



**REPUBLIC OF TURKEY
UNIVERSITY OF YALOVA
INSTITUTE OF SCIENCE**

**DESIGN AND FABRICATION OF PRESSURE SENSORS FROM
THERMOPLASTIC ELASTOMER BASED NANOCOMPOSITES**

**MASTER' S THESIS
Ayşe TURGUT
175101001**

Polymer Engineering Department

Polymer Engineering Programme

Advisor: Assist.Prof.Dr. Hatice Aylin KARAHAN TOPRAKÇI

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Ayşe TURGUT, a M.Sc. student of University of YALOVA Institute of Science with student ID number **175101001**, defended the thesis entitled “**DESIGN AND FABRICATION OF PRESSURE SENSORS FROM THERMOPLASTIC ELASTOMER BASED NANOCOMPOSITES**”, which she prepared after fulfilling the requirements specified in the associated legislations, in front of the jury whose signatures are below and was found to be successful with unanimity/majority.

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(Accept/Reject)

Advisor :

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Committee Members:

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PREFACE

I want to dedicate the study;

To my lovely family

To my parents, Münüre and Turgut TURGUT, who live without denying anything from their children and taught us how to be a person without losing human values.

To my sisters, Pınar, Yudum and Zümrüt TURGUT whom I grew up with and left tough sleddings together.

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ABBREVIATIONS

AFM	: Atomic Force Microscope
CB	: Carbon Black
CNF	: Carbon Nanofiber
CNT	: Carbon Nanotube
CVD	: Chemical Vapor Deposition
CA	: Curing Agent
ESEM	: Environmental Scanning Electron Microscope
FESEM	: Field Emission Scanning Electron Microscope
GF	: Gauge Factor
GO	: Graphene Oxide
GCFS	: Graphene-Coated Foams
VGCNFs	: Vapor Growth Carbon Nanofibers
HDPE	: High Density Polyethylene
HOPG	: Highly Ordered Pyrolytic Graphite
HI	: Hydrogen Iodide
ICPs	: Intrinsically Conducting Polymers
LBL	: Layer by Layer
MLG	: Multilayer Graphene Nanoplatelets
MWNTs	: Multi-walled Nanotubes
NR	: Natural Rubber
NBR	: Acrylonitrile Butadiene Rubber
PDMS	: Polydimethylsiloxane
PEDOT	: Poly(3,4-ethylenedioxythiophene)
PVA	: Poly(vinyl alcohol)
PVDF	: Poly(vinylidene fluoride)
PAN	: Polyacrylonitrile
PANI	: Polyaniline
PBI	: Polybenzimidazole
PEO	: Polyethyleneoxide
PI	: Polyimide
PPy	: Polypyrrole
PTh	: Polythiophene
PU	: Polyurethane
PGS	: Polyurethane containing Graphene Sponge
PUS	: Polyurethane Sponge
PP	: Prepolymer
PSA	: Pressure Sensitive Array
rGO	: Reduced Graphene Oxide
SEM	: Styrene-b-ethylene-ran-butylene-b-styrene
SR	: Silicon Rubber
SEBS	: Styrene-b-ethylene-ran-butylene-b-styrene
THF	: Tetrahydrofuran



TPE : Thermoplastic Elastomer
TEM : Transmission Electron Microscope
VGCNFs : Vapor Grown Carbon Nanofibers





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DESIGN AND FABRICATION OF PRESSURE SENSORS FROM THERMOPLASTIC ELASTOMER BASED NANOCOMPOSITES

ABSTRACT

Polymers are one of the most commonly used materials regardless of the application area because of their tunable properties such as electrical, mechanical, thermal, and optical. Most of the commercial polymers are electrically insulating, on the other hand, it does not restrict the usage of these insulating polymers in conductive systems. With the addition of conductive fillers such as carbon black (CB), carbon nanofibers (CNFs), carbon nanotubes (CNTs), graphene and their derivatives, conductive polymer nanocomposites can be produced. These are the most common carbon-based conductive nanofillers with different conductivity values. In the study, to obtain tunable electrical conductance CB, vapor grown CNFs and reduced graphene oxide were used with thermoplastic elastomer matrix in order to fabricate flexible pressure sensors. With the morphological, electrical, and electromechanical characterization, the working range of the conductive polymer nanocomposites was determined.

Key Words: Conductive polymer nanocomposites; Carbon black; Carbon nanofiber; Reduced graphene oxide; Piezoresistive pressure sensors; Flexible electronics



TERMOPLASTİK ELASTOMER ESASLI NANOKOMPOZİTLERDEN BASINÇ SENSÖRLERİNİN TASARIM ve ÜRETİMİ

ÖZET

Polimerler uygulama alanı fark etmeksizin yaygın olarak kullanılan malzemelerdir. Bunun en önemli sebebi ise ayarlanabilen elektriksel, mekanik, termal ve optik özelliklere sahip olmalarıdır. Ticari olarak kullanılan polimerlerin çoğu elektriksel olarak yalıtkan özellik göstermektedir. Fakat, bu özelliğe sahip olmaları iletken sistemlerde kullanımlarını sınırlandırmamaktadır. Karbon siyahı, karbon nanolifleri, karbon nanotüp, grafen ve bunların türevleri gibi iletken dolgu maddelerinin ilavesi ile iletken polimer nanokompozitler üretilebilmektedir. Bu dolgu maddeleri farklı iletkenliklere sahip en çok kullanılan karbon esaslı malzemelerdir. Çalışmada, esnek basınç sensörleri üretmek amacı ile elektriksel iletkenlikleri ayarlanabilen, karbon siyahı, buhar biriktirme yöntemi ile üretilmiş karbon nanolifleri ve indirgenmiş grafen oksit dolgu malzemeleri ve termoplastik elastomer bir matris kullanılmıştır. Üretilen iletken nanokompozit malzemelerinin morfolojik, elektriksel ve elektromekanik karakterizasyonu yapılarak etkin çalışma aralıkları belirlenmiştir.

Anahtar Kelimeler: İletken polimer nanokompozitler; Karbon siyahı; Karbon nanofiber; İndirgenmiş grafen oksit; Piezoresistif basınç sensorleri; Esnek elektronikler



1. INTRODUCTION

In recent years, flexible electronics created an attractive field in material science with widespread applications. Sensors, energy harvesting and data storage are the most common applications of flexible electronics. In the flexible electronics field, polymers are mostly used because of their superior properties such as being flexible, light weight, low cost with high resilience, dimensional stability, easy processing and tunable electrical and mechanical properties. In terms of electrical conductivity, polymers can be classified as intrinsically conducting polymers (ICPs) such as polypyrrole (PPy), polyaniline (PANI) and insulating polymers. Most of the commercial polymers are electrically insulating and this property provides usage of the polymers in insulating applications. Elastomers and thermoplastic elastomers (TPEs) exhibit appropriate properties to be used in flexible electronics. Besides all these, with the addition of conductive fillers, these polymers can show electrical conductivity. The most commonly used conductive fillers in flexible electronics are the carbon black (CB), carbon nanofibers (CNFs), carbon nanotubes (CNTs), graphene and its derivatives. All these carbon based fillers have different conductance values. With the combination of insulating elastomeric polymer matrix and conductive filler, electrically conductive polymer nanocomposites with high mechanical properties can be produced. The electrical response of the materials can show differences depending on basically properties of components. On the other hand, if the electrical response of the material change with a stimuli such as pressure, strain or bending, these material exhibit piezoresistive response.

In the study, it was aimed to produce electrically conductive polymer nanocomposites and investigate their morphological, electrical and electromechanical properties. Another aim of the present study is to design and fabricate thermoplastic elastomer based, flexible piezoresistive pressure sensors with various range of response and sensitivity.



2. LITERATURE

2.1. Sensors

A sensor is specified as a material that transforms a stimulus to the electrical signal (Figure 2.1) [1, 2]. The stimuli term express the property, condition or quantity of the input physical data. The output electrical signal can be modified, amplified and channeled by a proper system and the signal format can be in the form of charge, voltage and current [2].

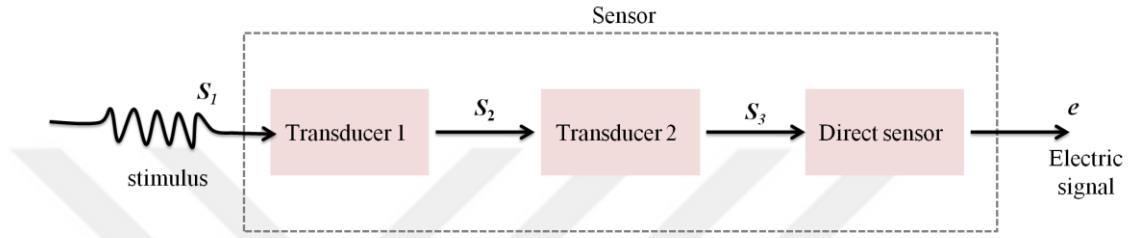


Figure 2.1 Schematic illustration of the sensor (The S_1 , S_2 and S_3 are the different energy types) [2]

Depending on the mechanism of the sensors, it processes the information or data related with the environment to perform its specific tasks [3]. The task of the sensor specifies its application areas. There are many sensor types that have been designed and used for many years such as capacitive, inductive, chemical, optical, piezoelectric and piezoresistive sensors. In this section, we will only focus on the piezoresistive sensors in order to be parallel with the experimental part.

2.1.1. Piezoresistive Sensors

Piezoresistive sensors exhibit change in resistance when the material is deformed. The materials used for piezoresistive sensors should be conductive or semiconductive. Depending on the shape, rigidity and flexibility of the material deformation causes to change in dimensions (length, diameter, thickness etc.) and resistance. Generally, semiconductor materials that show high sensitivity are preferred as a sensing material. Silicon is the most commonly used in piezoresistive sensors. On the other hand, elastomers and thermoplastic elastomer based conductive composites also exhibit piezoresistive behavior with the addition of conductive fillers [1, 3, 4].

Piezoresistive sensors can be used in order to sense gas [5, 6], temperature [7-9], or mechanical stimuli [10-12]. The sensors that are used in order to determine the

mechanical stimuli are called electromechanical piezoresistive sensors. If the output mechanical stimulus is a force, piezoresistive sensor can be classified as bending [13-15], strain [11, 16] and pressure sensors [17-19].

In terms of materials that can be used as piezoresistive materials, conductive elastomers and thermoplastic elastomers are preferred due to their high flexibility, high strain and compression deformation ability and good resilience. With the addition of conductive fillers, these insulating polymers can be turned to conductive materials. The conductance levels of the materials depend on the filler concentration, the mutual distance of fillers. In addition to these parameters, the stimulus also can affect the conductance of the material. The electrical resistance of the material can exhibit differences in the case of strain or pressure is applied. With the effect of compression or strain, the resistance shows different characters as a negative and positive piezoresistive response. The negative piezoresistive response is defined as the decrease in resistance under applied strain or pressure[20]. With the effect of stimuli, filler-filler distance decreases. This decrease leads to the formation of new conductive networks and resistance decreases. On the other hand, the positive piezoresistive response is defined as the increase in resistance with the effect of stimuli[21]. This response shows that the filler-filler distance increases and the conductive network is destructed by the effect of the stimuli [3].

The most important property for a sensor is that the sensor must exhibit meaningful (linear) character in its working range. In addition to the linear character, the sensor should show no or minimum hysteresis and creep and exhibit relatively sensitive and stable, repeatable response with high accuracy for long cycle times. Also the sensor should be suitable for reproduction with low cost [3].

2.1.1.1. Piezoresistive strain sensors

Piezoresistive strain sensors are used to detect the strain level by monitoring electrical signal. Resistance of the material changes with the strain effect. The piezoresistive strain sensors that are based on elastomeric matrix can be used in the field of wearable health monitoring systems due to their high flexibility and easy deformability [22-25]. For the production of piezoresistive strain sensors many filler can be used as graphene and derivatives [26-29], carbon black (CB) [30, 31], carbon nanofibers (CNFs) [16, 32], carbon nanotubes (CNTs) [21, 33, 34], metal particles [35-38] etc.

2.1.1.2. Piezoresistive pressure sensors

Piezoresistive pressure sensors are used to detect the pressure level or deformation ratio by monitoring the electrical signal. The resistance of the sensor changes with the applied pressure. The stimulus is the pressure and it affects the resistance that is the output response of the system. Pressure sensor can be used in many areas such as tactile skin sensors [39-41], pulse monitoring [42-44] and speech recognition [17]. For the production of piezoresistive pressure sensors many fillers can be used as graphene and derivatives [45-50], carbon black (CB) [47, 51-53], carbon nanofibers (CNFs) [18, 54], carbon nanotubes (CNTs) [55-57] and metal particles [20, 58-61].

2.2. Conductive Polymers and Conductive Polymer Composites

Polymer nanocomposites are materials those consist of a polymeric matrix and nano-sized fillers. For the production of polymeric nanocomposites many filler types can be used. These fillers can be natural or synthesized materials including metal, clay, ceramic and carbon based fillers. With the addition of nanofillers, electrical, thermal and mechanical properties are enhanced [62-66]. Depending on the application and the required properties; filler type changes. To enhance the electrical properties of polymers, the most commonly used nanomaterials are carbonaceous ones including graphene and derivatives [67-72], carbon black (CB) [73-77], carbon nanofibers (CNFs) [78-81], carbon nanotubes (CNTs) [82-85], etc.

Materials can be classified based on their conductivity as insulators (10^{-20} – 10^6 S/cm), semi-conductors (10^{-4} – 10^2 S/cm) and conductors (10^4 – 10^6 S/cm) [86]. In addition, depending on the electrical properties, polymers can be separated into two subclasses as intrinsically conducting polymers (ICPs) and insulating polymers [87, 88]. ICPs are organic polymers with the ability of conducting electrical current because of the conjugated double bonds in the molecular chains (Figure 2.2). With the delocalization of p-electrons on the conjugated bonds, current is conducted [89]. The intrinsically conducting polymers are obtained by chemical or electrochemical processes [89].

ICPS can be produced by different technics. The chemical synthesis for obtaining conducting polymers is based on the polymerization that provides large scale manufacturing even though the synthesis process is more complicated [88]. The most commonly produced ICPs are polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT) [87, 89, 90].

On the other hand, electrochemical synthesis is based on the polymerization under electrochemical conditions. In this method, ICP is deposited on a substrate by the effect of electrical energy and thickness can be controlled. The electromechanical synthesis is a very simple, cleaner, more effective process and also appropriate for manufacturing [65, 91-95].

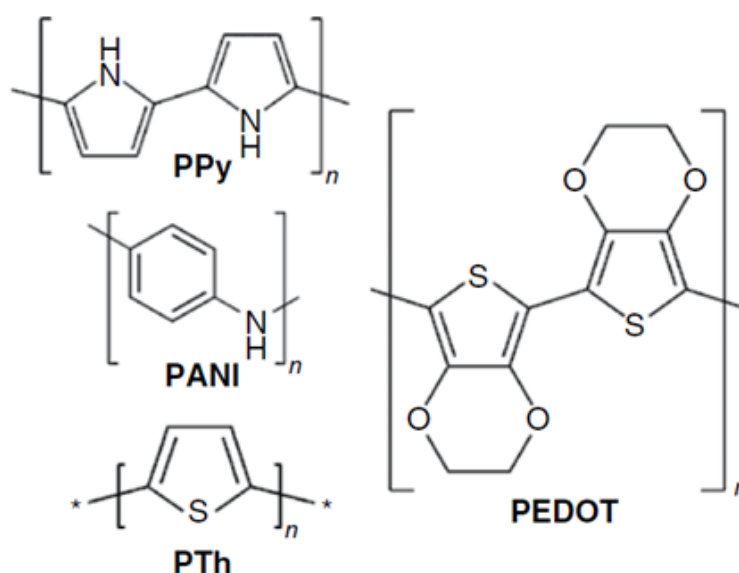


Figure 2.2 Chemical structure of some common conducting polymers [89]

Since polymers show high electrical resistivity, the electrical response can be tuned with the addition of electrically conductive nanomaterials. With the addition of sufficient amount of conductive fillers into the insulating matrix, electrically conductive polymer nanocomposites can be produced. As mentioned before, graphene [48, 49, 96, 97], graphene oxide (GO) [49, 98], reduced graphene oxide (rGO) [99], carbon black (CB) [44, 53, 100, 101], carbon nanofibers (CNFs) [18, 54] carbon nanotubes (CNTs) [102-104] are the mostly used carbon based fillers [89]. Resistivity of the polymer nanocomposite decreases with the formation of conductive network through the nanocomposite [89, 105].

For the production of electrically conductive polymer composites; melt processing [106-108], solution casting [109, 110] and in situ polymerization [111] methods can be used [89]. Melt processing is based on mixing conductive filler into molten polymer at high temperatures under shear and pressure. It is commonly used in polymer industry especially for large scale manufacturing [112, 113]. The solution casting process is carried out with an appropriate solvent. Polymer is dissolved in the solvent and conductive filler is mixed into the polymer solution. After the evaporation of solvent, polymer nanocomposite is obtained [16, 114].

The electrical response of the polymer nanocomposite changes depending on the filler concentration. There is a critical concentration for each polymer matrix that resistivity changes drastically and the material becomes more conductive. The filler concentration range that shows a drastic change in resistivity is expressed as the percolation threshold and it is clarified by percolation theory [16, 114, 115].

Factors that affect the electrical properties of conductive polymer composites:

- Polymer type (thermoplastic, thermoset, elastomer, rubber) [16, 114]
- Electrical properties of polymer (intrinsically conducting polymers, insulating polymers) [16, 82]
- Physical and morphological properties of insulating polymeric matrix (molecular weight, surface tension, viscosity, crystallinity) [16, 114, 116, 117]
- Grade of conductive filler [70, 85, 118]

- Physical and morphological properties of filler (geometrical shape, type, size, aspect ratio, porosity, surface area) [82, 119]
- Concentration of filler in the polymer matrix (insulating, percolation, saturation) [16, 114, 116-118]
- Morphological properties of conductive polymer nanocomposite (dispersion and alignment of filler into matrix, interface between filler and polymer) [16, 77, 82, 116, 117, 120]
- Processing type and conditions (melt processing, solution casting, latex technology, in situ polymerization, solubility parameter of solvent, amount of solvent, mixing type, processing time, temperature, and pressure) [16, 82, 114, 121]

The percolation theory explains the conductivity of the composite material as a function of filler concentration. The electrical response changes depending on the alignment, interactions and concentration of the conductive fillers [115]. When the filler concentration is low in the composite, resistivity of the system is close to insulating matrix. Since the fillers are highly separated from each other, composite presents insulating character. With the increase in filler concentration, fillers create island like structures in the matrix and resistivity decreases. This region is also called as insulating region. After a critical filler concentration, the resistivity shows a drastic decrease by few orders of magnitude and this region is called as percolation region. Through the composite, conductive network formation comprises. Since the electrical charge can easily be transferred through the conductive networks, the electrical character of the system can be evaluated as conductors [122-124]. Above the percolation, the resistivity of composite is not affected by the increase in filler concentration and saturation region is observed. The fillers create 2 or 3D network structure in the polymeric matrix and then material reaches its maximum conductivity values. Although percolation behavior is almost the same for both nano and micro composites; as expected the percolation threshold is observed at relatively lower filler concentrations for nanocomposites [125-133].

2.2.1. Percolation Theory

The percolation theory can be expressed by the following equations **(Eq.1)**:

$$\sigma = \sigma_1(f - f_c)^\alpha \quad (1)$$

In the percolation theory, f_c is defined as percolation threshold, f is the filler volume fraction, σ represents the polymer nanocomposite conductivity, conductivity of filler (σ_1) [115, 134].

In the case of $f > f_c$, filler concentration is above the percolation threshold and conductive network is already formed throughout the matrix. The conductivity of polymer nanocomposite, σ , can be calculated by using f , f_c and the σ_1 as given in Eq.1. Critical exponent of the system is expressed as α and it changes between 1.1-1.3 for 2D and 1.6-2.0 for a 3D network systems. The conductivity of the nanocomposite is calculated as **(Eq.2)**:

$$\sigma \approx \sigma_2(f_c - f)^{-\beta} \quad (2)$$

If the $f < f_c$, in other words concentration of filler in the matrix is below the percolation threshold; conductivity of matrix (σ_2) is used to calculate the critical exponent (β) of the composite system **(Eq.2)**. β can be found between 1.1-1.3 for 2D and 0.7-1.0 for 3D system.

In the last case, $|f - f_c| \rightarrow 0$, the transition regions of first and second case, the conductivity of nanocomposite is expressed as **(Eq.3)**:

$$\alpha \propto \alpha_2^\gamma \alpha_1^{1-\gamma} \quad (3)$$

And $\gamma = \alpha/(\alpha + \beta)$. These calculations are simply express the conductivity of nanocomposites [115, 134].

2.3. Carbon Black Filled Elastomeric Piezoresistive Pressure Sensors

2.3.1. Carbon Black

Carbon black (CB) is one of the most common electrically conductive materials in the world with conductivity in the range of 10^{-2} to 10^1 S/cm. By using CB, electrically conductive polymer nanocomposites can be produced [17, 47, 101, 135, 136]. Although there are various types of CB in the market, in the case of conductive polymer composite production, the most important point is the amount of CB incorporated into polymeric matrix. In other words, it is expected to reach high conductivity values at low CB concentrations, the lower percolation threshold is preferred. Since amount of CB also affects the processing and cost of the material, electrically conductive special CB grades are preferred instead of conventional CB grades [74].

The electrical conductivity is provided by the formation of conductive network through the polymeric matrix. In a CB filled composite, the interactions between CB aggregates create networks and depending on the CB concentration, conductivity of the composite changes. In here, the crucial point is the structure of CB such as particle size, surface area and void volume because the percolation behavior is directly affected by the CB morphology. To obtain conductivity at low percolation threshold and to provide stable conductive network, high structure CB is one of the most used CB grades [74].

The electrical conductivity of the CB increases with the graphitic character of the structure. Graphitic layers are arranged in the form of parallel stacks in carbon atoms. The primary carbon particles consist of turbostratic or graphitic domains. The most important structural differences observed in conductive carbon black are that the conductive carbon black is formed by spherical primary carbon particles. Their average diameter is in the range of nanometers to micrometers [74, 118].

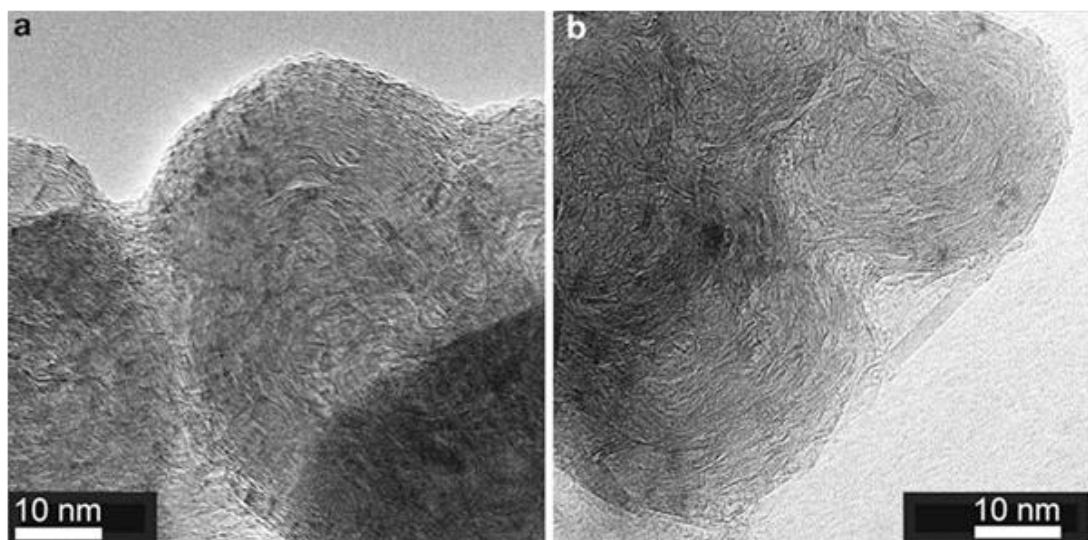


Figure 2.3 High resolution TEM images of primary CB particles for a) ENSACO® 250G and b) acetylene black

Since CBs are nanoparticles, the high level of interaction between particles may lead to formation of strong covalent bonds between carbon particles as shown in Figure 2.3 and they appear as fused. As a consequence of that, particles show the tendency to create coalescent units and branched morphology as shown in Figure 2.3 and 2.4. These branches form the aggregates and agglomerates by the effects of physical interactions. As given in Figure 2.4 while single CB particle's size can be around 20-40 nm, the aggregates and agglomerates can be in the size of couple of hundred nanometers (Figure 2.4a, b) [74].

