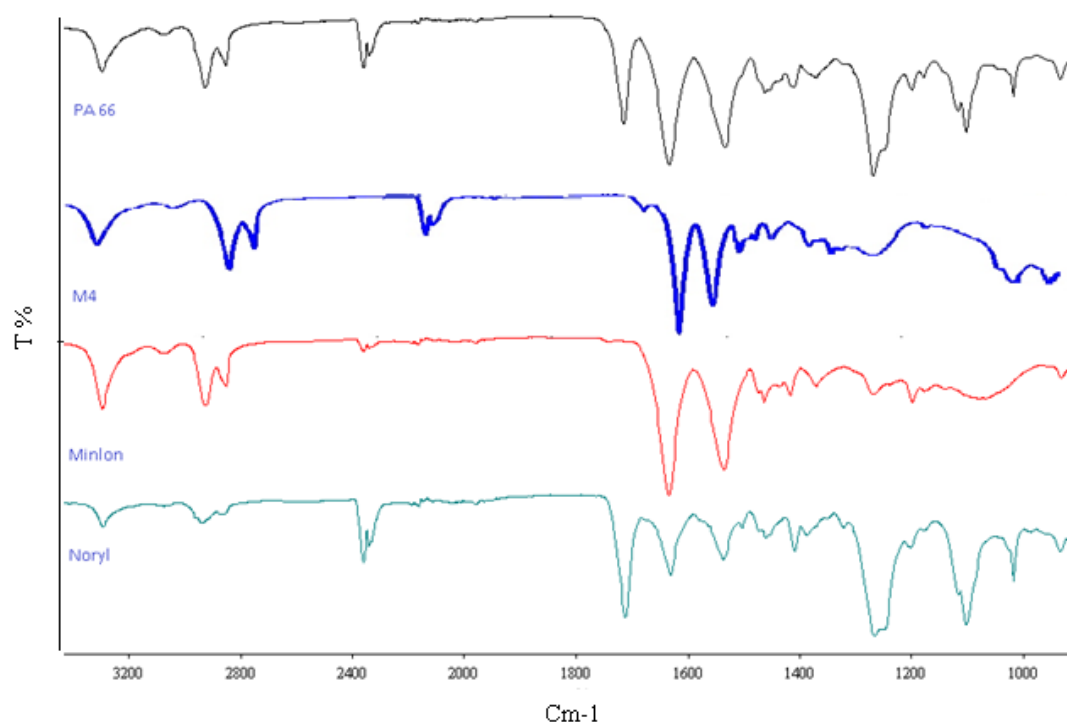


Figure 5.13 : FTIR curves for PA 6,6, M4, Minlon and Noryl.

5.5 Mechanical Properties

Tensile test have been done on the samples and reported in Table 5.2. Four samples of each composites formula were used each time for measuring the mechanical properties and for increasing the accuracy of data, the average of the data has been reported.

Table 5.2: Mechanical properties of composite samples.

Sample No.	Tensile stress MPa	Tensile strain %	Stress at break MPa	Elongation at break %	L ₀ mm	d ₀ cm	S ₀ mm ²
M1	40.92	59.49	37	62.6	20.00	0.241	4.56
M3	39.22	81.9	37.66	85.16	20.00	0.230	4.18
M4	52.27	14.77	48.33	16.43	20.00	0.197	3.05
M5	37.30	76.22	35	80.73	20.00	0.253	5.06
M6	31.81	72.03	30	75	20.00	0.202	3.22
M7	53.32	23.94	50	25.25	20.00	0.197	3.07
M8	48.55	16.58	45.5	18.37	20.00	0.206	3.34

By increasing amount of CB and CF in the matrix, some portions of polymer may be trapped by filler networks. Besides, polymer-filler interaction may reduce portion of polymer chains mobility due to the absorption of polymer segments to filler surface. Therefore, the polymer will face the rising of viscosity and modulus and tensile strength while elongation at break will be decreased. From Table 5.2 information, especially samples M4 and M5, it can be concluded that increasing CF is more effective than CB in enhancing tensile strength and decreasing elongation at break. This is because of greater strength of carbon fiber. These results were expected since polymer matrix can transfer the stress more easily to the filler with higher amount of aspect ratio and CF has a better reinforcement compared to CB. Other composites formulas have similar mechanical properties. Since the price of the final product for M4 sample was the lowest with the desired mechanical and electrical properties So M4 was chosen as optimum composite formulation that covers the requirements of the projects.