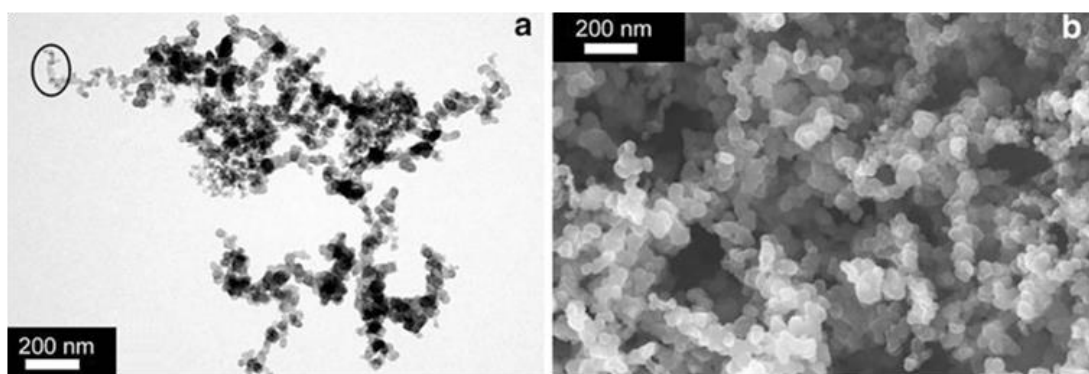


Figure 2.4 The a) TEM and b) SEM images of carbon black particles [74]

This special agglomerated structure leads to formation of the high void volume CB structure. The void volume is affected by the shape, size, fraction of the primary CB and CB agglomerations in the total volume. For CBs, high porosity is an indication of high surface area and high conductivity [137]. Because of the higher porosity, the density of the surface features increases and contact resistance between the particles decreases as a result of that conductivity of CB increases. In other words, higher the surface area, higher the conductivity [74, 136, 138-140].

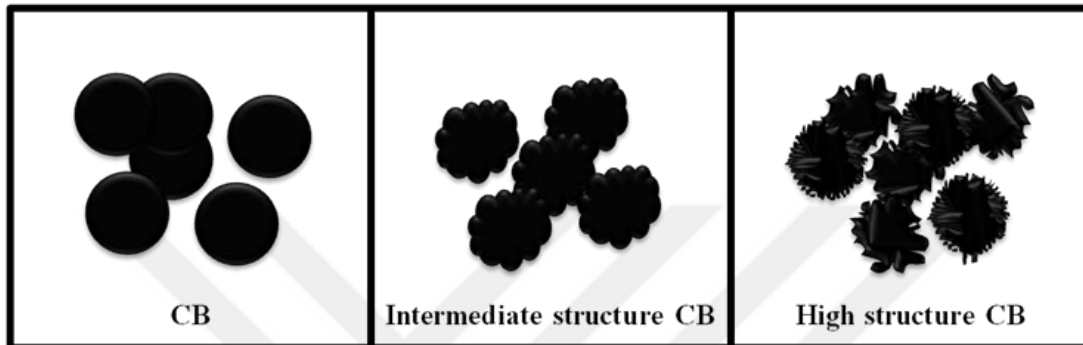


Figure 2.5 Carbon black particles with different morphological structure [117]

2.3.2. Production of Carbon Black

Carbon black (CB) is a one of the most commonly used material because of its superior properties. It is used for conductivity, reinforcement, and pigmentation. Chemically inert CB is generally found in the form of fluffy powder with high surface area. Depending on the processing type and conditions, particle size is ranging from nanometers to micrometers [141].

For the large scale manufacturing of CB, there are many processes as [138, 141]:

- Oil furnace black process,
- Gas Furnace Black Process
- Channel Black (Gas Black/ Impingement) Process,
- Thermal Black Process,
- Acetylene Black Process,
- Lampblack Process,
- Carbon Black Formed as Byproduct

From each processing types different CB grades can be produced. The production principle of CB is based on combustion of gaseous or liquid hydrocarbons under desired conditions [138]. Carbon black can be produced by thermal decomposition of hydrocarbons, processing with (oxidative) and without oxygen (oxygen free) [142, 143]. The most important part in manufacturing processes is the generation of primary CB with high degree of branched aggregates [74].

2.3.2.1. Oil furnace black process

The oil furnace black process is basically based on the oxidative decomposition of the hydrocarbon fuel and residual aromatic oils. Today, oil furnace black is one of the most common technics used for CB manufacturing since it has high yield with relatively low cost. In addition to these, most of the CB grades can be produced with this process because process parameters are tunable and any CB structure can be obtained easily [74, 138, 141].

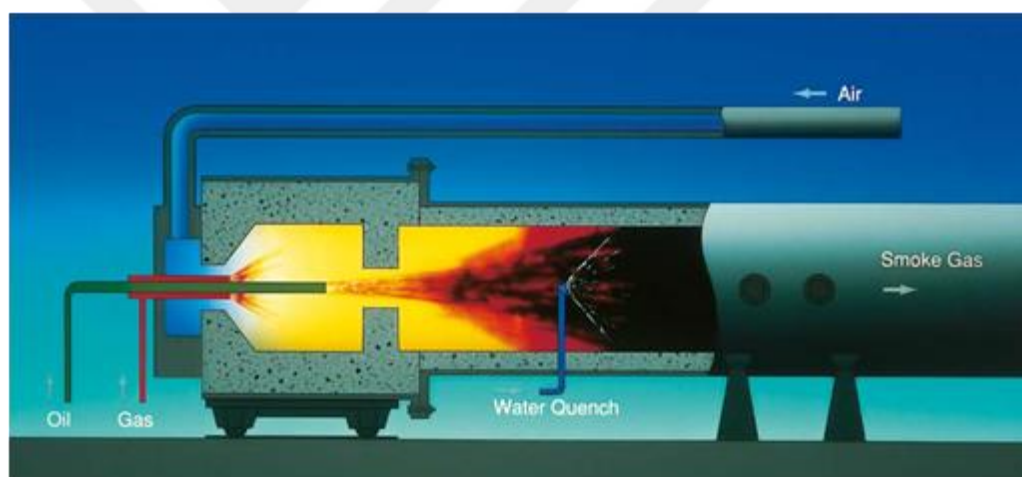


Figure 2.6 CB production by using furnace black process [144]

As shown in Figure 2.6, the process is carried out in a closed reactor and it is a continuous process. Air is sent in by an air blower to create turbulent flow and also oil and other combustion gases are sent into the reactor. Air is preheated in order to make combustion easier. Oil is sprayed through the combustion gas stream. The required temperature for the formation of CB is approximately in the range of 1400 to 1800 °C [74, 138, 141].

For the quenching of the CB particles, water is sprayed through the gas stream. For the filtration, more water is used to cool stream gas. In the filtration part, undesired particles and materials are separated from tail gas including water vapor, hydrogen, carbon dioxide, carbon monoxide, nitrogen [74, 138, 141].



Figure 2.7 Carbon black in the form of a) wet pelletized, b) dry pelletized, c) powder [144]

The filtrated CB powder is mixed with water in a pin mixer to form wet pelletized CB granules (Figure 2.7a). In the next step, the granules are dried in rotary dryers. The dried CB powder can be packaged (Figure 2.7b, c) [74, 138, 141].

2.3.2.2. Gas furnace black process (historic)

Furnace black process basically classified as gas furnace and oil furnace process. In the gas furnace black process, unlike the oil furnace black process, gaseous hydrocarbons such as natural gas were used as a raw material. With the oxidative decomposition of natural gas, CB was formed with large particles [138].

2.3.2.3. Channel black (gas black/ impingement) process

In the channel black manufacturing process, natural gas is used as a CB source. This process is carried out in an open system and it is very similar to the oil-furnace black process. For the production of CB, pre-heated carrier gas and pre-heated oil are sent into the system and the air is fed into the reactor tanks (Figure 2.8.). With the impingement of the burned oil stream from the ceramic openings through the surface of iron channels that filled with water, CB is cooled down [145]. The cooled CB is swept with a screw system and collected. On the other hand this process is used for special cases only because of some environmental concerns (lack of filtration, emission of CB to the air) and lower yield compared to oil furnace black process [138].

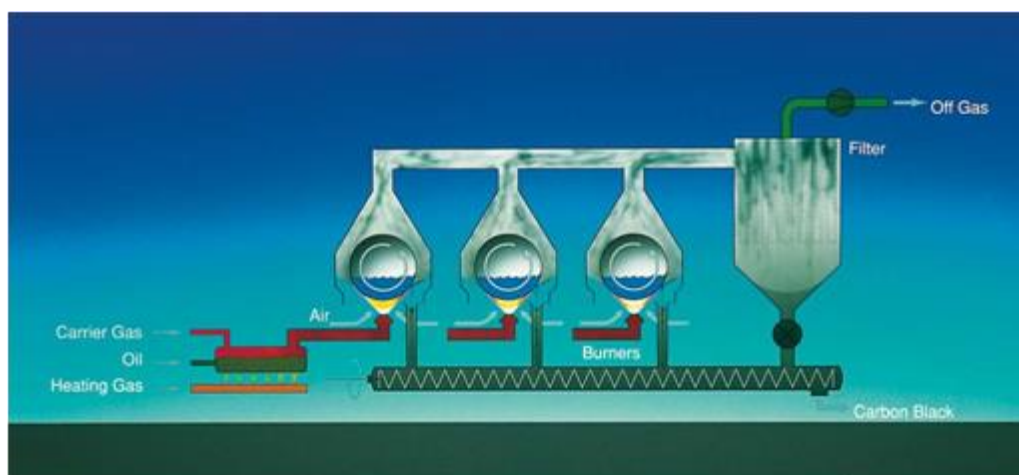


Figure 2.8 CB production by using channel black process [144]

2.3.2.4. Thermal black process

Thermal black process is a cyclic, closed and oxygen-free process based on the thermal decomposition. In the thermal black process system, there are two chambers for the heating and the decomposition cycles as illustrated in Figure 2.9. During the heating cycle, gas and air are fed into the chamber and gas is burned until desired temperature level. Then, entry of air into the chamber is prevented and gas valves are closed. The preheated gas stream decomposed into CB and hydrogen. The separation processes of the CB and gas stream is done same as the furnace black process mentioned above [135, 146].

After thermal decomposition, hydrogen can be used to heat the reactor that makes the process more effective [135].

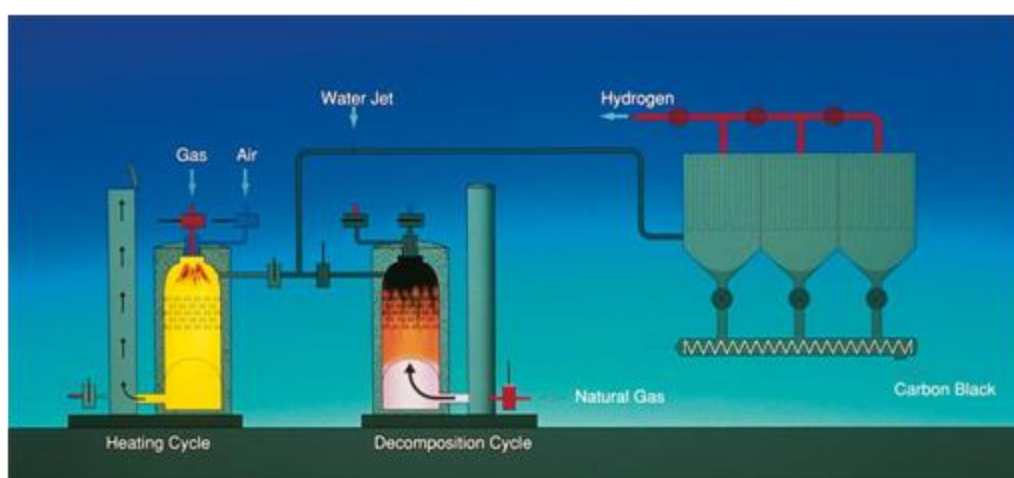


Figure 2.9 CB production by using thermal black process [144]

The processing parameters of thermal black process such as residence time and temperature are not similar to oxidative type CB manufacturing processes. This leads to the structural differences between CBs produced by different methods. Thermal black process is operated at relatively low temperatures with longer residence times. Since the residence time is long, the growth of the CB particles takes time and filament like CB morphology can be observed. In addition to that, particle size of CB can reach to 500 nm levels and this increases the percolation concentration in conductive polymer composites [135].

The CBs produced by thermal black process can be used in polymer industry due to their good compounding properties and relatively low cost [138].

2.3.2.5. Acetylene black process

The acetylene black process is carried out in closed systems without oxygen. As can be understood easily (Figure 2.10), it is basically a thermally decomposing process of acetylene gas. During the CB synthesis (above 2000°C), high amount of heat is released as a result of acetylene is splitting into hydrogen and CB. In order to provide heat transfer, reactors with water-cooling systems are used. Because of the raw material and synthesis conditions, acetylene black shows different properties. The most important advantage of this process is providing high structured CBs with higher surface area, crystallinity and conductivity. Because of that it is commonly used for electrically conductive polymer composites. On the other hand, this process is not flexible to produce different grades [138].

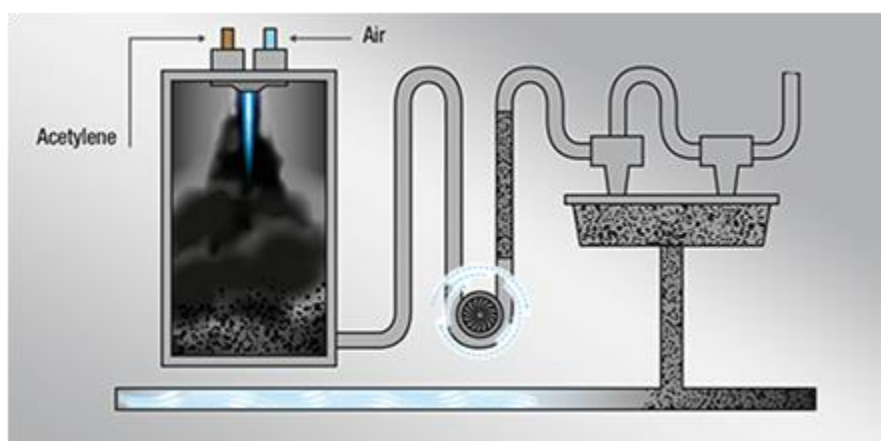


Figure 2.10 CB production by using acetylene black process [147]

2.3.2.6. Lampblack process

Carbon black is not only used for polymer composites but also used for inks, paints or systems used for coloration. Lampblack process is basically combustion of pine resin. At elevated temperatures, CB is formed and precipitated in the combustion chamber (Figure 2.11). After filtration and separation CB is obtained and used for coloration. It one of the oldest known processes used for the CB fabrication since ancient times [138].

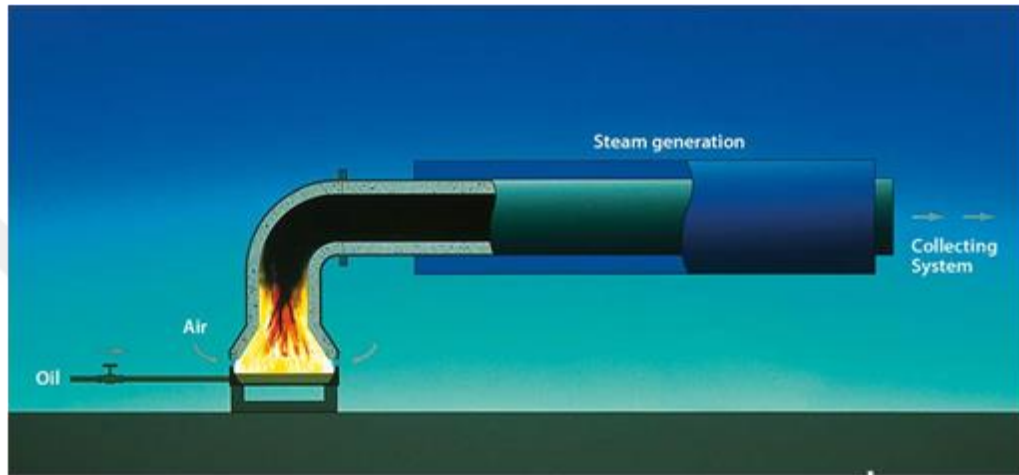


Figure 2.11 CB production by using lamp black process [144]

2.3.2.7. Carbon black formed as a byproduct

Until now, the explained processes are based on the CB production. On the other hand, CB can be formed as a byproduct at the end of the synthesis gas production and electric arc process. Very small amount of CB is produced by the incomplete combustion of heavy oil especially in large scale manufacturing. In addition, in the electric arc process with the thermally decomposition of hydrocarbon acetylene can be produced and then, CB is obtained [138].

2.3.3. Carbon Black Filled Elastomeric Piezoresistive Pressure Sensors

In this part, previous studies are going to be reviewed. In the review, carbon black filled elastomeric piezoresistive polymer composites are going to be given. In these studies, polyisoprene [53, 100], natural rubber (NR) [148], acrylonitrile butadiene rubber (NBR) [149], silicone rubber [30, 44, 52, 136, 150, 151], polyurethane [17] and poly(styrene-*b*-ethylene-*ran*-butylene-*b*-styrene) (SEBS) [47, 101] polymers were used as the matrix and various carbon black including fast extrusion furnace black [149] were used.

Knite et al. have studied piezoresistive properties of carbon black filled polyisoprene and aimed to find the most appropriate composition for sensing systems. This is the only study that investigated the piezoresistive properties of polyisoprene filled CB composites under pressure effect. Production technique of the composites was not given in the study. Sensor samples were vulcanized under pressure and cut into the appropriate sizes. Copper foils were adhered to both sides of samples as electrodes. The test system can be seen in Figure 2.12a. As seen, sample was placed between the jaws and electrical resistance of system was measured. In Figure 2.12b, insulator was used for minimizing the hysteresis of material [53, 100].

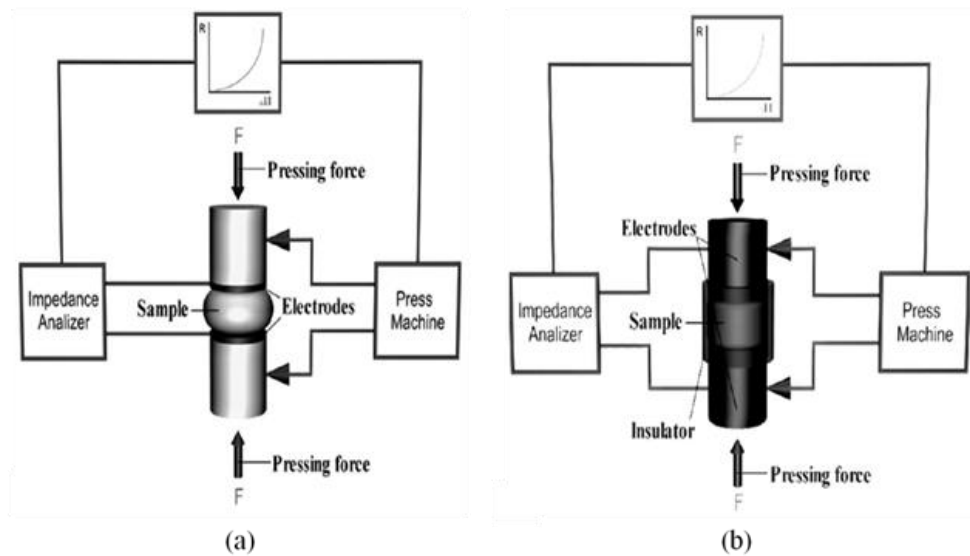


Figure 2.12 Electrical resistance measurement system for nanocomposites a) with and b) without insulator [53, 100]

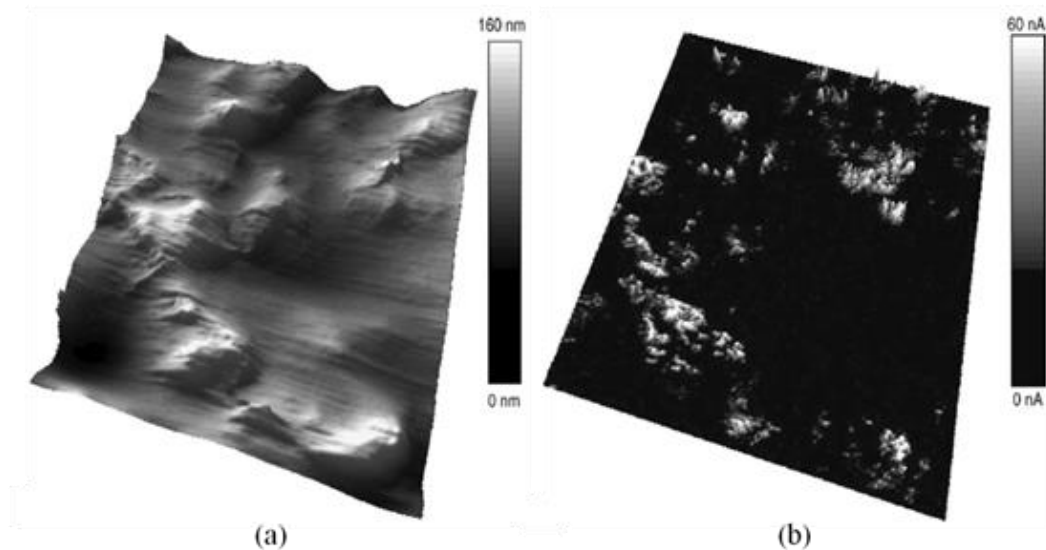


Figure 2.13 Atomic force microscope (AFM) images of the surface belongs to 20 wt% CB/polyisoprene polymer nanocomposites a) CB surface morphology, b) conductive network [53, 100]

AFM images of the samples gives information about surface topology and conductive channel paths. Figure 2.13a belongs to surface and shows the rough areas that shows CB nanoparticles and in Figure 2.13b conductive network of CB particles throughout the CB/ polyisoprene composite can be seen. Dark sections represent the SR insulating matrix and grey sections represent the CB nanoparticles [53, 100].

For the piezoresistive measurements, five conductive nanocomposites were prepared and they were separated from each other with brass sheets to increase efficiency of conductive channels. Then they were replaced in the equipment [53, 100].

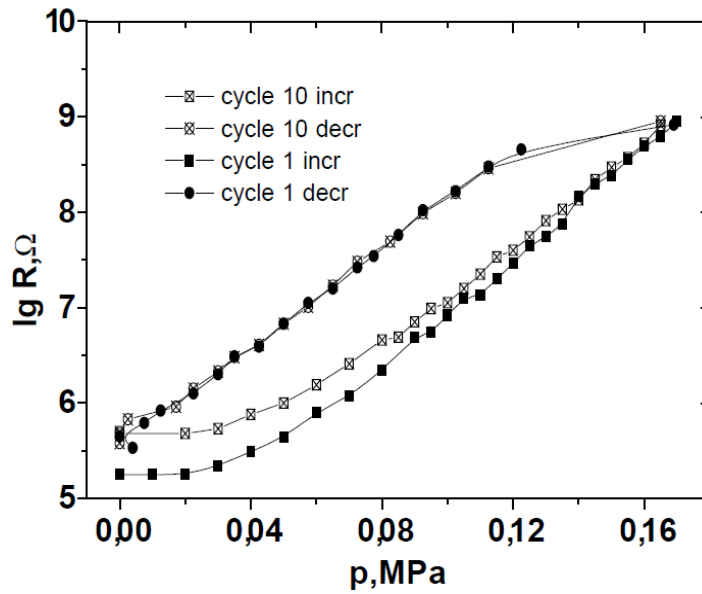


Figure 2.14 Resistance of the sample as a function of cyclic pressure (1st and 10th, without insulator) [53, 100]

In Figure 2.14, resistance of composite as a function of applied pressure at the 1st and 10th cycles can be seen. The general behavior of the composites against applied pressure was observed as increase in resistance due to the separation of conductive fillers and destruction of conductive paths. When the pressure was removed resistance decreased. The resistance value of the composite at the same pressure values was reported to be much higher when compared with unloading value. It can be seen that after the 10th cycle, the resistance of the material turned back to the initial value that is an indication of good recoverability of the composite due to the elastomeric structure of the matrix [53, 100].

To summarize, in the study, CB filler and polyisoprene were used but the production process and material properties were not given. Topology and electrically conductive network were characterized by an AFM. Electromechanical characterization was measured and resistance of composite returned to initial values after force was removed due to the elastic structure of rubber matrix but in cyclic measurements, deformation rate was not given. Depending on the deformation rate, all response could change [53, 100].

In the following study, for the characterization of piezoresistive properties, natural rubber (NR) was used. Job et al., investigated the electrical properties of natural carbon black (CB) filled rubber (NR) composites and their sensing behavior under pressure. Natural latex, stabilized by using ammonium hydroxide, was used as a matrix and carbon black was chosen as conductive filler. Five different CB/NR composites (5/95, 10/90, 15/85, 20/80, 25/75 wt%) were prepared. Casting method was used for composite preparation after all components were mechanically mixed and their electrical properties were determined [148].

For electromechanical characterization, various levels of pressure was applied in the range of 0-2.4 MPa and electrical data was monitored by using an electrometer [148].

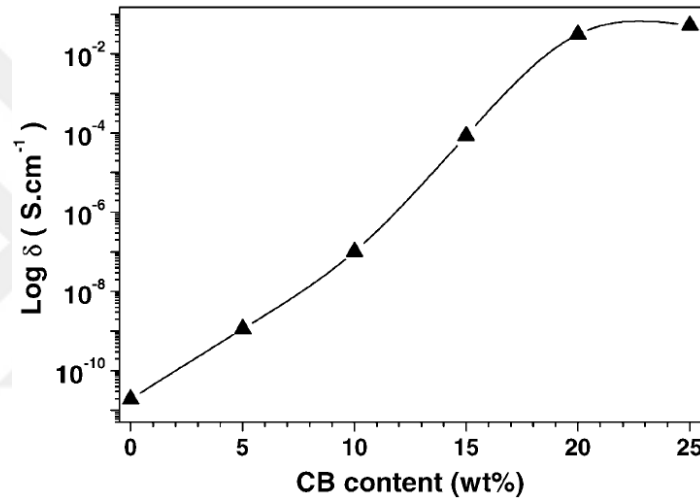


Figure 2.15 Percolation threshold graph of CB/NR composites [148]

Evaluation of the conductivity of CB/NR composites were given in Figure 2.15. This is a typical graph that shows percolation threshold of the composites. It gives the change in electrical conductivity of composites as a function of CB wt% in NR matrix. As obvious from the Figure 2.15, with the increase in filler concentration, conductivity of the composites increased. Up to 20 wt% CB, conductivity was reported to change around nine orders of magnitude and after this point no big change in conductivity was observed [148].

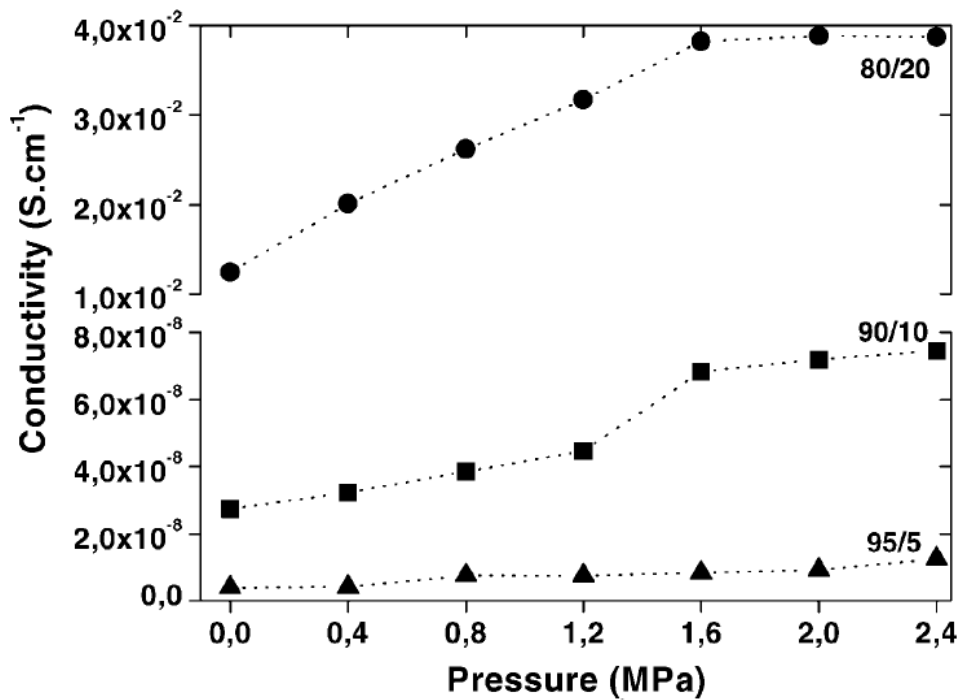


Figure 2.16 Electrical conductivity of the composites as a function of pressure for composites (5-10-20 % wt CB) [148]

In order to characterize the piezoresistive behavior of the composites, three specimens were selected from three regions of the percolation graph as 5, 10, 20 wt% CB/NR. Figure 2.16 gives the conductivity of the composites as a function of applied pressure. Change in conductance with applied pressure in the range of 0 to 2.4MPa on three different composites can be seen from Figure 2.16. This graph was given in order to show the concentration effect on piezoresistive behavior under pressure. When pressure was applied, 5 wt% CB containing composite showed small increase in conductivity. Since it has relatively low filler concentration, applied pressure values were not enough to form conductive networks. For 10 wt% CB containing composite, change in conductivity took place in two steps. In the first step up to 1.2MPa it increased slowly and after this pressure value increase was obvious and after that point it was almost constant. And lastly, 20 wt% CB containing composite showed unambiguously response to pressure with increase in conductivity. Because its concentration was much higher, under given pressure values many conductive networks formed. From these three samples, 20/80 CB/NR composite was found more applicable and sensitive as a pressure sensor especially between 0 to 1.6 MPa range [148].

The study showed the effects of filler concentration and pressure on sensing properties. As mentioned previously, increase in conductive CB filler content led to increase in conductivity. On the other hand, in material section function of stabilizer, cross-linking process and also cross-linking density were not mentioned. As known the cross-linking density of a material directly affects the sensing properties. In addition to these for calculation of electrical conductivity (Eq.4):

$$\sigma = \frac{L \cdot I}{A \cdot V} \quad (4)$$

equation was given but size of specimens, one of the most important parameter, was not given and also the system was not given detailed [148].

For the investigation of piezoresistive properties of materials, rubbers are the most commonly used. In present study, acrylonitrile butadiene rubber (NBR) was used. Mahmoud et al., investigated the electrical and piezoresistive properties of carbon black (CB, with 38 nm average particle size and 45 m²/g surface area) filled acrylonitrile butadiene rubber (NBR) composites[149]. For the preparation of rubber compound, activators (stearic acid and zinc oxide), an antioxidant (phenyl-β-naphthyl amine), a semi-ultra accelerator (dibenzthiazyl disulphide), a vulcanizing agent (sulfur) and a plasticizer (dioctyle phthalate) were used in appropriate rates and mixed by using a two roll mill. After getting the homogenous mixture, rubber compound vulcanized at high temperature under pressure. NX was given as the sample code where X denotes the CB content (phr) [149].

Electrodes were connected to the sample and pressure was applied by a mechanical testing system and digital electrometer was used for electrical characterization [149].

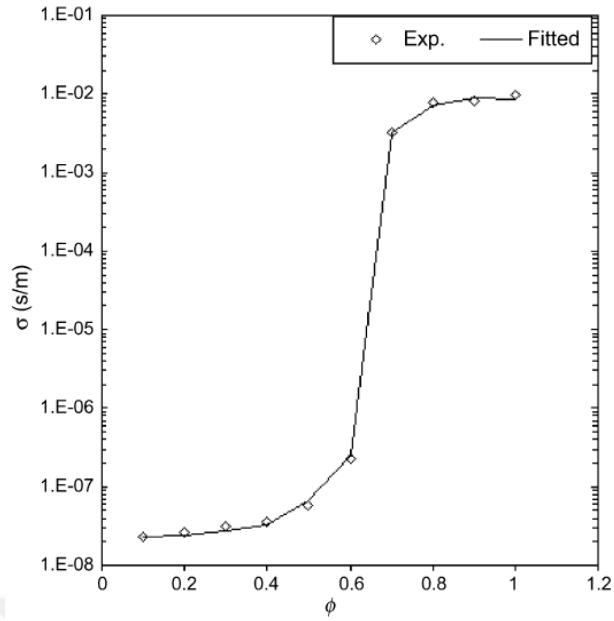


Figure 2.17 Percolation threshold of CB/NBR composites [149]

Conductivity of the composites as a function of CB volume fraction can be seen from Figure 2.17. As seen, there are three regions in the graph as insulating region at the beginning with low conductance then, percolation or transition region that showed obvious increase in conductance and lastly, saturation or conductive region that reaches the plateau or saturation region [149].

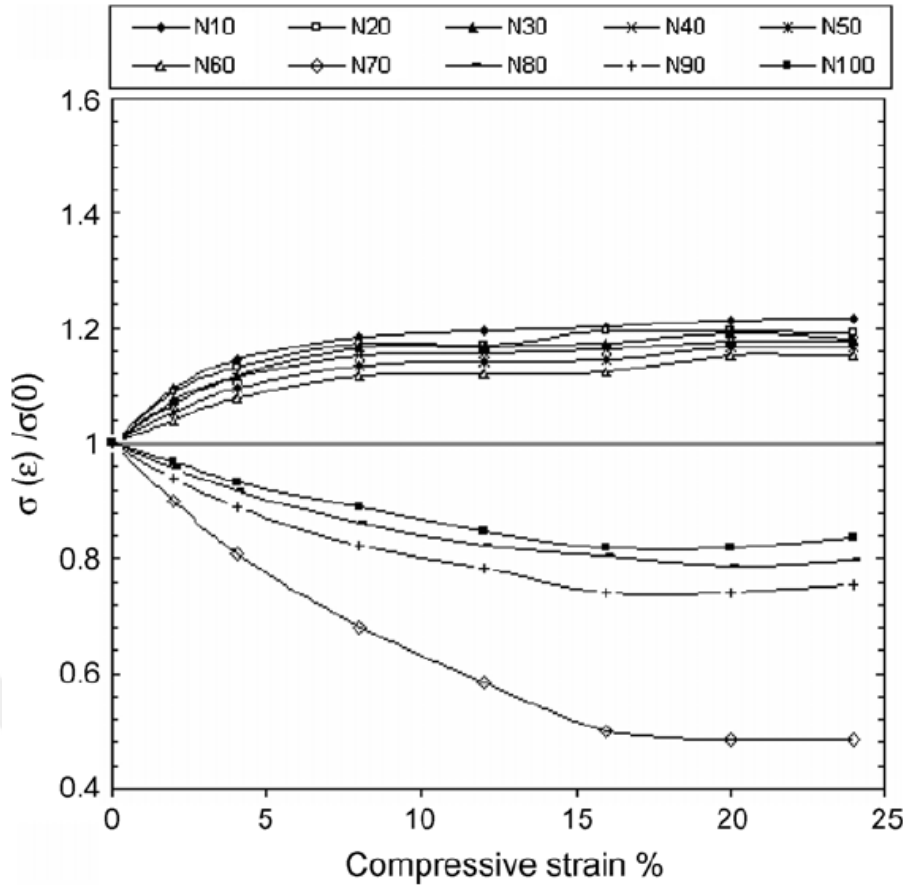


Figure 2.18 The relative conductivity as a function of compressive strain [127]

In Figure 2.18, relative conductivity of all composites under compressive strain can be seen. While one set of samples showed positive, the other set showed negative piezoresistance. The conductivity of composites under percolation region increase up to 8% compressive strain. On the other hand, conductivity of composites that is in and above the percolation region decreased up to 16% [149].

At lower filler concentrations, filler-filler distance is relatively lower when compared with the samples at higher filler concentrations (percolation region, saturation region). At lower filler concentrations with the effect of compression, conductance increased. Separated fillers came closer. On the other hand, at higher filler concentrations, compression caused to increase the filler-filler distance and conductance of composite decreased. After the percolation region, increase in CB content led to decrease the sensitivity of the system. Consequently, N70 composite showed the most sensitive response against to applied compressive strain [149].

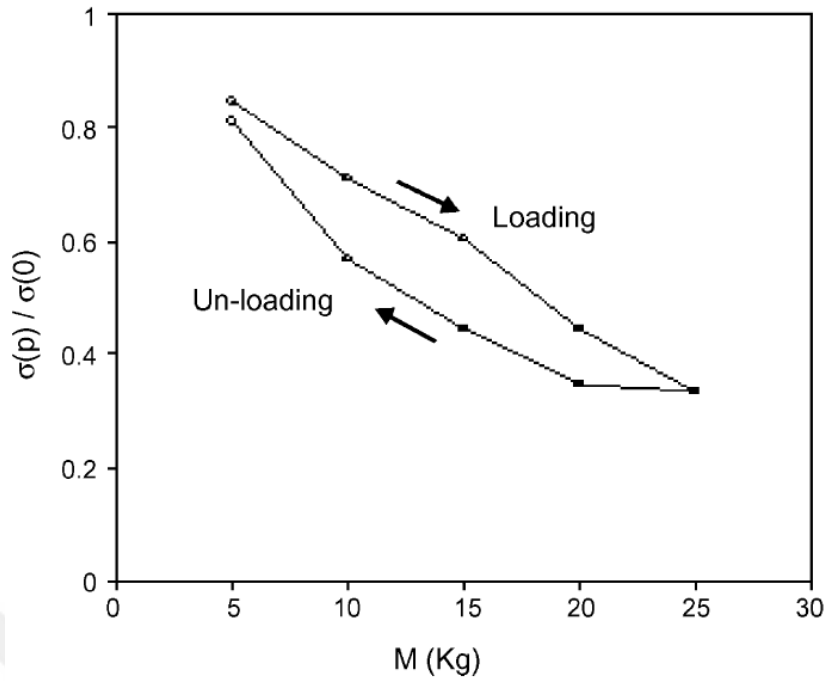


Figure 2. 19 Relative conductivity of N70 composite as a function of applied load [149]

Relative conductivity of the preconditioned N70 composite under cyclic load can be seen in Figure 2.19. The area between loading and unloading cycles represents the formation of hysteresis. The increase in load caused to the dimensional deformation of the composite and that lead to irreversible electrical behavior [149].

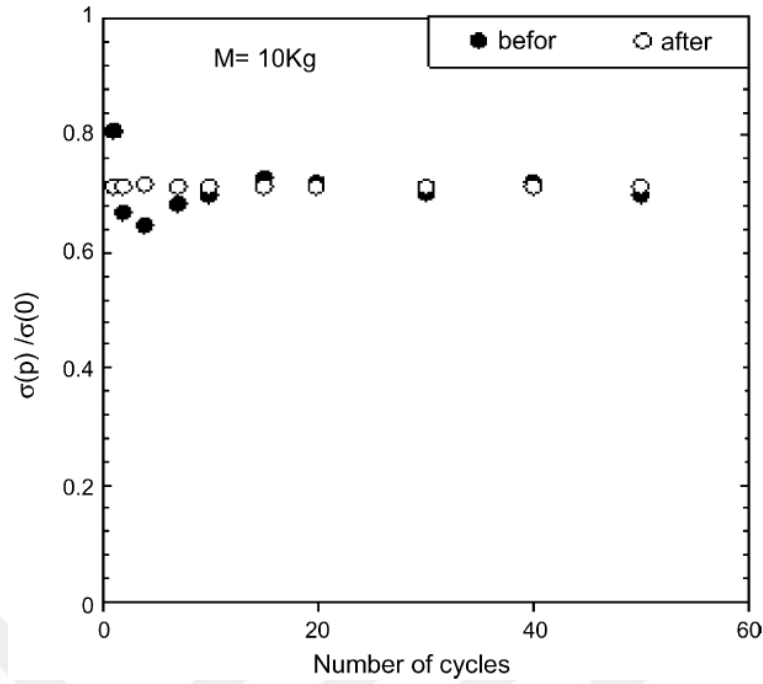


Figure 2.20 Relative conductivity of N70 sample under 10 kg constant load before and after preconditioning [149]

To examine the effect of preconditioning on relative resistance, 10 kg constant load was applied to the sample before and after conditioning process. As seen from Figure 2.20, the variation of the relative resistance after preconditioning was reported to be less and that supports the necessity of preconditioning [149].

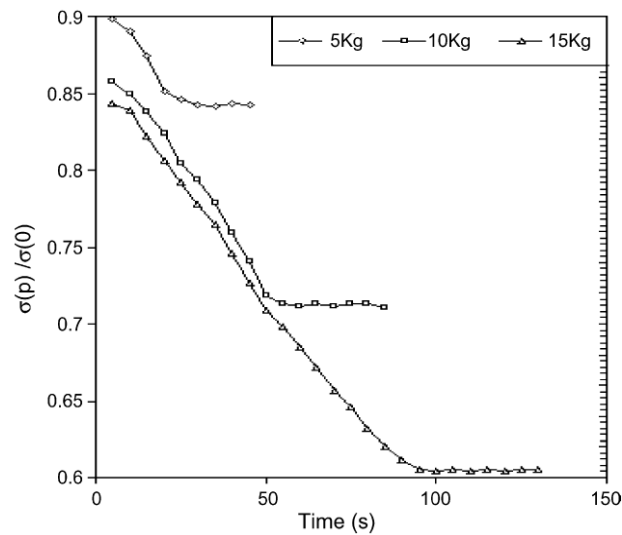


Figure 2.21 Relative conductivity of N70 sample under 10 kg constant load before and after preconditioning [149]

Sensitivity of the N70 composite under different constant loads was shown in Figure 2.21. The time required for a constant response for different loads were unlike from each other. In the case of higher level of load, more time was needed in order to obtain a stable response. When the applied load was increased, sample required more time to reach equilibrium [149].

To summarize, in the study, CB/NBR composites were prepared at different CB volume fractions and their electrical, electromechanical characterizations were carried out. Through all the composites, N70 was selected as the most sensitive pressure sensor. In order to examine electrical conductance of the composite, cyclic test was done and hysteresis were controlled with the preconditioning of the composite. Applied load effect on conductance was also investigated and it was clearly shown that, magnitude of the constant applied load was found significant in terms of obtaining a stable response [149].

Another most commonly used material for the fabrication of piezoresistive properties is silicone rubber (SR). Wang et al. studied with the CB and SR materials. In the study effects of type, surface area, resistivity, and mechanical properties of the carbon black were investigated on the electrical and sensing behavior of the polymer composites. Composites were prepared by solvent based method by using hexane. In addition to that, ethyl silicate and nano alumina powder were used as a cross-linker and a dispersant respectively. Silicone rubber (SR) was used as a matrix. The volume ratio of CB was between 5-60 % in the composites.

In order to disperse the fillers, mechanical stirring and ultrasonic mixing were used. After evaporation of the solvent samples were compression molded into disks at 165 °C, under 14.7 MPa pressure for 10 min [136]. Although process of CB/SR composites was given in a detailed way, there is no information about fabrication of CB/HDPE composites. Also, there is no explanation why HDPE was chosen. In the first step in order to choose the best matrix 35 v% carbon black containing composites were fabricated by using HDPE and SR (SL-10/HDPE and SL-10/SR).

After analyzing the compression behavior of two matrixes, SR was chosen because of its relatively lower elastic modulus and higher compressibility. In the study, percolation behavior of the composites was determined by a multimeter. Piezoresistive properties were determined by using a mechanical testing system and a digital multimeter. As can be seen from Figure 2.22, sample was placed between two steel plates and electrical resistance of the samples were measured when pressure was applied [136].

Table 2.1 : Properties of Carbon Black and Polymer [136]

CCB	Specific surface area (m ² /g)	pH	Heating loss (%)	Electrical resistivity (Ω cm)	Young's modulus (MPa)
SL-10	58	7.0	1.0	0.8	1.0×10^5
SL-20	140	7.0	1.0	0.5	1.0×10^5
SL-30	320	6.8	2.0	0.4	1.2×10^5
SL-32	430	7.0	2.0	0.4	1.2×10^5
SL-36	780	6.3	3.0	0.2	1.5×10^5
Polymer	Dielectric constant	Electrical resistivity (Ω cm)	Dielectric strength (KV/mm)	Density (g/cm ³)	Solid Young's modulus (MPa)
QD234	3.3	9.0×10^{14}	13	0.96	6.0
PE602D	4.0	8.2×10^{13}	20	0.94	100

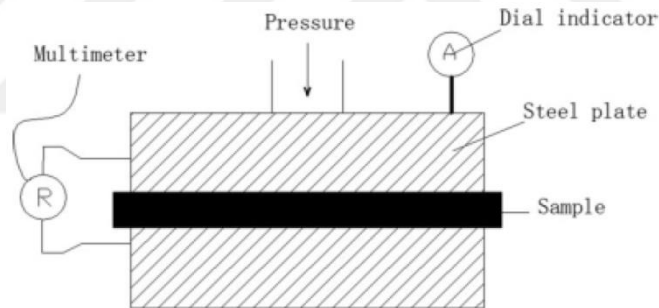


Figure 2.22 Uniaxial compression system for piezoresistance measurement [136]

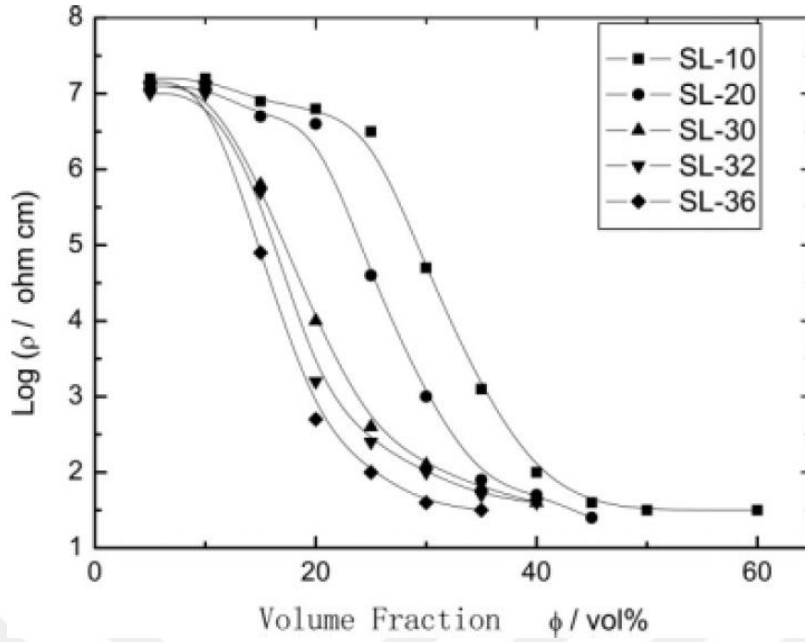


Figure 2.23 Percolation threshold of different CB powders with SR [136]

Figure 2.23 shows electrical resistivity as a function of CB concentration for different fillers. As can be seen from the graph, for all sets, increase in CB content causes a decrease in electrical resistivity to a certain extent then CB concentration does not affect the electrical resistivity. In other words, all samples set showed a classical percolation behavior. In addition to that, filler type was found significant in terms of electrical resistivity. SL-36/SR composites showed the lower percolation threshold that is probably caused by high surface area and low resistivity values of SL-36 [136].

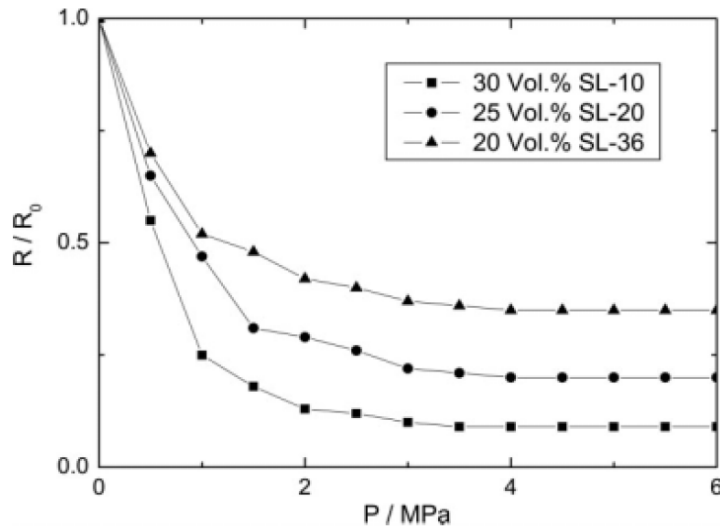


Figure 2.24 Piezoresistance of carbon black/ silicone rubber composites [136]

In order to determine the piezoresistive behavior, SL-10 (30 v%), SL-20 (25 v%), SL-36 (20 v%) filled composites were chosen. Filler content was determined according to percolation threshold so all samples had different filler concentration. R/R_0 values of the composites as a function of pressure is given in Figure 2.24. All samples showed negative piezoresistance up to a certain value around 3MPa. However, SL-10/SR composite showed the higher sensitivity. This is probably caused by the resistivity value of the so called filler. As given in Table 2.1, SL-10 has the highest resistivity. As known, when pressure was applied, particle separation and resistance decreased. Since SL-10 has the highest resistivity, in other words the effect of pressure was more obvious [136].