5.6 Hardness Tests

The aim of the test was to determine the hardness of the paint film based on TSH 3131G 4,5 and the results have been reported in Table 5.3.

Table 5.3 : Hardness test results for M4, Minlon and Noryl.

Part description	Hardness measurement result	Judgment
M4	HB	OK
Minlon	HB	OK
Noryl	HB	OK



Figure 5.14 : Hardness test.

Based on the information in Table 5.3 all samples have met the requirements and the hardness value of the film paint is HB.

5.7 Dropped Weight Impact Tests

The purpose of this analysis is to observe the wheel cap impact behavior by throwing weights based on the TIS 01202-00N08 7. Results for dropped weight impact test can be seen in Table 5.4 to Table 5.9.

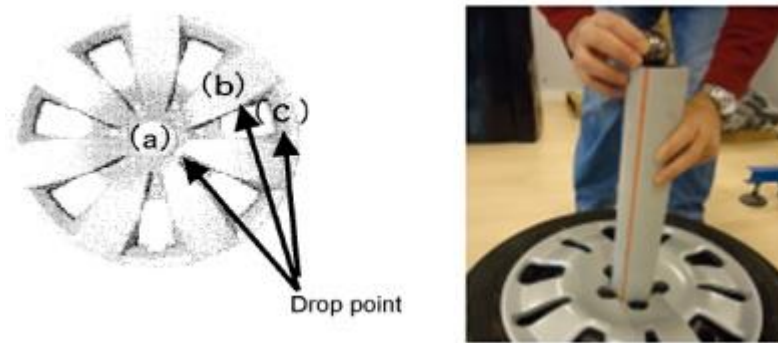


Figure 5.15 : Drop weight impact test.

Table 5.4 : Evaluation results of M4 when placed on plane.

Evaluation Results of M4 when placed on plane							
	Drop point	Number of round	Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall evaluation
a	Center of cap	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	
b	Spoke of portion	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	
c	Outer circumferential portion	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	

Table 5.5 : Evaluation results Minlon when placed on plane.

Evaluation Results of Minlon when placed on plane							
	Drop point	Number of round	Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall evaluation
a	Center of cap	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	
b	Spoke of portion	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	
c	Outer circumferential portion	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	

Table 5.6 : Evaluation results Noryl when placed on plane.

Evaluation Results of Noryl when placed on plane							
	Drop point	Number of round	Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall evaluation
a	Center of cap	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	
b	Spoke of portion	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	
c	Outer circumferential portion	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	

Table 5.7 : Evaluation results M4 when titled at 45°.

Evaluation Results of Minlon when tilted at 45°						
Drop point	Number of round	Flaw and scratch	Cracking and peeling of surface	Cracking and fracture	Judgment	Overall evaluation
a	Center of cap	First	OK	OK	OK	OK
		Second	OK	OK	OK	
		Third	OK	OK	OK	
b	Spoke of portion	First	OK	OK	OK	OK
		Second	OK	OK	OK	
		Third	OK	OK	OK	
c	Outer circumferential portion	First	OK	OK	OK	OK
		Second	OK	OK	OK	
		Third	OK	OK	OK	

Table 5.8 : Evaluation results Minlon when tilted at 45°.

Evaluation Results of Minlon when tilted at 45°						
Drop point	Number of round	Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall evaluation
a	Center of cap	First	OK	OK	OK	OK
		Second	OK	OK	OK	
		Third	OK	OK	OK	
b	Spoke of portion	First	OK	OK	OK	OK
		Second	OK	OK	OK	
		Third	OK	OK	OK	
c	Outer circumferential portion	First	OK	OK	OK	OK
		Second	OK	OK	OK	
		Third	OK	OK	OK	

Table 5.9 : Evaluation results Noryl when tilted at 45°.