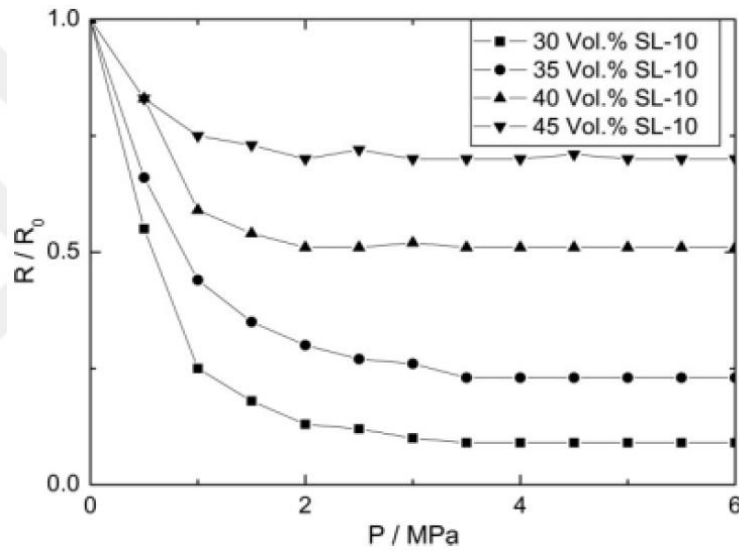


Figure 2.25 Effect of filler volume fraction of SL-10 CB filler/SR composites on piezoresistive behavior [136]

The piezoresistive behavior of SL-10 containing composites with different filler concentrations was tested. Figure 2.25 shows that 30 v% CB containing composite has the most sensitive response to applied pressure because it is in the percolation region. As known, amount of filler is lower at this region when compared with saturation region and fillers are free to move and change their position. Because of that, any external effect can lead to drastic changes in the resistance [136].

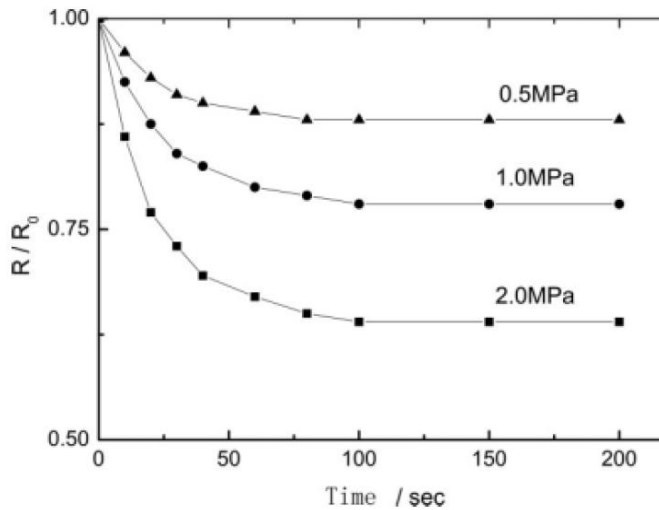


Figure 2.26 Resistance change under constant pressure [136]

In addition to piezoresistive characterization, 35 v% CB (SL-10) filled SR composite was used to examine the effect of constant pressure on piezoresistance. Pressure values with the magnitude of 0.5, 1, 2 MPa was applied for 200 sec. which can be seen in Figure 2.26. Relative resistance showed three regions for all cases. While in the first region (0-30 sec.) change in resistance was quickly and relatively slower in the second region (30-100 sec.) and it was almost constant in the third region (100-200 sec.). Because the system needed time to reach a constant pressure value. After reaching target pressure value, resistivity did not change. When the magnitude of applied pressure was compared, 2 MPa showed the most sensitive response (in the first region) that was probably caused by the highest number of conductive network formation under this condition [136].

To summarize, this study simply evaluated the effects of filler properties on mechanical, electrical and sensing behavior of the polymer composites. To explain these phenomenon, five different CBs were used. In the study, the amount of solvent, cross-linker and dispersant were not mentioned. As a conclusion, type, resistivity, surface area and mechanical properties of the carbon black were found to directly change the response of the composites against mechanical stimulant [136].

In another study, Luheng et al., studied the effect of conductive filler content on electromechanical properties of carbon black (CB) filled silicon rubber (SR) composites. Specific surface area of CB was reported as 780 m²/g. Composites were prepared by using solution casting method and all materials were mixed with hexane by using a mechanical stirrer and a sonicator, respectively to obtain homogeneous dispersion of filler into the matrix. The ratio of CB in the structure varied between 0.08:1 to 0.24:1 (7,41 wt%-19,35 wt%) (the mass ratio between CB and SR was referred as F) [150].

Table 2.2: Properties of CB and SR

	Specific surface area	pH	Volatile content ^a	Light transmittance of toluene extract
Carbon black	780 (m ² /g)	6.25	3.0 (%)	100 (%)
	Dielectric constant	Hardness	Tearing resistance	Dielectric strength
Silicone rubber	3.0	35 (Shore)	4 (kg/cm)	18 (kV/mm)

^a Condition: drying temperature: 105 °C, drying time: 1 h.

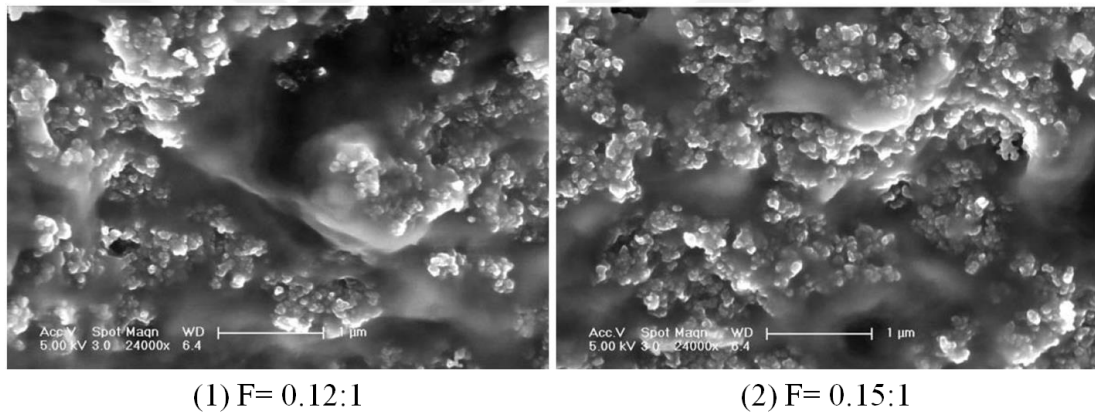


Figure 2.27 SEM images of composites (1) F= 0.12:1, (2) F= 0.15:1 [150]

Properties of CB and SR were given in Table 2.2. Morphological structures of composites were analyzed by SEM images in Figure 2.27. In the SEM images black and dark grey parts denoted the SR matrix and light grey parts that have particles denoted the CB filler and as seen from fractured surface of the composites, carbon black was dispersed homogenously [150].

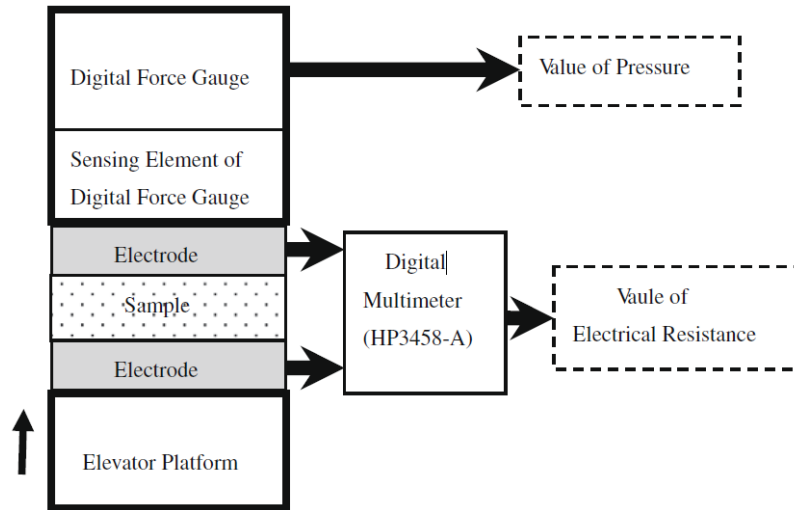


Figure 2.28 Piezoresistance measurement system [150]

Electromechanical test system can be seen from Figure 2.28. In the study, sample was placed between two electrodes connected to a digital multimeter. Pressure was applied by the moving the elevator upwards. Electrical resistance was monitored during the application of uniaxial pressure [150].

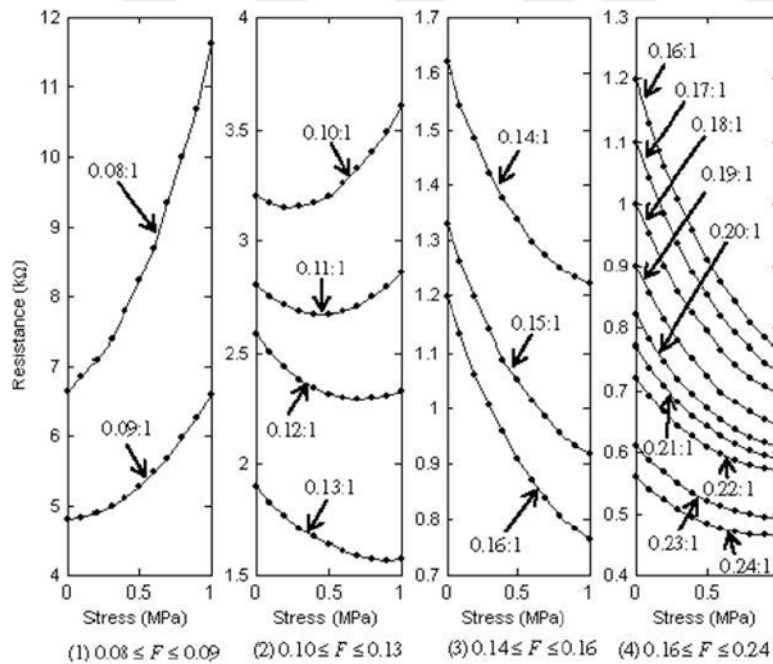


Figure 2. 29 Resistance of composites as a function of pressure in the range of 0 to 1 MPa [150]

Electromechanical responses of the composites can be seen from Figure 2.29. Resistance values of the composites were given as a function of pressure at different CB concentrations. As reported in the study, depending on the mass ratio of CB to SR matrix, referred as F , resistance of the composites showed three different behavior. If F value was smaller than 0.09 (1), resistance of composite increased. That was assumed to be caused by the destruction of the conductive network. As known at lower filler concentrations, it is easier to separate the fillers and destruct the conductive network. When the F value was between 0,10 to 0,13 (2), resistance firstly decreased and after a critical pressure value it started to increase. The decrease in resistance was seen due to the formation of new conductive networks under low pressure values. However, the increase in resistance after a critical pressure value was an indication of filler separation. Lastly, if F was bigger than 0.14 (3,4), the resistance of composites decreased by applying pressure and it indicated the conductive network formation dominance [150].

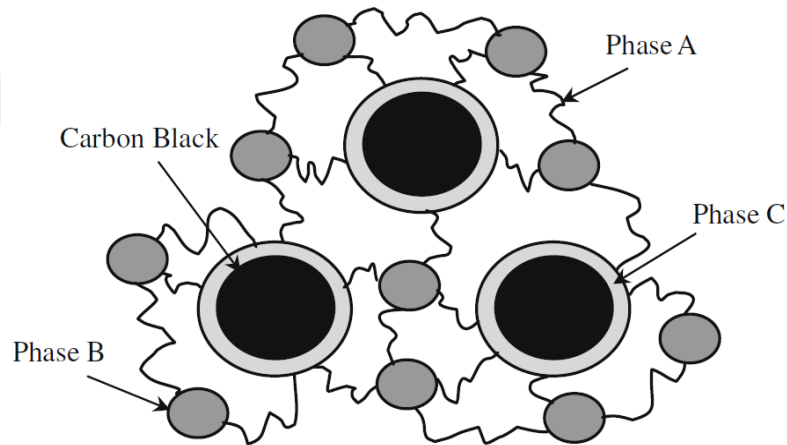


Figure 2.30 Shell model for the explanation of conductivity [150]

Mechanism of resistance change was explained by the shell structure model as illustrated in Figure 2.30. As shown, there are different phases in 3D network structure. Phase A represents the SR chains, Phase B is cross-linking points of SR and Phase C is formed with absorption of SB onto the surface of CB particles. Conductive network forms when CB particles come close enough to each other that is due to the tunneling effect and then resistance of composite decreases [150].

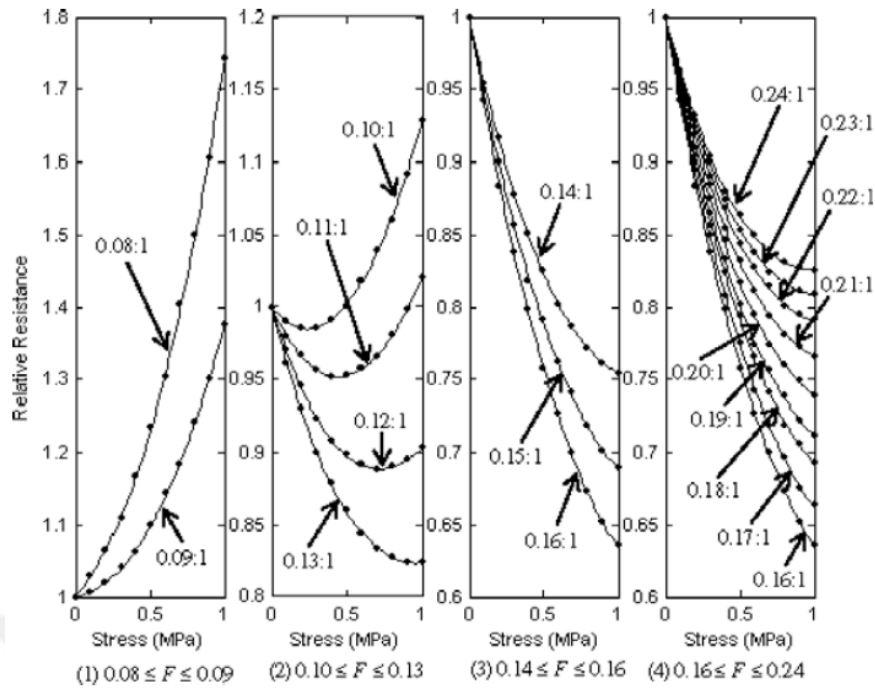


Figure 2.31 Relative resistance of composites as a function of pressure [150]

Relative resistance change as a function of pressure was given in Figure 2.31. The first case was obtained for the F value between 0.08 to 0.09 (1) and composites showed positive piezoresistive behavior. When F was between 0.10 to 0.13 (2), composites showed two different behavior as negative to positive piezoresistive behavior. There was a critical pressure value for each composite in this group and it increased with CB content. In the third case, F was between 0.14 to 0.16 (3), composites have negative piezoresistive behavior. Since gauge factor was maximum, sensitivity of the composites in this group was found close to each other. In the case of F value between 0.16 to 0.24 (4), composites showed negative piezoresistive behavior. On the other hand, with the increase in CB content gauge factor decreased and as a consequence of that, sensitivity of composites also decreased [150].

To summarize, in the study, CB/SR composites were prepared by using solvent casting method and piezoresistive sensing properties were investigated. Resistance change was explained by the shell model and as expected depending on CB content resistance showed different behavior under pressure. Since, all sensing properties were measured by discontinuous system because of that sensing repeatability and limits are not known [150].

In another study, Wang et al., investigated the piezoresistive response of carbon black (CB) containing silicone rubber (SR) composites under cyclic compression. CB and SR were mixed by hexane and the mass ration of CB to SR was 0.08:1. Dispersion of CB into the SR matrix was provided by mechanical mixing and ultrasonic vibration. After evaporation of the solvent, viscous mixture was molded and vulcanized at room temperature. Composites were placed between two steel plate electrodes and one was movable and other one was fixed [52].

In order to investigate the cyclic behavior of the composites 40 cycles were completed. The cyclic test was divided into four levels and applied pressure values gradually increased for each level as 0, 0.4, 0.6, 0.8, 1MPa. During the cyclic test, composites were loaded and unloaded between determined pressure values. In the first level (1st-10th cycles), 1st cycle, first pre-compression, was completed under 0.4 MPa and following nine cycles, pressure value was set to 0.15MPa. Before starting the next step, pressure was completely removed and sample was relaxed for 6 h and this procedure was repeated until the test was completed. In the second level (11th-20th cycles), 11th cycle, second pre-compression, was carried out under 0.6 MPa and the other cycles were completed under 0.35 MPa. In the third level (21th-30th cycles), 21th cycle, third pre-compression value was 0.8 MPa and the other cycles in this level were completed under 0.5MPa. In the fourth level (31th-40th cycles), 31th cycle, fourth pre-compression, was completed under 1 MPa and following cycles were completed under 0.7MPa [52].

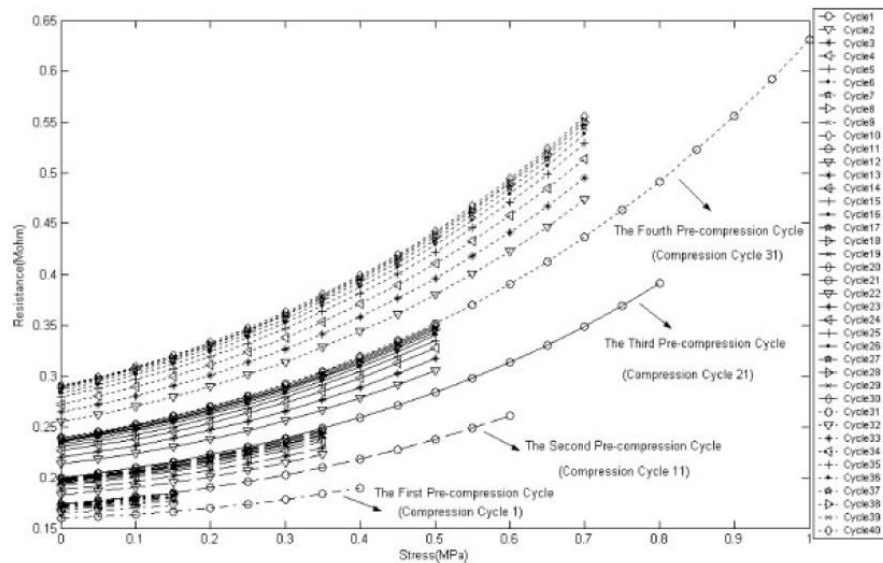


Figure 2.32 Resistance of CB filled SR composite as a function of stress under applied various forces [52]

Piezoresistive response of CB filled SR composite under cyclic pressure can be seen from Figure 2.32. CB/SR composite showed positive piezoresistive behavior. After all pre-compression cycles, the resistance of the composite increased. R_0 value of each level increased by increasing the cycle number. The difference between resistance values of the following cycles is decreased by increasing the cycle number. In other words, the difference between 2nd and 3rd cycles was more noticeable when compared with the difference between 9th and 10th cycles [52].

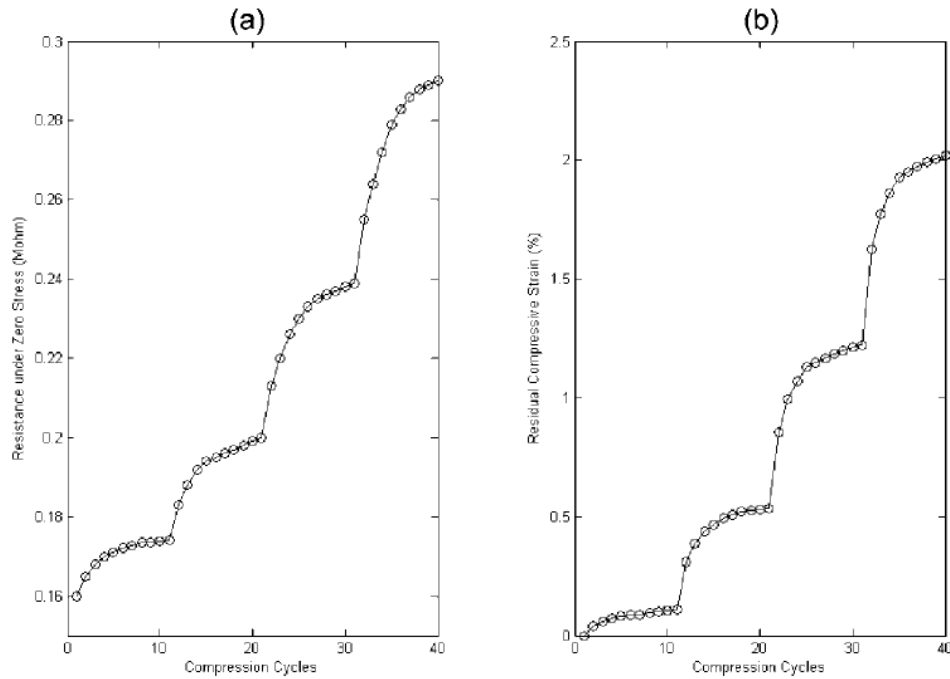


Figure 2.33 a) Resistance change when the pressure was removed on the composite, b) Residual compressive strain as a function of compression cycle number [52]

Figure 2.33a gives the change in resistance as a function of compression cycle numbers. In the same compression level, resistance at zero pressure value increased and as previously mentioned, degree of increase in resistance relatively decreased. This behavior has arisen from the formed conductive network due to the previous cycles. The residual compressive strain as a function of compression cycle was given in Figure 2.33b. When composite was exposed to cyclic pressure, the increase in residual compressive strain was found to be higher because of stress softening property of composite [52].

The increase in resistance during cyclic test was reported to be caused by two reasons. Firstly, under pressure, destabilized CB particles changed their positions and resistance increased. Secondly, after pressure was removed, composite could not return to its initial position and increase in cycle number caused to increase in resistance [52].

In the study, CB filled SR composites were produced by using solution casting method. The piezoresistive response of the composite was characterized under gradually increased cyclic pressure. The cyclic test was carried out at four different pressure levels (0.4, 0.6, 0.8, 1 MPa). CB/SR composite showed positive piezoresistive response under pressure. Pre-compression cycles were useful step such as conditioning [52].

Another interesting study was carried out by Wang et al.. They have developed a method for the production of relatively cheap, thin, and flexible pressure sensor with high accuracy. In the study, silicon rubber (SR, RTV) and carbon black (CB) (with 780 m²/g specific surface area) were used to obtain conductive polymer composites that is suitable for sensing element production [151].

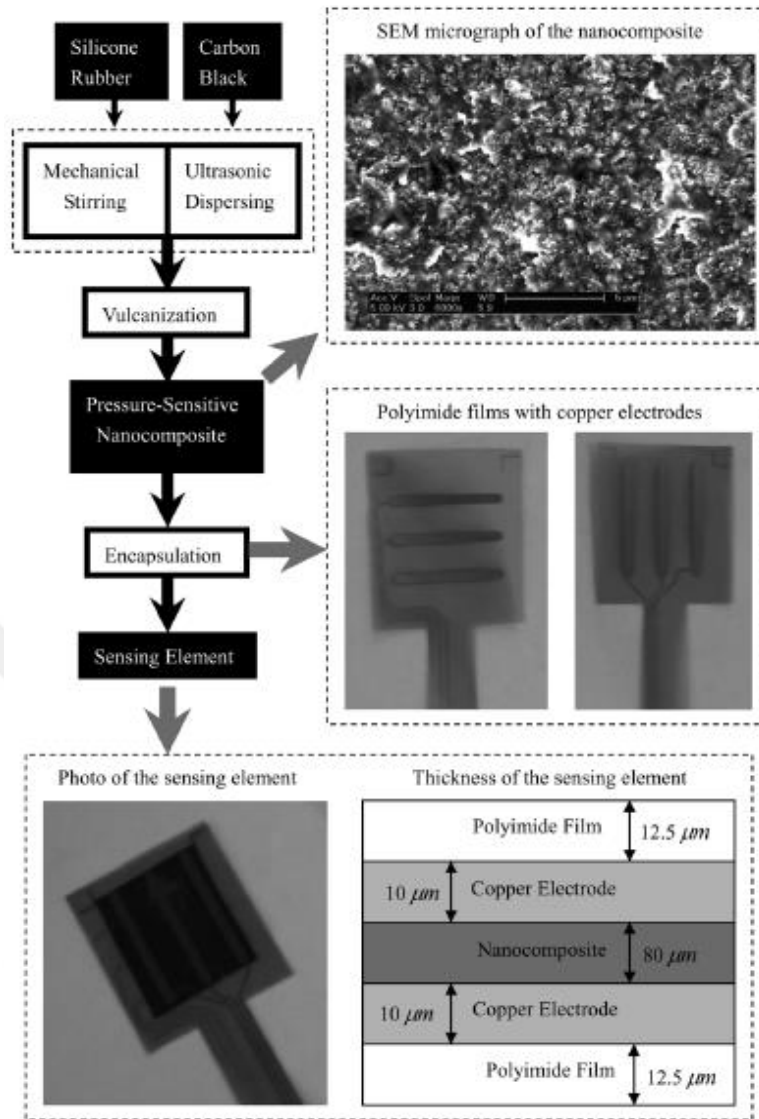


Figure 2.34 Fabrication steps of the sensing system and SEM image of the composite [151]

Preparation of pressure sensing element can be seen in Figure 2.34 step by step. At the beginning, SR and CB were mixed together in the presence of hexane as a solvent and for better dispersion ultrasonic vibration and mechanical stirring were used. For the production of composites, approximately 125 μm , spin coating method was used and then they were vulcanized. Vulcanized CB/SR composite was encapsulated by polyimide films with copper electrodes. Morphology of the composites was characterized by SEM as given in Figure 2.34. In the image, black parts represent the SR matrix and light grey parts represent the CB particles. CB filler was homogeneously dispersed in SR matrix [151].

For finding appropriate composition, different CB containing composites were prepared. When the mass ratio of CB to SR was 0.06:1, composite resistance was found very high for sensing applications. On the other hand, if the ratio was higher than 0.10:1 resistance of the composites did not change at all. The optimum range was reported to be between 0.07-0.09:1 and in the study the mass ratio of CB/SR is used as 0.08:1 [151].

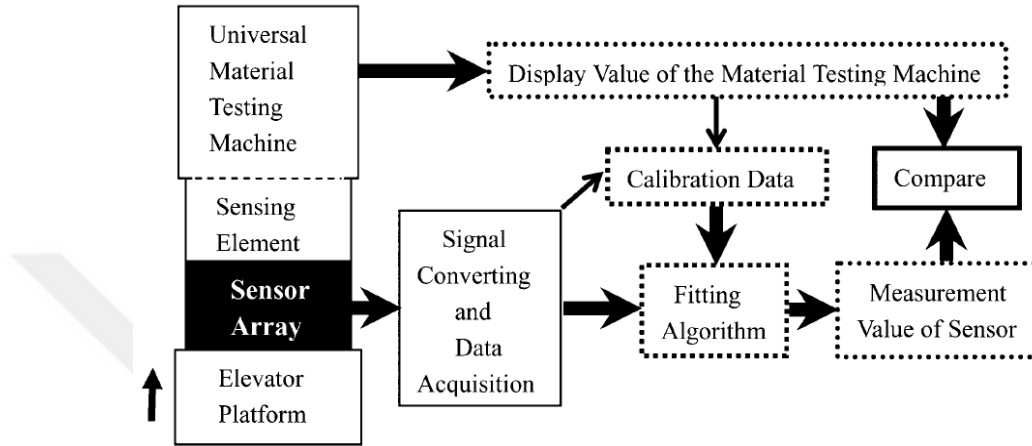


Figure 2.35 Experimental set up for electromechanical characterization [151]

Electromechanical characterization system is given in Figure 2.35. As seen, the sensor array is located and pressure was applied by an elevator platform and resistance was monitored [151].

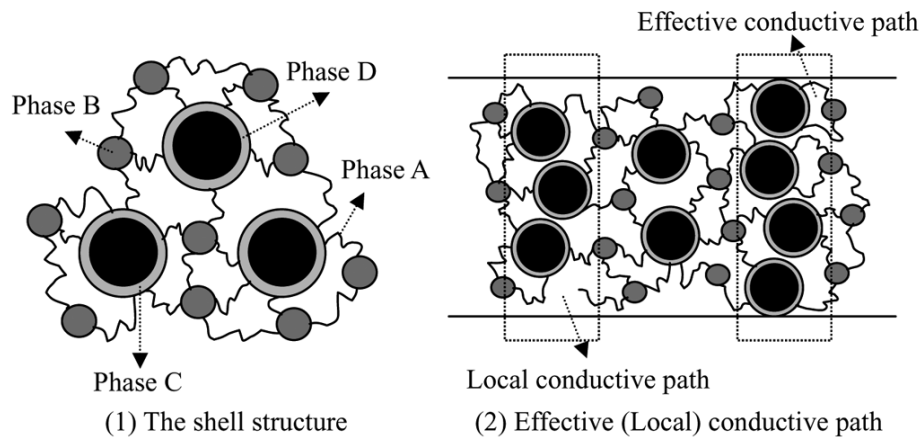


Figure 2.36 Illustration of conductive network [151]

Piezoresistance mechanism of composites under pressure was explained by the shell structure model as mentioned in another study made by Luheng et al. [150].

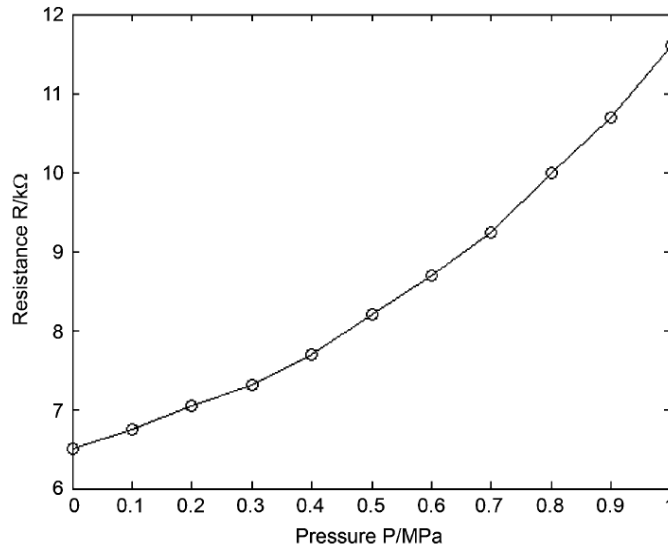


Figure 2. 37 Resistance change of composite as a function of pressure (CB:SR is 0.08:1) [151]

Electromechanical properties of the composite, the mass ratio of CB/SR is 0.08:1, is given in Figure 2.37 as resistance vs. pressure. As seen, resistance of composite increased with pressure due to the destruction of conductive networks [151].

To summarize, in the study, CB/SR composites were produced and the most appropriate one selected for the sensor array fabrication. SR cross-linking density was not mentioned and given data were not enough to understand electromechanical properties of the composite. Resistance change was given only for the first pressure loading. There is neither unloading nor cyclic data [151].

Another SR based sensor was developed by Shu et al. In the study, a durable, comfortable and highly sensitive flexible pressure sensor was fabricated to monitor the heart rate by carbon black filled silicone rubber nanocomposites [44].

The design of pressure sensor was illustrated as given in Figure 2.38. The pressure sensor contains four basic layers. Two nanocomposite layers were located inner side of the sensor (Figure 2.38b). Conductive nanocomposites and two electrodes placed on the outer sides of the sensor (Figure 2.38a). In addition to these, extra two adhesive layers were used for the isolation of the sensor (Figure 2.38d) [44].

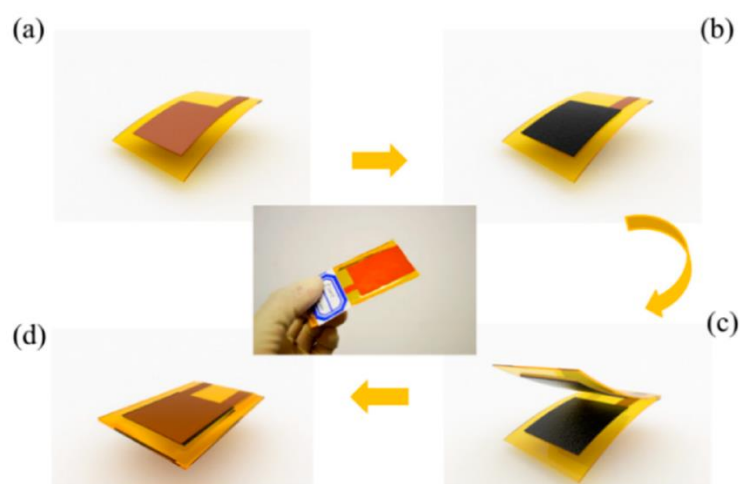


Figure 2.38 Schematic illustration of the CB/SR nanocomposite pressure sensor design. a) the electrodes of sensor, b) connection of the nanocomposite on electrode, c) placement of sensor and electrodes face to face with the another, d) insulation of sensor system [44]

CB, SR and n-hexane were mixed at appropriate rates. The dispersion of CB into the matrix was provided by using an ultrasonic mixer and a magnetic stirrer. The film was obtained by spin coating of the mixture [44].

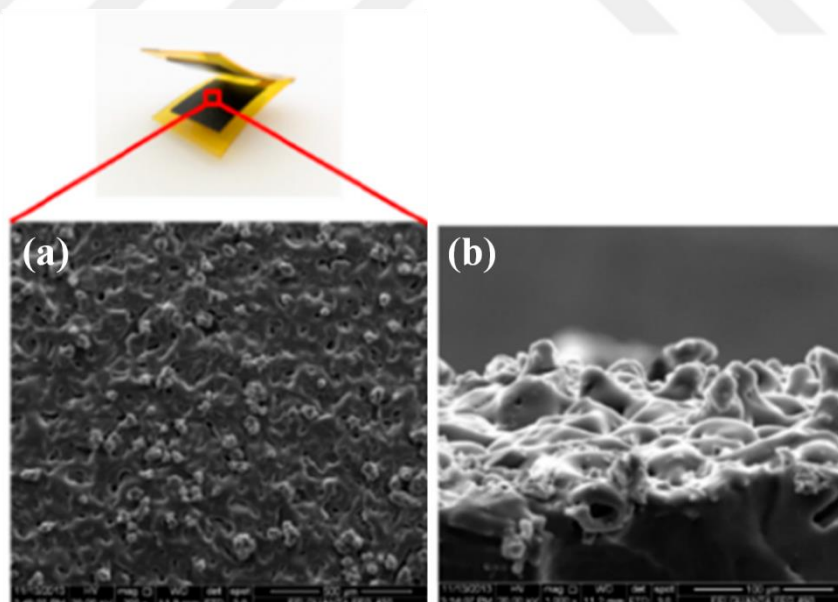


Figure 2.39 Morphological structure of the modified surface a) and side perspective view b) of CB/SR pressure sensor [44]

The surface of the nanocomposites was modified by using "micrometer-scale bump structures" Figure 2.39a-b. The SEM images show the surface and side perspective view of the surface. Moreover, these micro-bumps on the surface increase the sensitivity of the sensor [44].

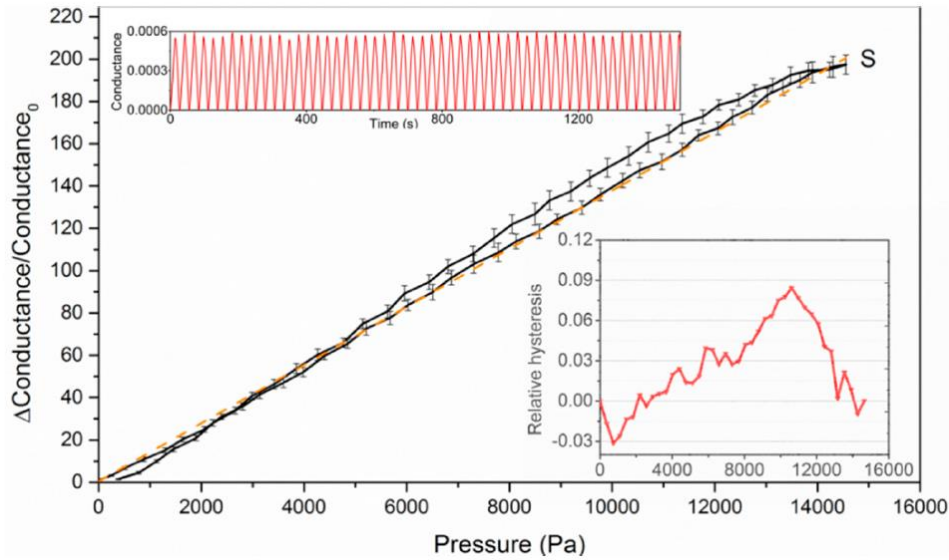


Figure 2.40 The relative conductance of the material as a function of pressure, inset graph at the lower-right corner is the relative hysteresis as a function of pressure and the inset graph at top left corner [44]

The characterization of piezoresistive behavior of pressure sensor can be seen from Figure 2.40. The relative conductance was given and the sensitivity was reported to be 13.4 kPa^{-1} . The cyclic test result was given in the inset and pressure sensor showed stable response during 100 cycles. In addition to that hysteresis of pressure sensor was calculated and it was not more than 9% over the whole measurement [44].

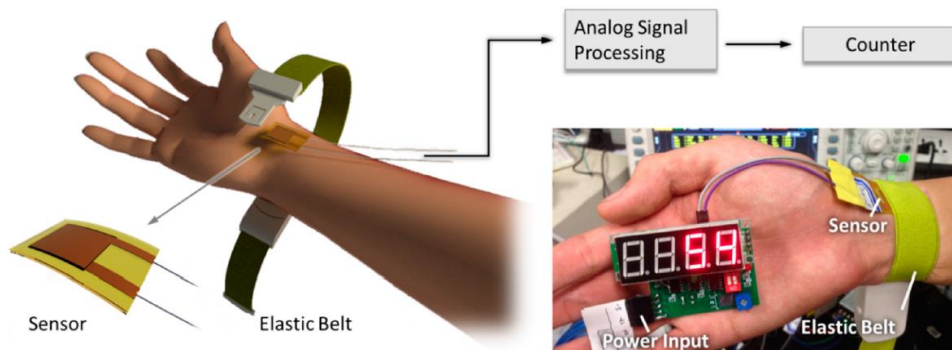


Figure 2.41 Illustration of designed heart monitoring system and inset shows the components of the device as a pressure sensor, an elastic band and a module [44]

Heart rate monitoring device can be seen from Figure 2.41. The designed device consisted of three components as a sensor, an elastic band and a module. The sensor was placed onto the wrist and an elastic band was wrapped onto the wrist and the module monitored the data [44].

To summarize, the aim of the study was to design the pressure sensor from CB/SR nanocomposite to monitor the heart rate. By using the spin coating method, CB/SR nanocomposite was produced and a sensor system was designed. Furthermore, the piezoresistive properties were characterized by measuring cyclic behavior and the sensor was found suitable for heart rate monitoring [44].

Shang et al., investigated the electrical and compressive electromechanical properties of carbon black (CB) filled silicone rubber (SR) composites[30]. In the first step, CB and silane were mixed. Then, SR was dissolved in toluene. In the next step, CB-silane mixture and SR were mixed by mechanical and ultrasonic mixer. The curing agent was added to the mixture after solvent evaporation composites were vulcanized [30].

SEM was used in order to investigate the morphology of the CB/SR composites. Electrical measurements were done by an electrometer and a digital multimeter and pressure was applied by a mechanical testing system [30].

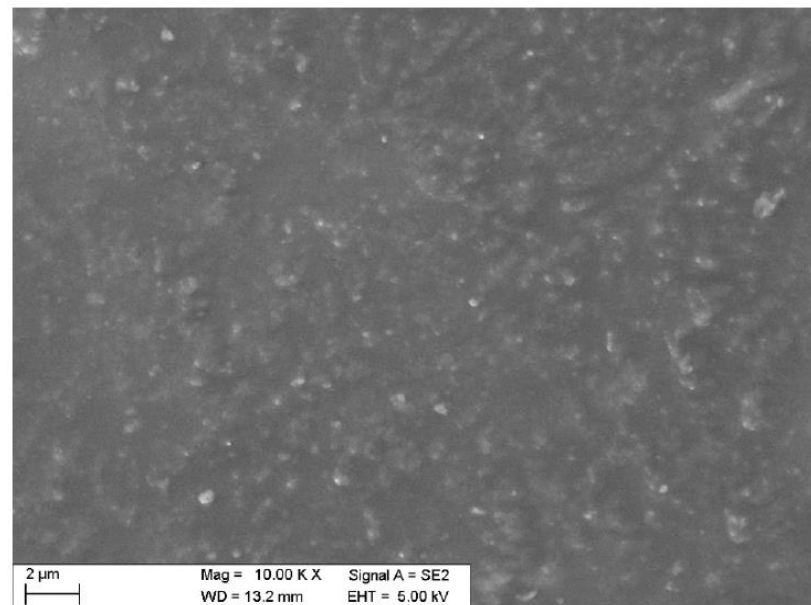


Figure 2.42 SEM image of CB/SR composite [30]

Morphology of CB/SR composite can be seen from Figure 2.42. The grey color denotes the SR matrix and light grey denotes the CB particles that were homogeneously dispersed into the matrix [30].

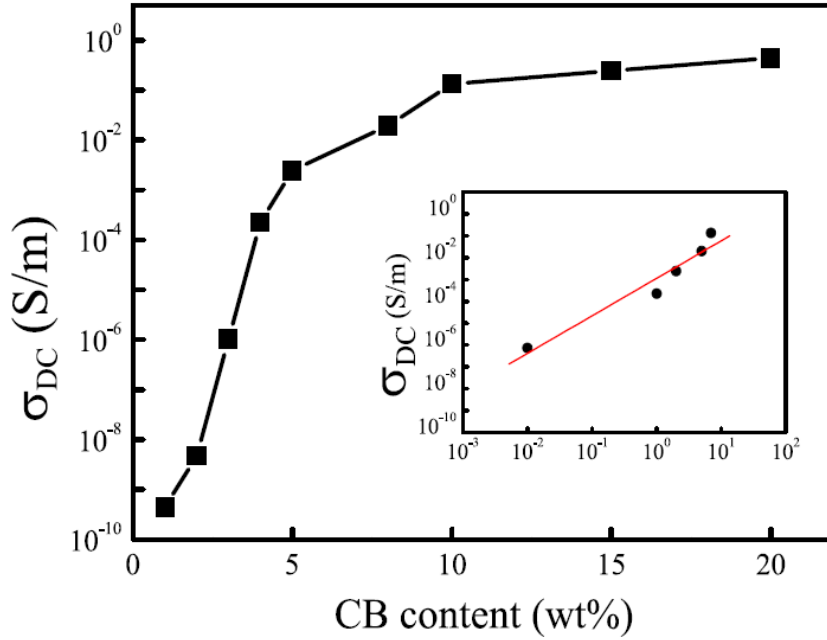


Figure 2.43 Percolation threshold of CB/SR composites [30]

The percolation graph of CB/SR composites can be seen in Figure 2.43. The graph gives the conductivity as a function of CB wt%. As can be seen, at the beginning, addition of CB filler (1-3 wt%) led to the formation of conductive network and conductivity increased. The most drastic change in conductivity was observed between 3-5 wt%. This region can be given as percolation region. After a certain point, 10-15 wt%, even though CB concentration was increased, change in conductivity was almost constant. In the study, 4-20 wt% CB containing samples were selected for the electromechanical characterization [30].

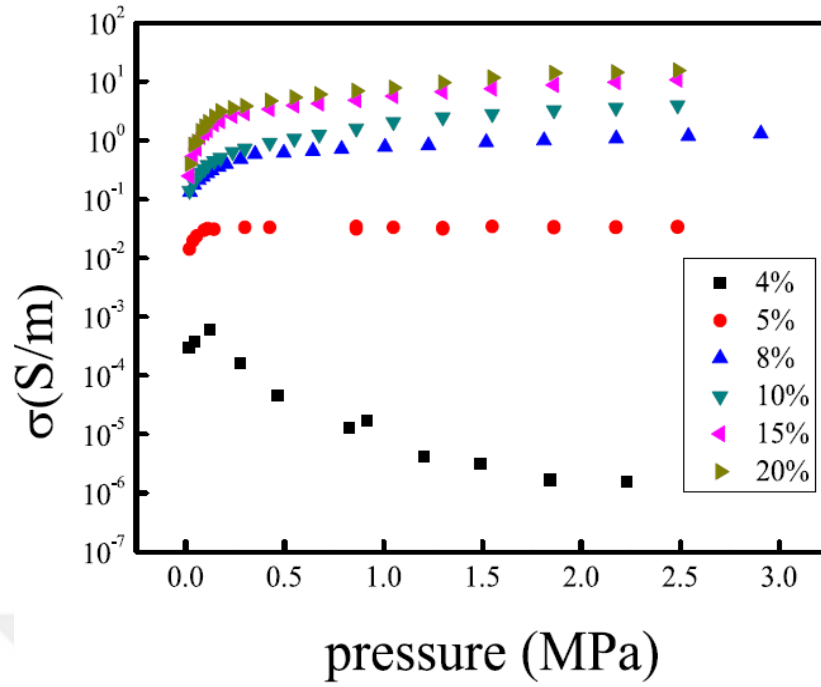


Figure 2.44 The conductivity of composites under pressure and each symbol represents the CB ratio in the composites [30]

The conductivity of the composites as a function of pressure can be seen in Figure 2.44. As seen, at low-pressure values, all composites showed increase in the conductivity. On the other hand, at higher pressure values, various responses were observed depending on the filler content. While 4 wt. % CB composite showed positive piezoresistivity, 5 wt% CB containing sample showed almost constant response. Other samples (8- 20 wt. % CB) showed slight increase when the pressure was increased [30].

As seen from Figure 2.44 depending on the filler content, there is a critical pressure value for each sample. Magnitude of the change in conductivity varies before and after critical pressure value. Since the density of conductive networks at 4 wt% CB is lower and network is not stable, after critical pressure electrical response totally changed. Theoretically with the increase in CB content, number of conductive networks increases and system becomes more stable. The stability of the conductivity under compression affects the formation and destruction of conductive networks. For 5 wt. % CB filled sample, regardless of the magnitude of the applied pressure, destruction and formation of the conductive networks took place simultaneously and conductivity did not change significantly under pressure [30].

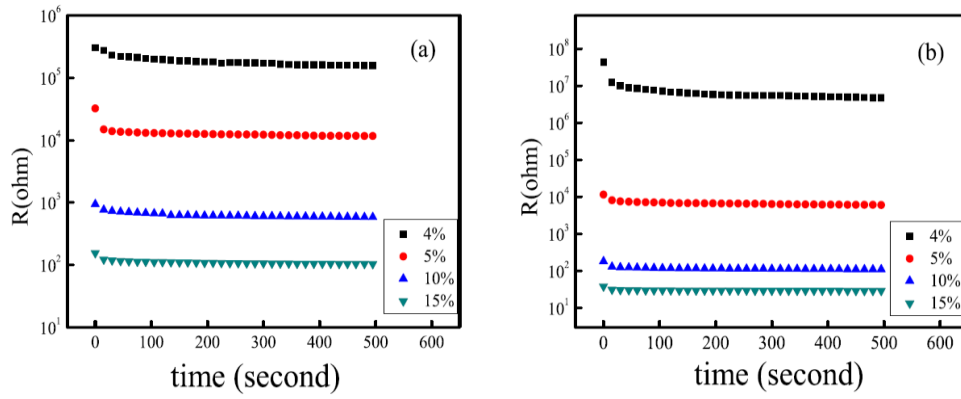


Figure 2.45 The creep behavior of resistance of composites with different CB contents under a) 0.1 MPa, b) 0.75 MPa pressure

Figure 2.45a,b show the creep behavior of resistance of composites with different CB contents. In order to understand the resistance change under constant pressure values, creep tests were carried out. Figure 2.45 shows change in resistance under constant pressure values (0.1 and 0.75 MPa) as a function of time. These pressure values were chosen because 0.1 MPa is lower than critical pressure and 0.75 MPa is higher than critical pressure of all samples. All samples showed decrease in resistance at the very beginning process then showed a stable response [30].