Evaluation Results of Noryl when tilted at 45°							
	Drop point	Number of round	Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall evaluation
a	Center of cap	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	
b	Spoke of portion	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	
c	Outer circumference portion	First	OK	OK	OK	OK	OK
		Second	OK	OK	OK	OK	
		Third	OK	OK	OK	OK	

Based on the results in Table 5.4 to Table 5.9 cover wheels have met the requirements.

5.8 Drop impact tests

The purpose of this analysis is to check the wheel cap dropping effect in terms of fracture, scratch based on the TIS 01202-00N08 8 and Results have been reported in Table 5.10 to Table 5.15.

Table 5.10 : Evaluation results of M4 parts when placed at 120 cm (initial state).

Evaluation temperature	Dropping posture	Evaluation Results of M4 parts when placed at 120 cm (Initial State)				
		Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall
Height 120 cm @ 23°C	a	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	b	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	c	1 st	-	-	-	OK
		2 nd	-	-	-	OK

Table 5.11 : Evaluation results of Minlon parts when placed at 120 cm (initial state).

Evaluation temperature	Dropping posture	Evaluation Results of Minlon parts when placed at 120 cm (Initial State)				
		Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall
Height 120 cm @ 23°C	a	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	b	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	c	1 st	-	-	-	OK
		2 nd	-	-	-	OK

Table 5.12 : Evaluation results of Noryl parts when placed at 120 cm (initial state).

Evaluation Results of Noryl parts when placed at 120 cm (Initial State)						
Evaluation temperature	Dropping posture	Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall
Height 120 cm @ 23°C	a	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	b	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	c	1 st	-	-	-	OK
		2 nd	-	-	-	OK

Table 5.13 : Evaluation results of M4 parts when placed at 60 cm (after ageing).

Evaluation Results of M4 parts when placed at 60 cm (Initial State)						
Evaluation temperature	Dropping posture	Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall
Height 60 cm @ -40°C	a	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	b	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	c	1 st	-	-	-	OK
		2 nd	-	-	-	OK

Table 5.14 : Evaluation results of Minlon parts when placed at 60 cm (after ageing).

Evaluation temperature	Dropping posture	Evaluation Results of Minlon parts when placed at 60 cm (Initial State)				
		Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall
Height 60 cm @ -40°C	a	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	b	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	c	1 st	-	-	-	OK
		2 nd	-	-	-	OK

Table 5.15 : Evaluation results of Noryl parts when placed at 60 cm (after ageing).

Evaluation temperature	Dropping posture	Evaluation Results of Noryl parts when placed at 60 cm (Initial State)				
		Flaw and scratch	Cracking and peeling of surface treatment	Cracking and fracture	Judgment	Overall
Height 60 cm @ -40°C	a	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	b	1 st	-	-	-	OK
		2 nd	-	-	-	OK
	c	1 st	-	-	-	OK
		2 nd	-	-	-	OK

Based on the information mentioned hubcaps have met the requirements.

5.9 Adhesive Resistance (Cross-Cut) Tests



Figure 5.16 : Adhesive resistance (Cross-Cut) test.

Table 5.16 : Adhesive resistance (Cross-Cut) test result for M4, minlon and nylon.

Part description	Peeling	Percentage of peeling
M4	No peeling is observed	0/100
Minlon	No peeling is observed	0/100
Noryl	No peeling is observed	0/100

The test was performed on the hubcaps and they met the requirements.

Cost of composites formulae

The price of composites per a kilo have been calculated and reported in Table 5.17.

Table 5.17 : Average price of composites per a kilo .

No	PA66 (gr)	Compatibilizer (gr)	CF (gr)	CNT (gr)	CB (gr)	Price (€/kg)
M1	97	-	-	3	-	73.5
M3	95	2	-	3	-	73.56
M3	95	2	-	3	-	73.56
M4	90	5	5	-	-	8.07
M5	94	5	-	1	-	26.94
M6	90	5	-	-	5	34.74
M7	89	5	4	-	1	19.64
M8	89	5	4	0,5	0,5	28.22

6. CONCLUSION

The composites were prepared by compounding of PA66 with different types of carbon (CB, CF, and CNT) with a twin-screw extruder. The FTIR spectra results showed that the composites have not undergone degradation. This showed the temperature zones of extruder have been well adjusted.