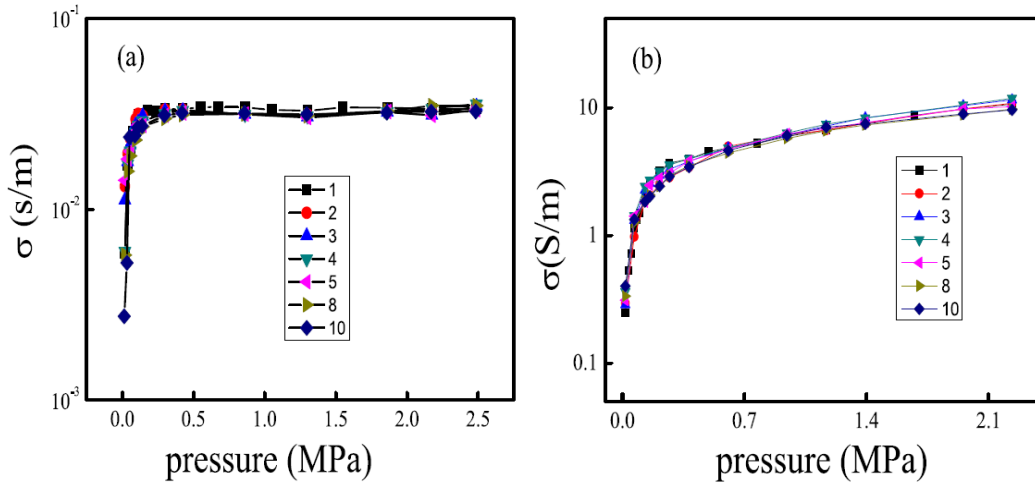


Figure 2.46 Conductivity of (a) 5 wt% (b) 15 wt% CB containing SR composites as a function of pressure under cyclic deformation (each symbol represents the number of cycles) [30]

In piezoresistive materials, reversibility is crucial. In the study, to examine the effect of filler content on reversibility was analyzed by cyclic tests for 5 and 15 wt% CB containing SR composites. As seen from Figure 2.46 both composites showed great repeatability [30].

To summarize, in this study, electrical, electromechanical and morphological properties were studied. The percolation region and optimum CB/SR composition were determined. Electromechanical properties were measured under pressure and critical pressure values were observed for each sample. In addition to these, electromechanical reversibility of the composites was measured by cyclic tests for ten cycles. It was reported that, all samples showed great reversibility due to the silicone matrix [30].

For the fabrication of piezoresistive pressure sensors, another material is the polyurethane sponges (PUSs). The interesting study was carried out by Wu et al.. They have developed flexible, versatile, highly sensitive and low-cost pressure sensors by creating micro-cracks in the sensor morphology inspired by spiders that are very sensitive to vibrations due to the morphology of their leg joints. For the determination of change in conductance, slit system of spiders (Figure 2.51) was taken as a model. CB conductive filler was used for their rigidity and spherical structure. In the study commercial product polyurethane sponges (PUSs) were used as the matrix. PUSs were dipped into the CB+ and CB- two oppositely charged suspensions respectively. Dipping was repeated 5, 10, 15, 20times and process was named as "*natural polymer-mediated water-based layer by layer (LBL) assembly*." Conductive silver was coated on the both sides of CB/PUS composite as electrodes and copper wires were connected to the silver to get current data under compression (Figure 2.47) [17].

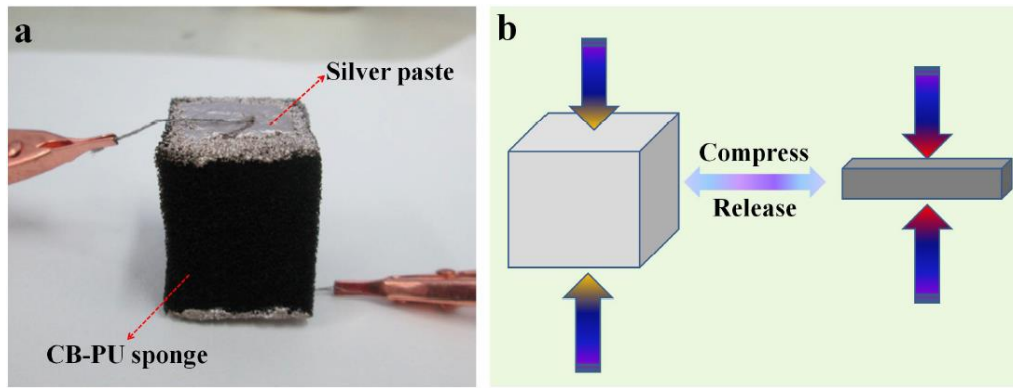


Figure 2.47 Piezoresistive CB/PUS pressure sensor a) photograph that coated with silver and b) compressive test illustration [17]

The piezoresistive characterization was measured by a two-point measurement source meter and tensile test machine for electrical and mechanical measurements, respectively. The researchers claimed that this was the first study in the field of bio-inspired pressure sensors that are versatile with high sensitivity by using very cheap materials with easy processing [17].

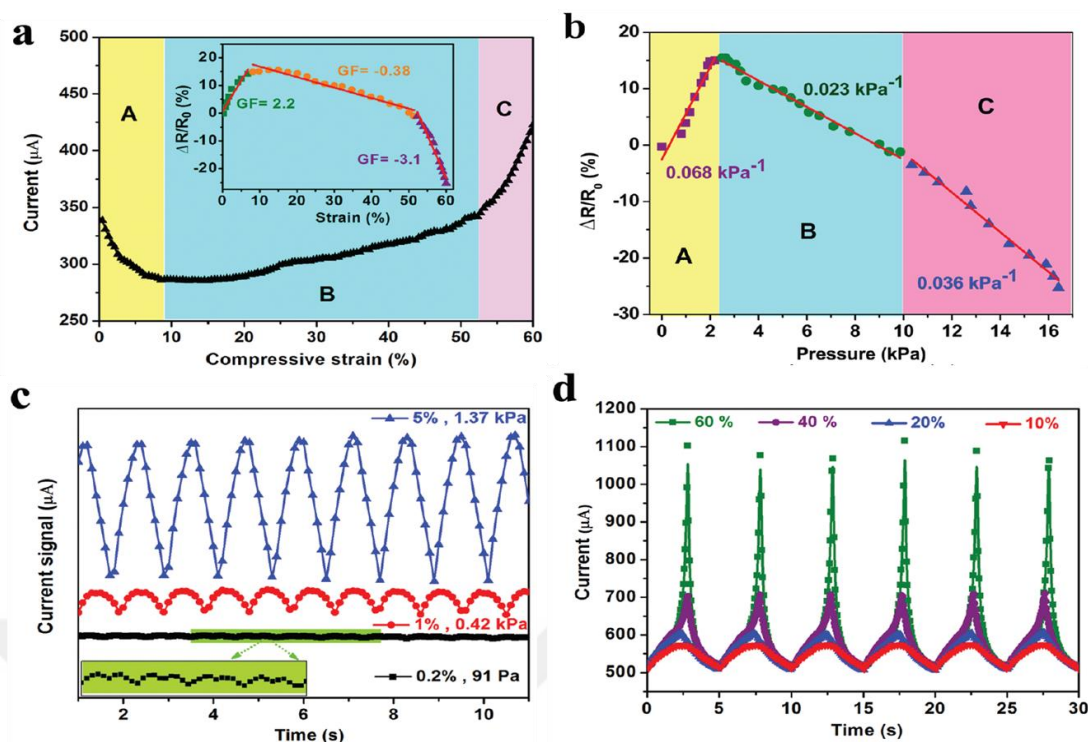


Figure 2.48 a) Current change in CB/PUS sensor as a function of compressive strain and variations in GF for each region (inset). (b) Relative resistance change under pressure. Cyclic electromechanical test (c) for low range (0.2-5 %), (d) high range (10-60 %) of compressive strain values [17]

As shown in Figure 2.48 electromechanical behavior of CB/PUS (15 LBL) composite was measured at a constant voltage and current was monitored until 60% compressive strain. As seen, there are 3 basic regions. In the first region (between 0-9 % compressive strain), electrical resistance increases. This behavior was attributed to the separation of micro-cracks in CB layers as given in SEM images from Figure 2.49 [17].

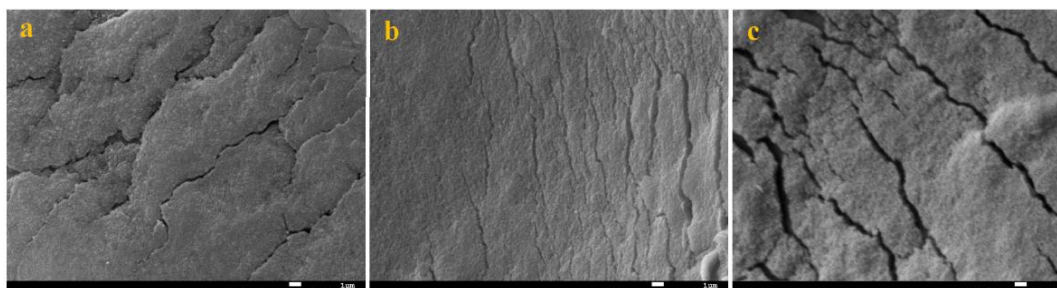


Figure 2.49 Micro-crack propagation under compressive strain at (a) 0 %, (b) 20 %, (c) 40 %, magnification: 4000X [17]

In the second region (between 9-52 % compressive strain), resistance decreased because of the formation of new conductive networks. In the third region (above 52% compressive strain) the resistance decreased since high deformation rates caused to increase the interaction between CB and PUS. Gauge factors (GF) of composite for three-stage were calculated and given in Figure 2.48a inset. In the first and third regions or at low and high compressive strain values sensitivity of the sensor was very high compared to the second region [17].

In Figure 2.48b, sensitivity of CB/PUS composite was investigated in terms of relative resistance change as a function of pressure. The change in sensitivity was examined in three regions. In the A region, relative resistance increased with an increase in pressure and positive piezoresistive behavior was observed. In this region, micro-crack formation caused the increase in resistance. In the B and C regions, with the increase in pressure value response of the sensor changed and relative resistance decreased and showed negative piezoresistive behavior. The decrease in relative resistance caused by the increase in contact area between CB layers and PUS [17].

In Figure 2.48b, electromechanical properties of CB/PUS sensor was investigated under different compressive strain values. Depending on the compressive strain ratio, current, resistance and also sensitivity limits of sensor was changed and very low pressure value was determined by sensor system. To specify the working range of the sensor, the high compressive strain rates were studied as shown in Figure 2.48d. Each strain rate shows different intensities and signal peaks. With the increase in compressive strain value, peak became sharper and higher conductance value was obtained. This behavior led to an increase in the ability of the sensor to determine the maximum pressure value [17].

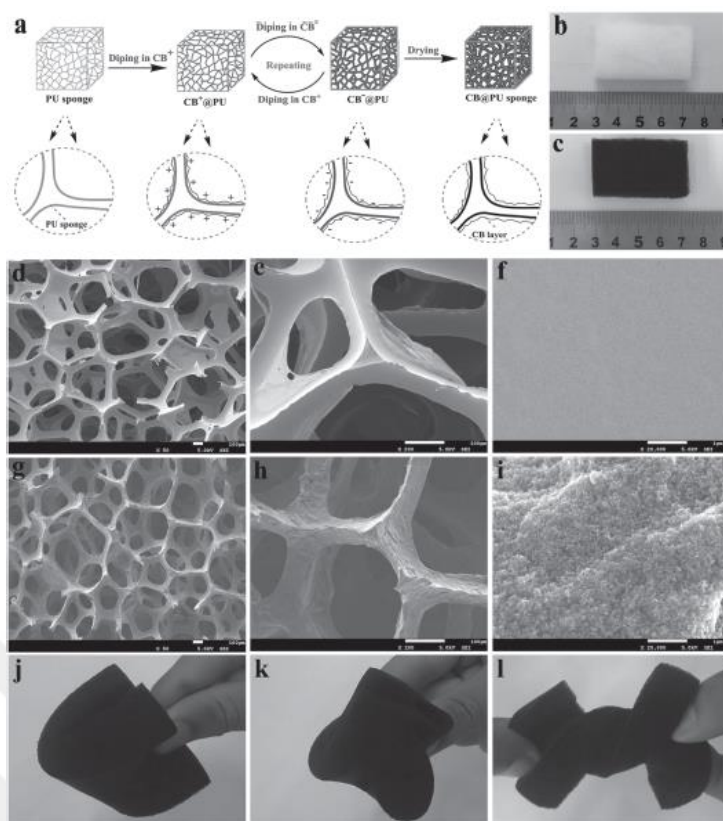


Figure 2.50 a) Fabrication process of CB/PUSs. b) Images of a commercial PUS. c) CB/PUS (15 LBL). d-f) Commercial PUS and g-i) SEM images of CB/PUS. Magnification of SEM images d) and g) 50x, e) and h) 200x, f) and i) 20,000x, and images of sponges to show their ability to be j) bent, k) compressed and l) twisted [17]

It is clearly seen from SEM images in Figure 2.50d,e that PUS has a 3D open porous structure. After dipping of PUS in CB solutions, surface morphology was changed and CB particles deposited on PUS. To express the ability of sponges to be j) bent, k) compressed and l) twisted digital photos were taken [17].

The sensibility of CB/PUS sensor to small and large range motions were gained by creating micro-cracks in the coating layer morphology as seen from Figure 2.51c,d. When force was applied to the sensors, micro-cracks were created in the CB layers and after removing the force the gaps between cracks were closed. The change in gaps (Figure 2.51b) between crack edges under continuous loading- unloading cycles resulted in variations in the conductance even in the case of slight movements [17].

As known with the increase in applied force, compressive stain will also increase and samples deform more. As a result of this recover ability and sensing performance might change. (Figure 2.51,i) [17].

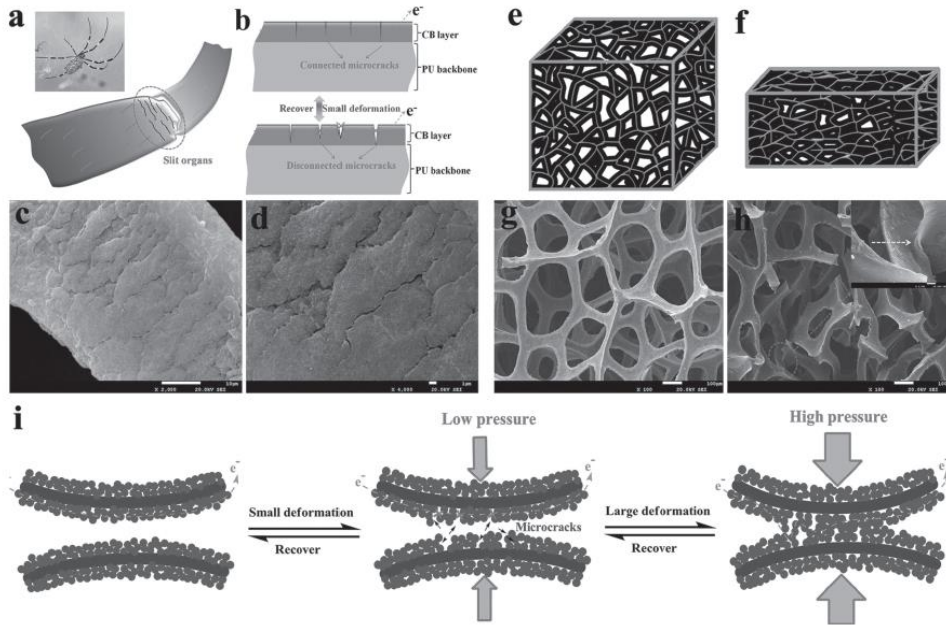


Figure 2.51 a) Illustration of "crack shaped slit organs" of a spider. b) Connection and disconnection of micro-cracks in CB layer under small deformation values. SEM images of micro-cracks formation c) 2000x and d) 4000x. e,f) Schematic illustrations for high compression rate deformation of CB/PUS. SEM images of g)uncompressed and h) compressed CB/PUS, mag. 100x. i) Formation and destruction of conductive networks during cyclic deformation [17]

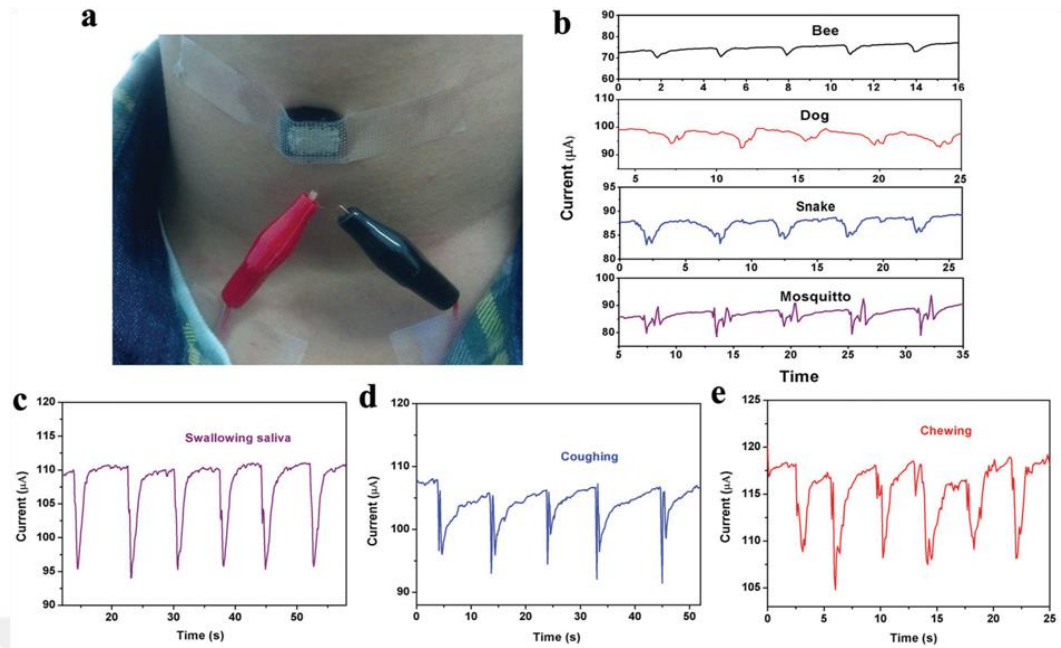


Figure 2.52 a) Digital image of CB/PUS throat sensor, current signal during b) speaking different words with time, c) swallowing saliva, d) coughing, e) chewing [17]

After determination of the sensing behavior of CB/PUS composite, some real case studies were carried out. In these studies, small and large scale movement monitoring were investigated. Small scale analysis and monitoring were carried out by throat, finger and pulse patches. Large scale analysis were carried out by a waistband [17].

One of the capabilities of the produced CB/PUS composite was the determination of small-scale motions. As given in Figure 2.52a throat patch sensor was placed on the neck to observe the muscle motions on throat. The changes in current were monitored during speaking. Since pronunciation of different words cause differences in current patterns due to the motions of various muscles; in each trial different words were chosen. As obvious from the Figure 2.52b cyclic performance of the system was found good for all cases. In addition to those, the change in resistance was monitored during swallowing saliva, coughing and chewing in Figure 2.52c-f. Characteristic response was obtained for each action. From these results, it can be concluded that; this systems can be used to recognize human's activities [17].

In summary, the study proposed to produce low-cost, versatile, flexible and highly sensitive pressure sensor by using water based LBL method. Highly sensitive sensor was gained by creating micro-cracks on CB layers. Due to these micro-cracks in the structure, sensor responded to small and large scale motions in a short time and voice recognition and health monitoring devices could be potential applications [17].

The other polymeric material that was used for the piezoresistive pressure sensors is poly(styrene-*b*-ethylene-*ran*-butylene-*b*-styrene) (SEBS). Kuester et al., determined the most appropriate processing conditions to obtain carbon black filled poly(styrene-*b*-ethylene-*ran*-butylene-*b*-styrene)(SEBS) composites and investigated their electrical properties [101]. In the study, SEBS polymer with 30% polystyrene content and CB (surface area is 1000 m²/g) were used as an insulating matrix and filler, respectively. For the production of CB containing SEBS composites torque rheometer was used. After mixing process, compression molding method was used to obtain films. The processing parameters were specified as 230 and 260 °C temperature, 7 and 15 min. mixing time and 50 and 150 rpm rotation speeds with different CB concentrations. For the characterization of composites 7 wt% CB containing SEBS composite was chosen [101].

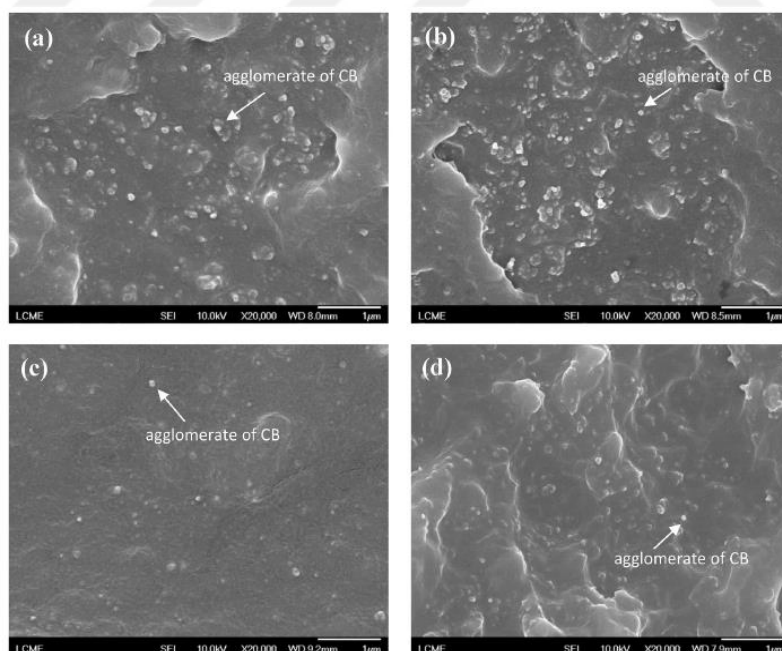


Figure 2.53 SEM images of CB/SEBS composites at different processing conditions. a) 230 °C, 50 rpm and 7 min; b) 230 °C, 50 rpm and 15 min; c) 230 °C, 150 rpm and 7 min; d) 260 °C, 150 rpm and 15 min. [101]

Morphological properties of the composite were characterized by SEM. As seen from Figure 2.53 processing conditions directly affected the dispersion of CB filler into the matrix and also electrical conductivity as given in Table 2.3. When the processing temperature and speed were kept constant and residence time was increased (Figure 2.53a-b), electrical conductivity increased (Table 2.3) because CB filler had more time to be dispersed and to form new conductive networks (But still CB agglomerations exist into the matrix). If rotation speed was changed (Figure 2.53a-c) and the temperature and time were kept constant, dispersion of CB increases as supported by SEM image (Figure 2.53c) but in terms of electrical conductivity, both composites had almost the same value (Table 2.3) with low rotation speed. High rotational speed can help for better dispersion of CB and lead to the destruction of existing conductive networks. When all processing parameters were changed, not any dominant effects on morphological and electrical properties were observed as seen from Figure 2.53d and Table 2.3. The most appropriate processing conditions in terms of both electrical and morphological properties were selected as 230 °C, 50 rpm and 15 min [101].

Table 2.3 : Electrical Conductivity of 7 wt% CB/SEBS composite under different processing conditions [101]

System	Additive (wt.%)	Processing parameters			Specific energy input (J g ⁻¹)	Electrical conductivity (S cm ⁻¹)
		Temperature (°C)	Processing time (min)	Rotational speed (rpm)		
SEBS	0	230	15	50	1200	$(2.5 \pm 0.7) \times 10^{-16}$
SEBS/CB	7	230	7	50	844	$(2.7 \pm 0.4) \times 10^{-3}$
SEBS/CB		230	15	50	1529	$(5.1 \pm 0.2) \times 10^{-2}$
SEBS/CB		230	7	150	2187	$(3.0 \pm 0.1) \times 10^{-3}$
SEBS/CB		230	15	150	3560	$(2.1 \pm 0.1) \times 10^{-2}$
SEBS/CB		260	7	50	546	$(2.3 \pm 0.3) \times 10^{-2}$
SEBS/CB		260	15	50	928	$(3.4 \pm 0.5) \times 10^{-2}$
SEBS/CB		260	7	150	1358	$(5.2 \pm 0.3) \times 10^{-2}$
SEBS/CB		260	15	150	2165	$(5.1 \pm 0.7) \times 10^{-2}$

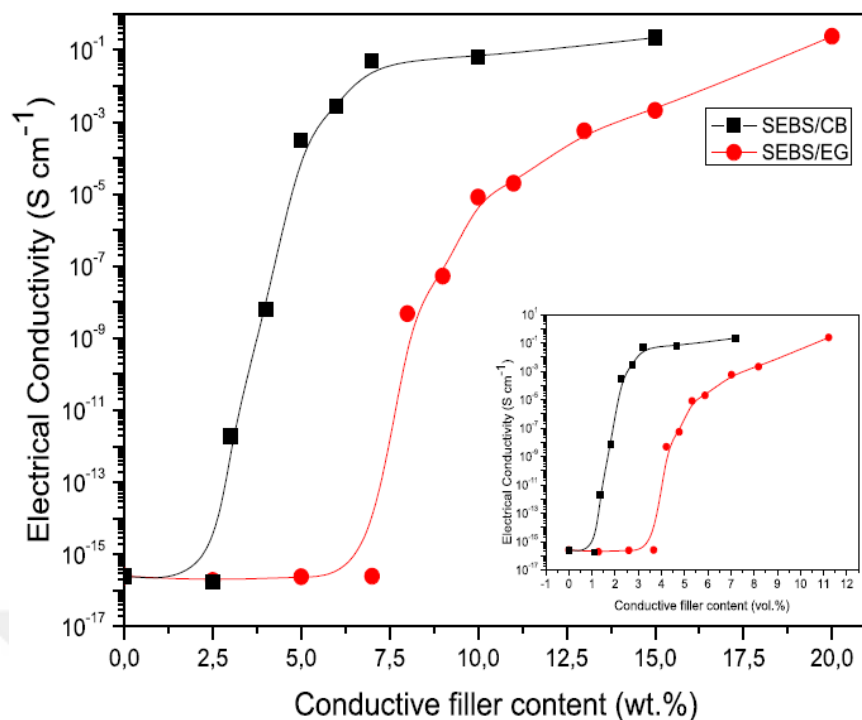


Figure 2.54 Electrical conductivity of CB/SEBS (black squares) composites as a function of CB filler content [101]

The percolation threshold of CB/SEBS composites was given in Figure 2.54. CB/SEBS composites were not electrically conductive between 0 to 4 wt%. When CB concentration was between 4 to 6 wt%, a sudden increase in conductivity was observed due to the connected conductive network. At 6 wt% CB concentration, composites reached relatively high conductivity levels and after 6 wt% CB further addition of CB did not change the conductivity of the system. This region is called saturation region. For CB/SEBS composites, the percolation threshold was determined as 5 wt% CB [101].

To summarize, in the study, CB conductive filler and SEBS thermoplastic elastomer were used and by changing processing parameters such as temperature, mixing time and rotation speed. Percolation threshold was determined as 5 wt% CB and the most appropriate parameters were determined as 230 °C processing temperature, 50 rpm rotation speed and 15 min mixing time in terms of morphology and electrical conductivity [101].

Another SEBS based sensor was developed Moreno et al.. They investigated the relation between electrical conductivity and compressive strain. For this purpose carbon black (CB with 250 μ m average size) and poly(styrene-b-ethylene-ran-butylene-b-styrene) (SEBS 33/67 S/EB) were chosen [47].

The CB/SEBS composites were prepared by using an internal mixer. For the electrical and electromechanical characterization, two probe technique and tensile testing machine were used [47].

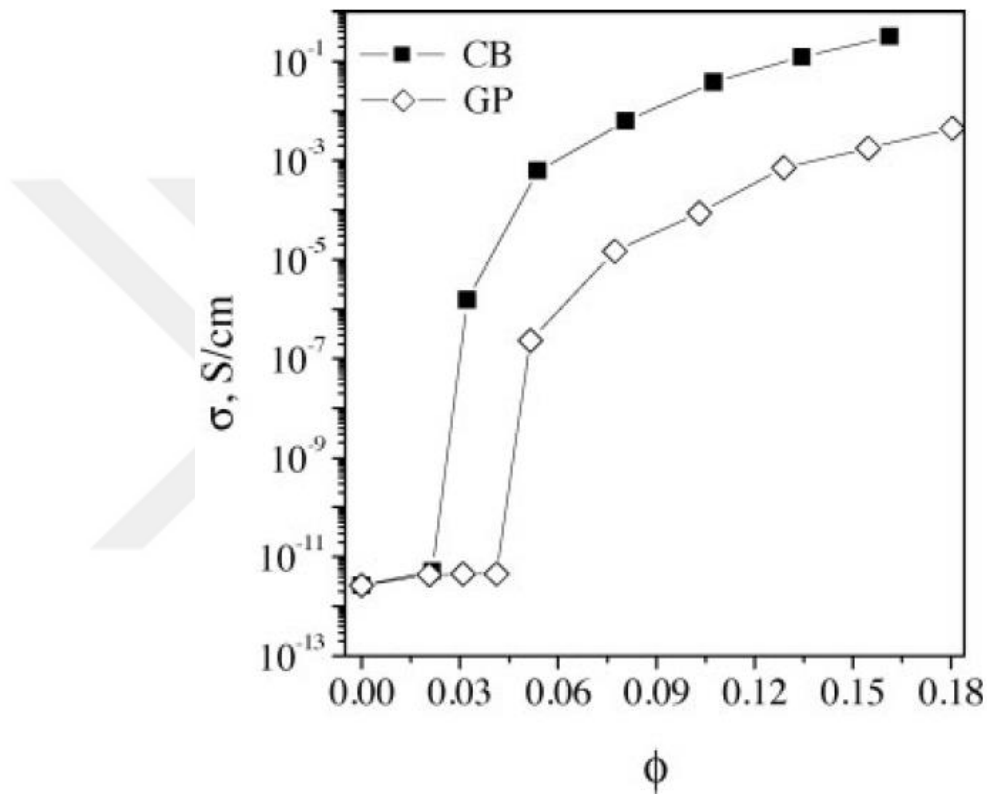


Figure 2.55 Percolation threshold of CB/SEBS composites (electrical conductivity versus volume fraction of CB) [47]

The electrical conductivity of composites was explained by using the percolation theory as given in Figure 2.55. The graph gives information about conductivity as a function of volume fraction of CB. At low filler concentration, below the 0.032 v % CB, conductivity changed slightly. The sudden increase in conductivity was seen at 0.032 v% CB due to effective conductive network formation. After this point, electrical conductivity increased very slowly [47].

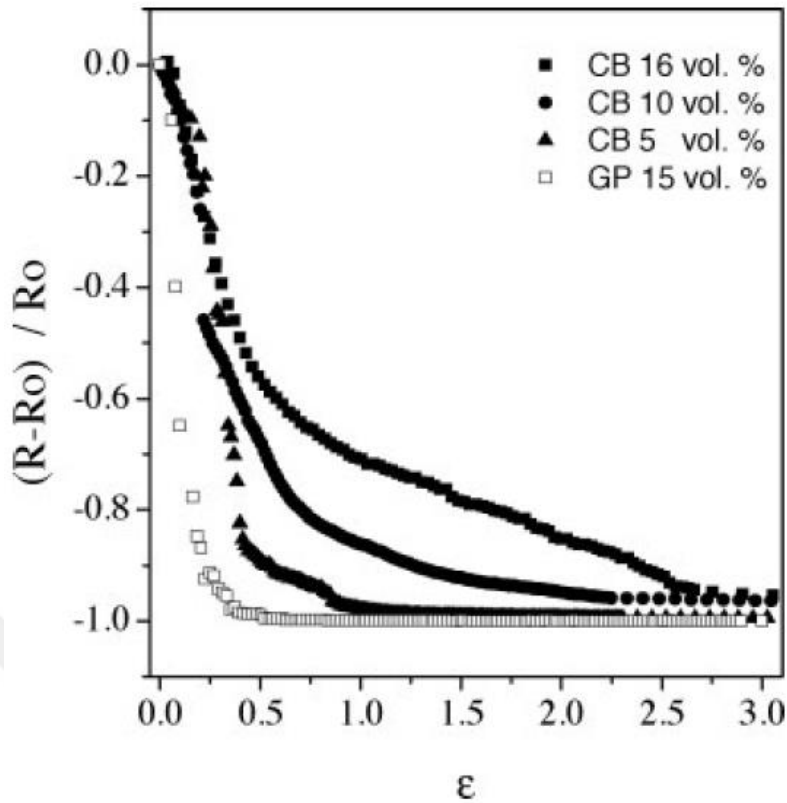


Figure 2. 56 The effect of compressive strain on the piezoresistive behavior of CB/SEBS composites [47]

Piezoresistive behavior of composites can be seen in Figure 2.56 as relative resistance vs. compressive strain for various CB composites. All composites show a decrease in relative resistance when the compressive strain increases. From the electromechanical response sensitivity and working range could be determined. In the range of 0 to 1 % compressive strain, 5 v% CB/SEBS composite showed the biggest drop in the relative resistance that is an indication of maximum sensitivity. On the other hand in the range of 1 to 2.75% compressive strain values, relative resistance change in 16 v% CB/SEBS composite is maximum [47].

As a summary, CB/SEBS was prepared by using an internal mixer. The electrical and piezoresistive properties of composites were investigated. Percolation threshold was determined as 0.032 v% CB concentration. For the piezoresistive characterization, different CB containing composites were chosen. 5 v% CB showed the highest sensitivity. It was clarified that depending on the filler content and compressive strain value, the working range and sensitivity of materials show changes [47].

2.4. Carbon Nanofiber Filled Elastomeric Piezoresistive Pressure Sensors

2.4.1. Carbon Nanofibers

Carbon nanofibers (CNFs) are one of the common carbonaceous nanomaterials in the form of discontinuous fibers with high specific surface area. CNFs can be found in various geometries including spiral, straight and helical. The diameter of CNFs is in the range of 50–200 nm and have aspect ratio (length/diameter) higher than 100 [78, 152-156]. Due to high electrical conductivity, chemical stability and superior mechanical properties, CNFs are commonly used for fabrication of polymer composites with good mechanical and conductive properties [157]. The electrical conductivity of CNFs is in the range of 10^3 - 10^5 S/cm [78, 155, 158, 159]. There are basically two synthesis methods for the production of CNFs. First one is based on the catalytic vapor deposition growth and the second one is the combination of electrospinning process and carbonization.

2.4.2. Production of Carbon Nanofiber

There are basically two synthesis methods for the production of CNFs. First one is based on the catalytic vapor deposition growth [152, 153, 160] and the second one is the combination of electrospinning process and carbonization [161-163].

2.4.2.1. Vapor growth carbon nanofiber production (VGCNFs)

Chemical vapor deposition is a deposition method used for fabrication of some nanoparticles under vacuum at elevated temperatures. The most important contribution of the so called process is to obtain high purity nanomaterials. This process is the most common process for the commercial CNFs. Since fibers are obtained by vapor deposition, CNFs are named as vapor grown carbon nanofibers (VGCNFs). The process is operated at elevated temperatures (400-950 °C) by using a carbon source and catalysts that can dissolve in the carbon source to constitute metal carbide. With the deposition and precipitation of formed metal carbide, graphitic structure VGCNFs are obtained [153, 160].

As a carbon source ethane [164, 165], ethylene [166], acetylene (ethyne) [167], methane [168-170], molybdenum [170] or synthesis gas (H_2/CO) [171] can be used. In addition, for the synthesis of VGCNFs various metal and alloy catalysts can be used such as nickel [169, 172], iron [167, 170, 173], cobalt [173, 174], vanadium [175] and chromium [157, 176-178].

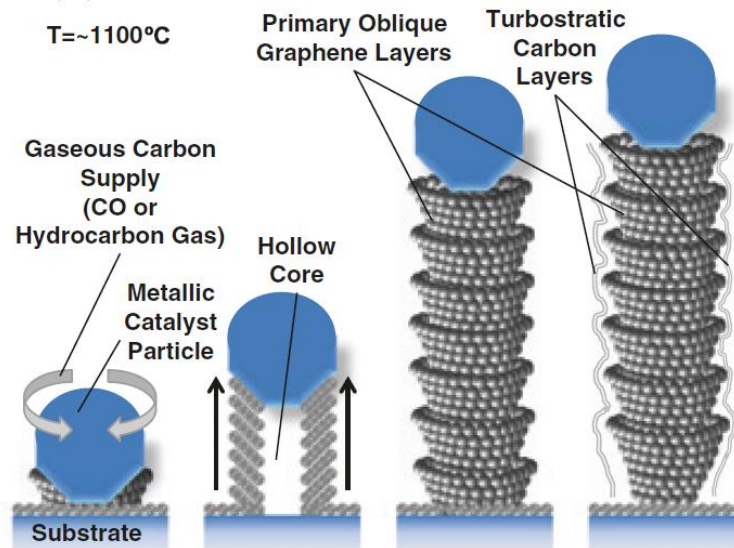


Figure 2.57 Demonstration of the synthesis [162]

The diameter and morphology of the VGCNFs are affected by the particle size and geometry of the catalyst [179]. The particle size of the catalyst is generally between 10 to 100 nm [180, 181]. Furthermore, catalyst and carbon source can change the arrangement and morphology of the layers in the VGCNFs (Figure 2.58). As a consequence of that conductivity and mechanical properties of the VGCNFs change [182].

VGCNFs can be classified depending on arrangement of graphitic layers to fiber axis [153, 180, 182, 183]

- Cup stacked/Conical/Herringbone VGCNFs (graphene layers are aligned at the tilted position) (Figure 2.58a)
- Stacked/Platelet (perpendicular alignment of the graphene layers to the fiber axis) (Figure 2.58b)

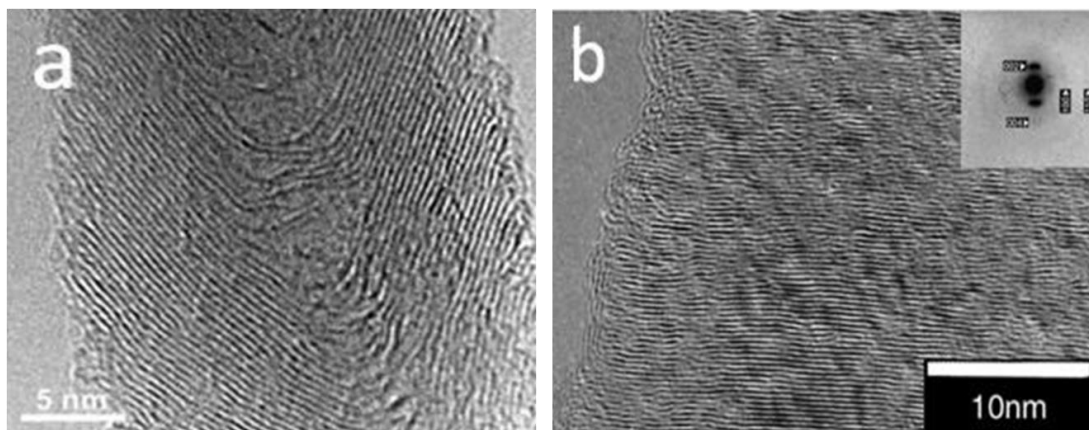


Figure 2.58 High resolution TEM images of a) cup- stacked VGCNF, b) platelet VGCNF [153, 181, 184]

The hollow core like structure of VGCNFs is formed with the folding the graphene layers through the fiber axis. The graphitic layers are placed with an angle and forms cup-stacked structure as shown in Figure 2.59a-c [182].

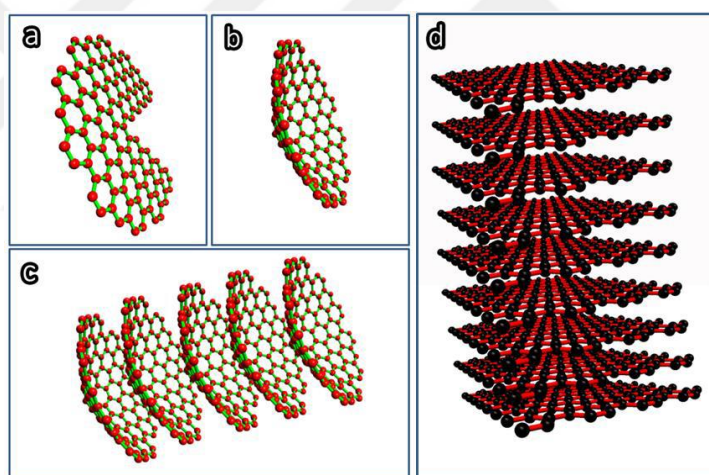


Figure 2.59 Formation of graphitic structure of a-c) cup-stacked VGCNFs, b) platelet VGCNFs [153]

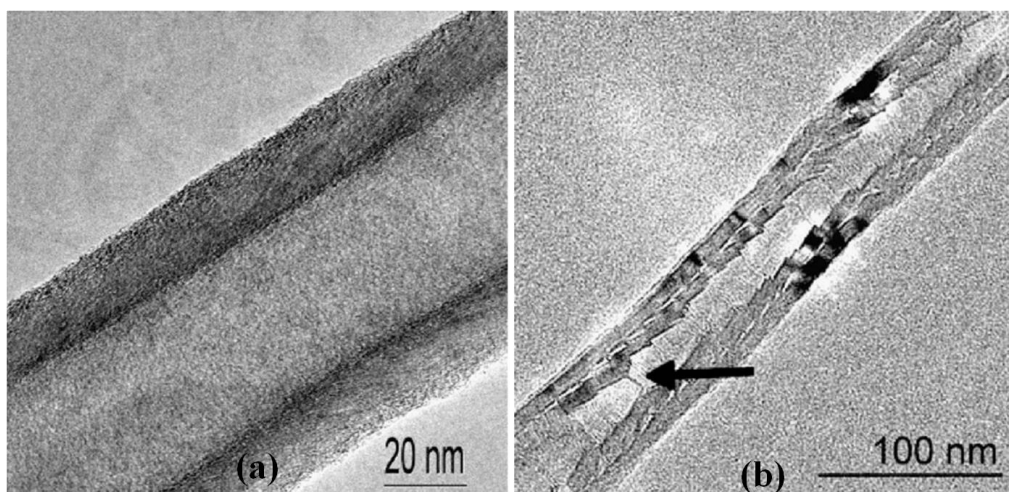


Figure 2.60 TEM image of a) single layer and b) double layer VGCNFs and the arrow shows the side walls of VGCNFs [155, 185]

VGCNFs can be comprised of a single or double layer with the stack of graphite planes as given in Figure 2.60 [185, 186]. As known graphite planes are composed of graphene layers and for VGCNFs, the distance between graphene layers are around 0.34 nm [78]. Because of that crystalline morphology, VGCNFs have good electrical conductivity.

2.4.2.2. Electrospun carbon nanofiber synthesis (ECNFS)

Electrospinning is an alternative method for the production of CNFs (Figure 2.61). This method consists of two steps as production of polymer nanofibers and heat treatment of these nanofibers to obtain CNFs. By using electrospinning system, polymer nanofibers can be produced from a polymer solution or polymer melt. For the production of nanofibers, polyacrylonitrile (PAN) [187-190], pitches [191-193], poly(vinylidene fluoride) (PVDF) [194], polyimides (PIs) [195-199], poly(vinyl alcohol) (PVA) [200-202], polybenzimidazole (PBI) [203-205], polyethyleneoxide (PEO) [194], lignin [206-208] and phenolic resins [209, 210] can be used [211]. However, PAN is the most commonly used polymer for the production of CNFs since it has a high carbon yield [160, 212]. PAN has a great spinnability and this makes it suitable for large scale production [162, 163].

The electrical, mechanical and thermal properties of CNFs are affected by the properties of polymer, solvent and processing conditions such as polymer concentration in solution, viscosity of the solution, solubility of the solvent, vapor pressure of the solvent, applied voltage, feed rate, working distance, temperature and humidity [213-216].

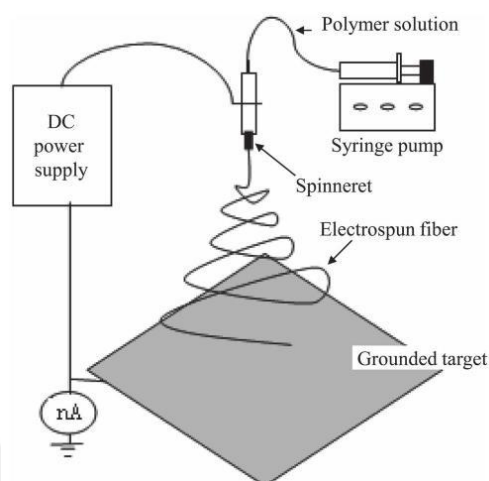


Figure 2.61 Electrospinning system for the production of nanofibers [211]

After electrospinning process, polymer nanofibers are generally in the form of nonwoven mat or web. To obtain CNFs, firstly stabilization of nanofibers are carried out and then carbonization is completed. Temperature range for the stabilization is in the range of 200-300 °C in air and for the carbonization, the temperature might increase up to 2800 °C under inert atmosphere [189, 216-221]. In addition, heat treatment conditions (temperature, atmosphere) also changes the CNFs properties such as diameter, morphology, crystallinity, purity and porosity. The weight and volume of the mats change and shrinkage is observed due to the carbonization process and diameter of CNFs decreases [153, 157, 216].

Depending on the precursor, spinning conditions and carbonization conditions morphology of the CNFs change. Although it may not be observed always, CNFs can show non-homogeneous “skin-core” structure can be seen as given in Figure 2.62.

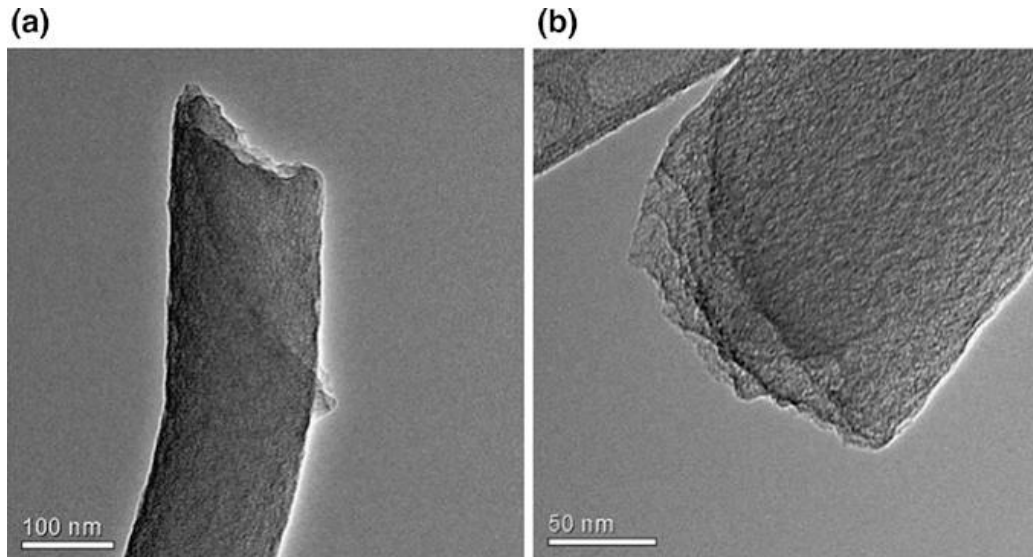


Figure 2.62 TEM image of a) outer layer, b) several layers of carbonized electrospun CNF [221]

2.4.3. Carbon Nanofiber Filled Elastomeric Piezoresistive Pressure Sensors

In this part of the study, previous studies are going to be reviewed. The review includes the piezoresistive CNFs containing elastomeric nanocomposites. In the literature, there are only a few studies in the field of piezoresistive pressure sensors that consist of carbon nanofibers (CNFs) and elastomeric matrix. In these studies PDMS was used as the polymeric matrix [18, 54]. The CNFs were vapor grown.

One of these studies belongs to Chowdhury et al..The research group investigated the piezoresistive properties of polydimethylsiloxane and VGCNFs based conductive polymer nanocomposites [54].

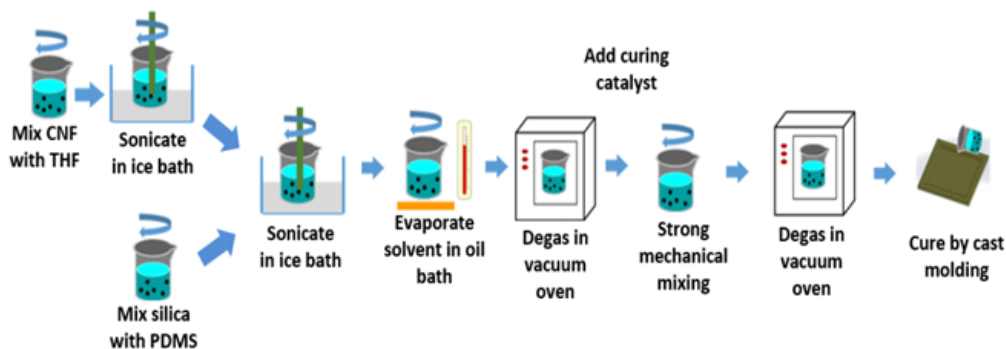


Figure 2.63 Fabrication process of CNFs/PDMS nanocomposites by using casting method [54]

In the study, PDMS and CNFs with 100 nm of average diameter were used. Nanocomposites were prepared by solution casting and tetrahydrofuran (THF) was used as a solvent. As shown in Fig. in the first step, CNFs were mixed with THF to get better filler dispersion. Meanwhile, PDMS mixture was prepared in another beaker. Then, PDMS and CNFs/THF mixture were mixed together in the ice bath until obtaining homogenous dispersion. For the evaporation of solvent, oil bath and vacuum oven were used. After that, curing catalyst was added into the media and mixed by a mechanical mixer. Followed that, the mixture was degassed in the vacuum oven, poured into a mold and cured (Figure 2.63) [54].