The electrical conductivity of composites had been investigated. Based on the electrical conductivity results, it can be concluded that even at lower concentration, CNT is more effective in decreasing electrical resistivity of composite than CB and CF.

Results obtained from the mechanical properties of the composites suggest that composites obtained by using CNT have more stiffness compared to one with CB but lower than composite filled with CF. On the other hand, elongation at break for CNT filled composites is lower compared to CB filled composites and higher than CF filled composites.

As a result, based on the mechanical, electrical properties and cost of composites, M4 (Minlon with 5wt. % CF and 5wt. % compatibilizer) was determined as a final composite for the requirement of wheel cover that suitable for EP. M4 was used to produced wheel cover and then these product was electrostatically painted and compared with the cover obtained from Minlon which had been painted with wet painting. The common tests such as hardness, cross cut, dropped weight impact, drop impact were applied in order to check the properties of final product and all tests showed that the M4 was matched with the requirements.

In conclusion, a conductive composite material based on PA and carbon material was obtained for automotive industry, which was suitable for electrostatic painting and had better mechanical properties compared to commercially available one.

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8. CURRICULUM VITAE

Amirhossein Nasri

nasri@itu.edu.tr +90 538 5463329

Home Address: Unit 1, No. 5, Plato APT. ,

Sahindler Skg., Paşa Mh., Ferikoy Mh., Istanbul, Turkey



Education

- **Master of Science in Polymer Science & Technology (GPA 3.31)**
Istanbul Technical University (ITU), Turkey (2013-2015)
Thesis title: Conductive polyamide with carbon black (CB), carbon fiber (CF) and carbon nanotube (CNT) for electrostatic painting
- **Bachelor of Science in Polymer science and Engineering (top 30%)**
Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran (2005-2011)
BSc graduation project: Physical- Mechanical properties of thermoplastic elastomers (TPEs) based on EPDM/PP.

Areas of Academic Interests

- Extrusion and Injection (processing and properties)
- Mixing and Compounding Plastics and Elastomers (Processing and properties)
- Thermoplastic elastomers (TPE) (Processing and properties)
- Composite and Nano composite (Processing and properties)

Patent

- New conductive polyamide 6,6 composite used in automotive industry (as hubcap). This CF filled composite was produced by extrusion method. (with the cooperation of ITU university and Mecaplast company)
Patent No. (Submitted in Turkey)

Laboratory and Computer Skills

- ATR-FTIR
- TEM, SEM
- DMA, TGA and DSC
- Two-Roll Mill, Injection, single and twin-screw Extruder and Internal Batch Mixer
- Microsoft Office, Windows XP & 7 , Adobe Acrobat, Familiar with AutoCAD and Photoshop
- Familiar with Pascal, Matlab , Gaussian and Chem office

Research & Teaching Experience

- **Research Assistant:** under supervision of Professor Esma Sezer, work on producing a conductive polyamide compound (CPAC) formula in order to use as raw material to produce hubcap (wheel cover) which is suitable for electrostatic painting (EP) system. (ITU university, Sep 2013-Oct 2014)
- **Teaching assistant:** giving lecture for “course recitation” sessions on physical chemistry (undergrad students) and helping students to solve problems, taking exams - Istanbul Technical University (Fall 2014 semester).

Work Experience

- Working in Atbin factory as a QC in Iran, fall 2011: one of the most successful manufacturers in the field of design and construction of industrial and laboratory furnaces
- Working in RADHA engineering Consultant Company as a junior process engineer, spring 2011: one of the biggest consultant companies in the oil, gas and petrochemical industry

Academic accomplishments and Honors

- One-year scholarship from SAN-TEZ
- Ranked 840th among 450,000 Participants in Iran Bachelors' Entrance Exam for engineering known as “KONKOOR”

Language

- English : TOEFL: Total : 84 (Reading 18 – Listening 26 – Speaking 20 – Writing 20)
- GRE
- The medium of instruction in Istanbul Technical University(Polymer science and technology program) is English.