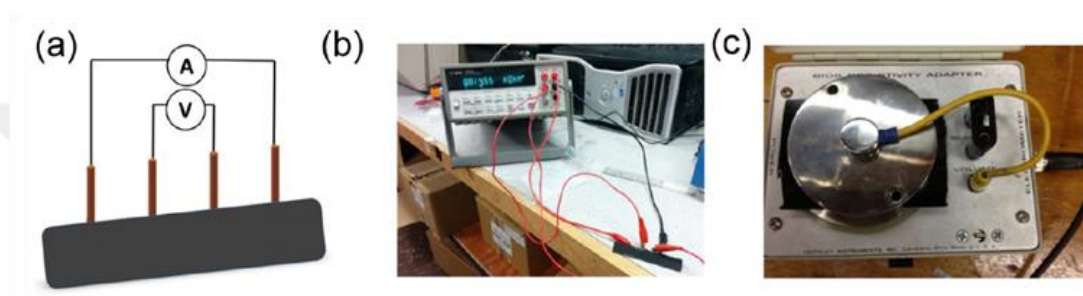


Figure 2.64 a) 4-probe technique b) set up used for 4-probe measurement c) electrometer system [54]

The electrical properties were measured by a four probe multimeter (Figure 2.64a,b) and silver paste was applied on the surface in order to reduce the contact resistance. The electrical conductivity of low CNFs containing composites was measured by an electrometer (Figure 2.64c) [54].

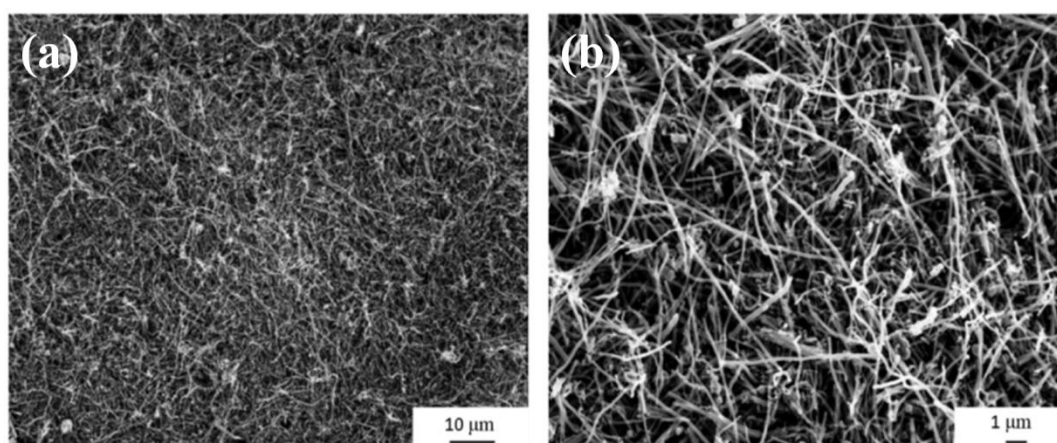


Figure 2.65 SEM images of CNFs at different magnifications [54]

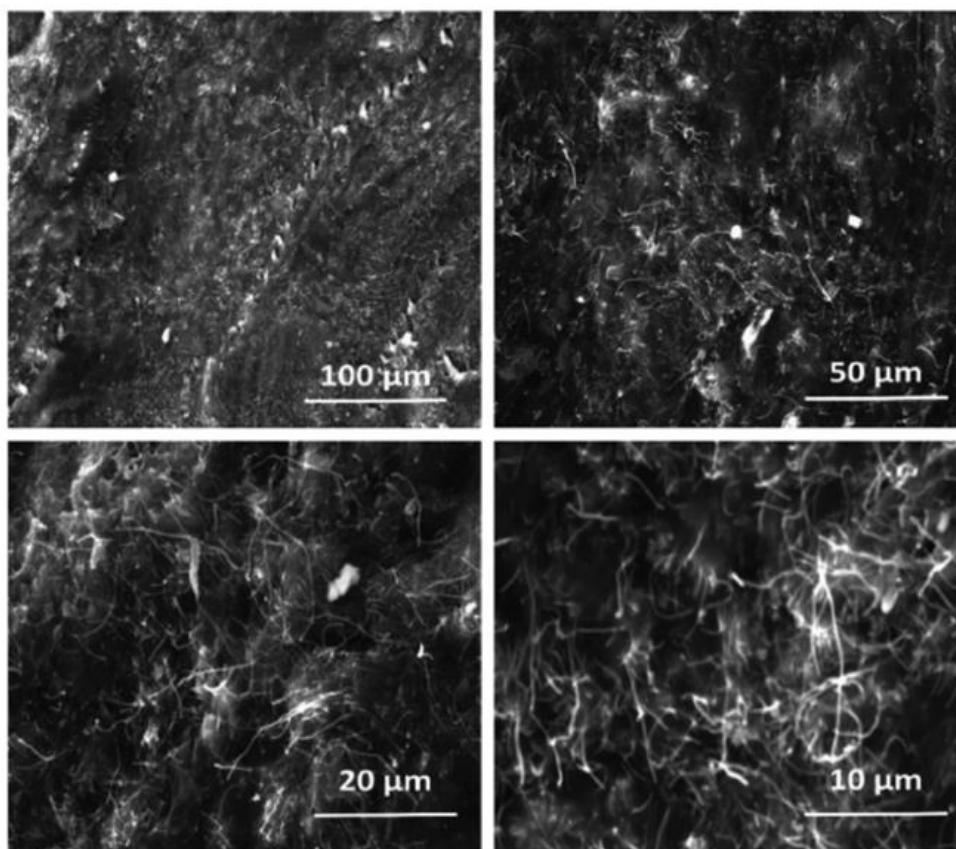


Figure 2.66 SEM images of 8 wt% CNFs/PDMS composites [54]

The dispersion of CNFs in PDMS was displayed by SEM images as seen from Figure 2.66. The black parts of images represent the PDMS matrix whereas light grey parts represent CNFs. As seen in Figure 2.66, homogeneous filler dispersion was achieved [54].

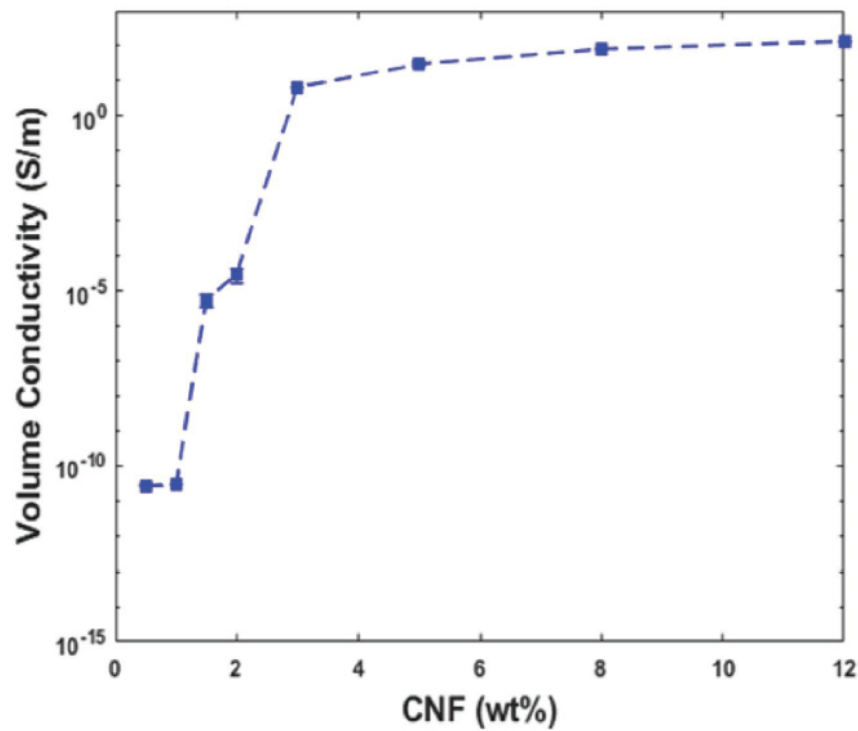


Figure 2.67 Volume conductivity of CNFs/PDMS nanocomposites [54]

In Figure 2.67, volume resistivity of CNF/PDMS nanocomposites can be seen as a function of wt% CNFs. As can be seen from Figure 2.67, concentration of CNFs affects the electrical properties of the composites. At low concentrations, there is almost no change because of the low filler content. On the other hand, the biggest change in volume resistivity was observed between 1 to 3 wt% CNFs concentrations. An increase in CNFs content supports the formation of conductive networks. After 3 wt% CNFs content change in volume resistivity is very low and system reached the saturation region due to the high filler content. The 8 and 12 wt% CNFs containing composites show excellent electrical conductivity due to the good dispersion of fillers into matrix. Due to the appropriate electrical properties 8 wt% CNFs in PDMS composite was chosen for electromechanical characterization [54].

For the piezoresistive characterization, two different composite geometries were fabricated as truncated cone and cylindrical shape. Compressive strain levels were determined as 3, 5, 10, 25%. Strain rate was 10 % stain/min [54].

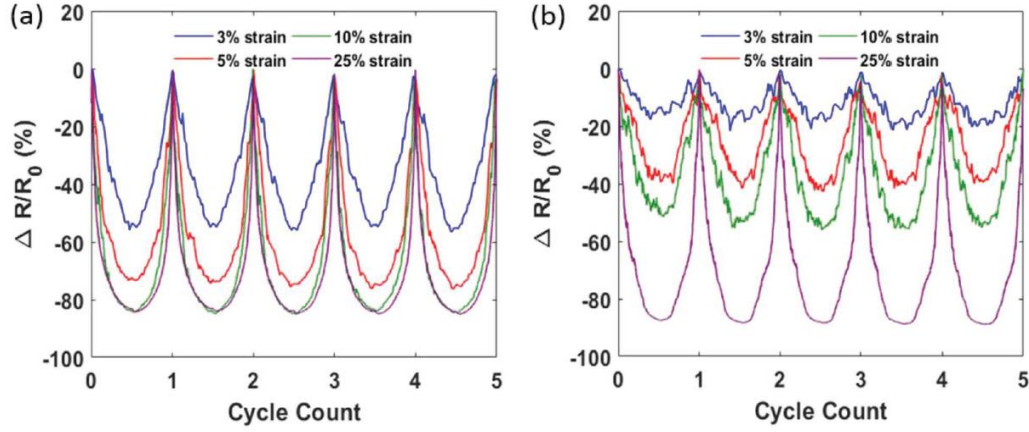


Figure 2.68 Relative resistance change under different cyclic deformation rates a) cylindrical sample, b) truncated cone sample [54]

The relative resistance change under different cyclic compression rates can be seen from Figure 2.68 for both composite geometries. When the pressure was applied, both samples showed negative piezoresistive behavior. During the unloading cycle, both samples showed positive piezoresistive behavior. Regardless of the composite geometry and compression level, all samples turn back to their initial values that are an indication of good resilience. However, cylindrical sample showed more stable response [54].

The compression level changes the piezoresistive behavior of the samples. In the case of higher level of compression, resistance change was showed to be higher. The sensitivity of the sample depending on the compression levels was determined by the Gauge factor (GF). The GFs of the cylindrical-shaped sample were given as 18.3, 14.8, 8.2, and 3.5, respectively for 3, 5, 10, 25 % compressive strain levels, as given in Figure 2.68a. The GFs of the truncated cone-shaped sensor are 6.3, 8.0, 5.5, and 3.5 for the 3, 5, 10, 25 % compressive strain level, as given in Figure 2.68b. As reported in the study, for tunable sensing capacity, various composite geometries could be used. According to piezoresistive properties (Figure 2.68a-b), cylindrical shaped samples were found sensitive at low compression levels, whereas truncated shaped samples were found sensitive at relatively high compression levels [54].

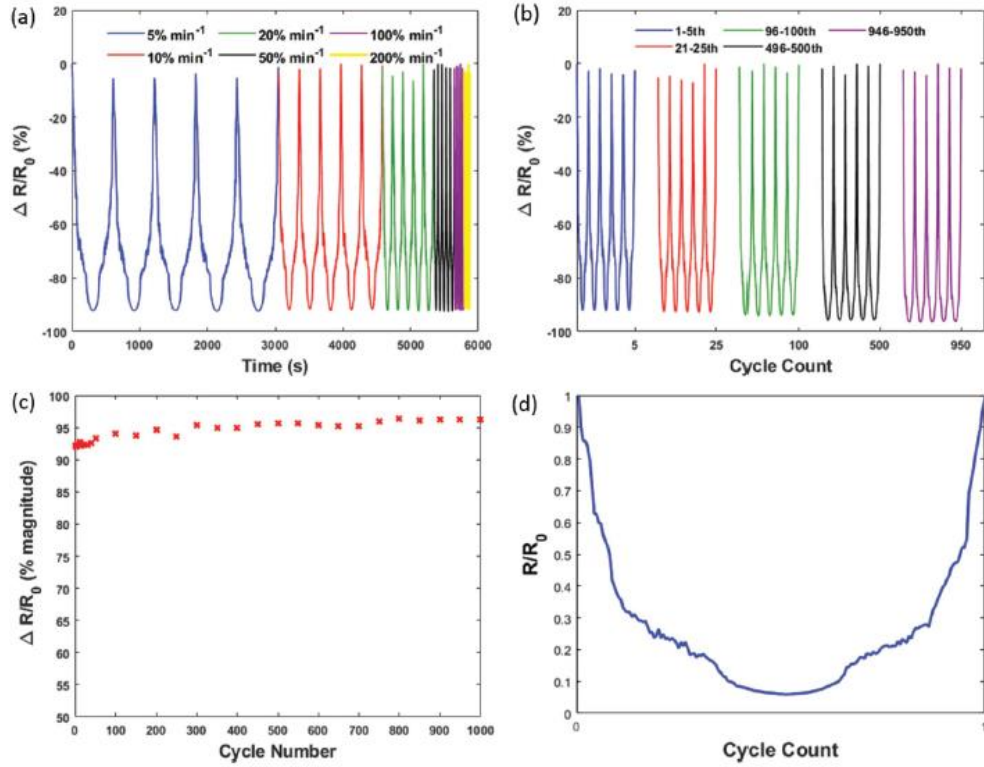


Figure 2.69 $\Delta R/R_0$ values of sensor under cyclic deformation rates a) as a function of time, b) as a function of cycle count to demonstrate the durability during 1000 cycles, c) variation in $\Delta R/R_0$ during 1000 cycles, d) R/R_0 of one cycle [54]

The piezoresistive behavior of the sample with truncated cone geometry at different deformation rates can be seen from Figure 2.69a. In all cases stable response was obtained. Little variations in relative resistance change was reported as shown in Figure 2.69b and the quantification of the change in relative resistance was almost 5 % as seen in Figure 2.69c. A single cycle was given in Figure 2.69d. After pressure was removed, the sensor returned to its initial relative resistance value with little hysteresis in other words, loading and unloading steps were almost symmetrical to each other [54].

In the study, electrically conductive flexible CNFs containing PDMS composites were prepared by solvent casting. Morphological, electrical and electromechanical properties were investigated. Two different geometrical shaped samples were fabricated and the effects of the sample shape on electromechanical properties were investigated. The cylindrical shaped sensor was found more sensitive to lower level of compression whereas the truncated cone shape sensor was reported to be more appropriate for high compression levels. Durability and stability of the sensors were determined by cyclic tests under different compression rates and compression strain levels. Totally, 1000 loading and unloading cycles were analyzed and piezoresistive behavior of sensors was found durable and stable in the long term and sensor response was reported to be independent of the compression rate [54].

In another study, Charara et al., studied the piezoresistive properties of the flexible porous CNFs/ PDMS composites. For the preparation of the porous template, brown sugar was used [18].

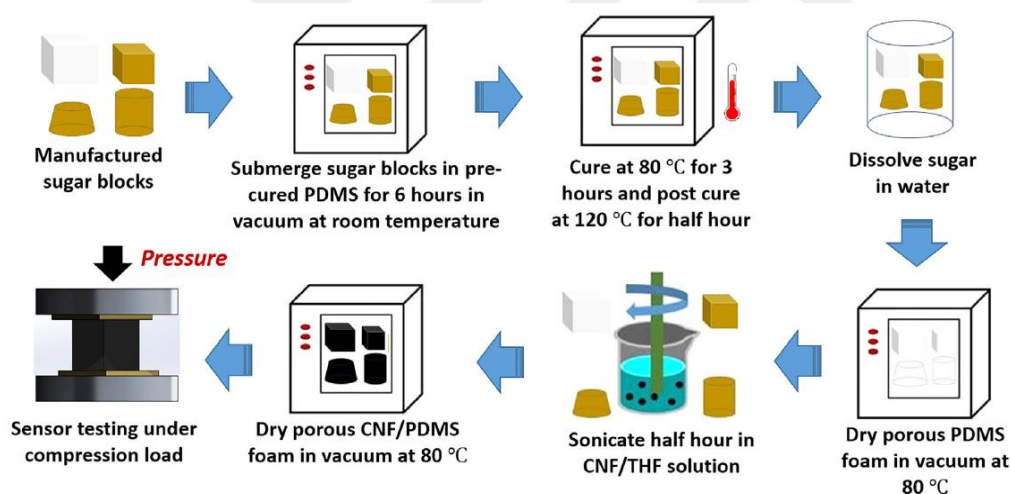


Figure 2.70 Porous CNFs/PDMS composite production [18]

Brown sugar was pressed into the mold in order to give the desired form. There were two main steps for the production of porous electrically conductive CNF/PDMS sponge composites. The first step was basically porous PDMS fabrication. Uncured PDMS was mixed with the curing agent and brown sugar template was immersed into the PDMS under vacuum to speed up the diffusion of the PDMS through the template. After a while PDMS was cured then brown sugar was removed by water as a result porous PDMS structure was obtained. The second step was the infiltration of CNF/THF mixture throughout the PDMS sponges to obtain electrically conductive composites. The process was carried out in a sonicator and after infiltration it was dried (Figure 2.70). Three different open cell conductive CNF/PDMS sponge composites were prepared (Table 2.4) [18].

Table 2.4 : The weight ratio of CNF/THF mixtures for composite production [18]

Nanocomposite type	CNF weight [g]	THF volume [mL]	CNF/THF weight to volume ratio
S1	0.07	100	0.07%
S2	0.30	100	0.3%
S3	0.70	100	0.7%

Morphological characterization of composites was made by SEM. The electrical properties of composites were characterized by using two- probe method. Both sides of sponges were coated with gold-palladium to decrease the contact resistance. For electromechanical characterization tensile test machine was used [18].

For the comparison of sensitivity between three different CNFs/PDMS sponge sensors, were tested at different deformation levels (7 to 70 %) and constant crosshead speed (0.5 mm/min). On the other hand, for the determination of the effect of test speed on piezoresistive behavior, different test speeds (0.5 to 30 mm/min) were used at a constant deformation level (70%). For the testing durability and repeatability of the sensors in the long term, cyclic tests (720 cycles) at 70% deformation level were carried out [18].

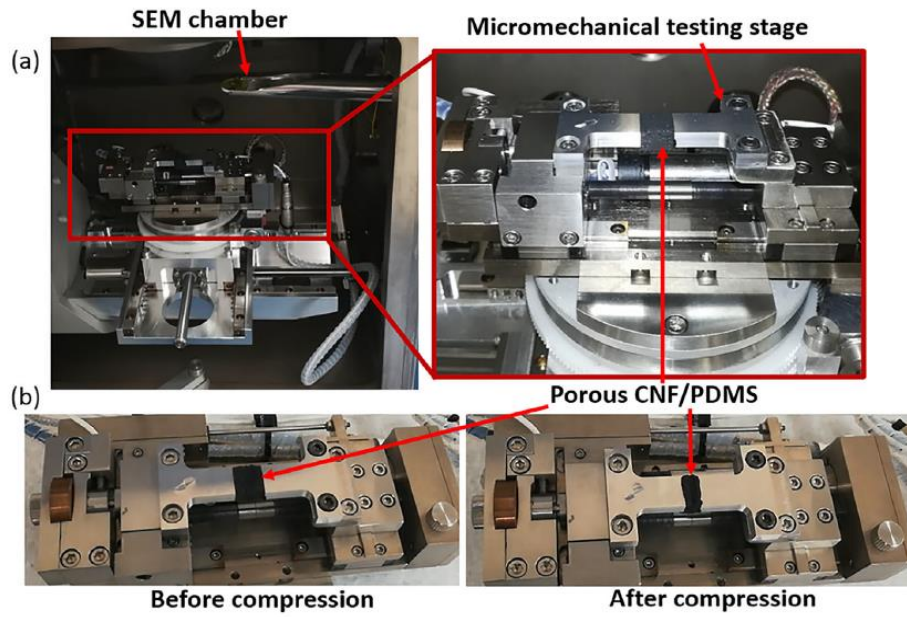


Figure 2.71 Piezoresistance measurement set up attached in SEM [18]

The morphology of CNFs/PDMS sponge composites morphology was characterized by the system in SEM as shown in Figure 2.71 [18].

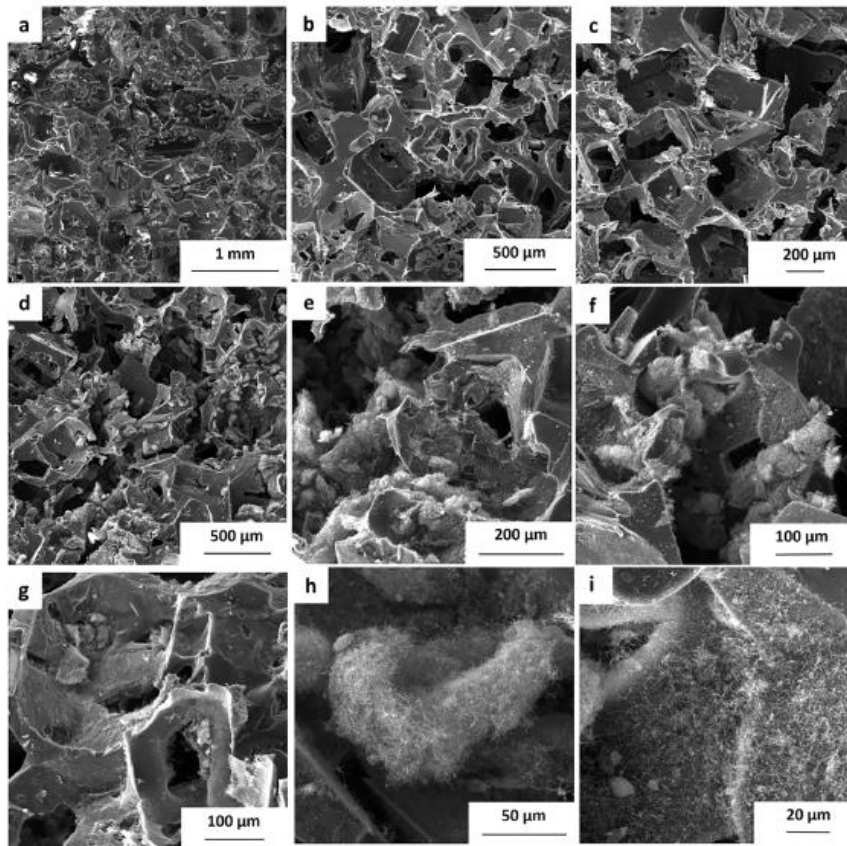


Figure 2.72 SEM images of a-c) neat PDMS sponge, d-i) CNF/PDMS sponge composite structures at different magnifications [18]

Morphology of neat PDMS sponge was given in Figure 2.72a-c at different magnifications. As seen, by dissolving the brown sugar, cubic open-cell porous structure was obtained and the mean pore size was reported to be around 351 μm . Additionally, the morphology of CNFs/PDMS sponge composites was given in Figure 2.72d-i at different magnifications. SEM images show that CNFs were successfully infiltrated on the walls of the open cells of PDMS sponge and dispersion of CNFs provides formation of the conductive networks [18].

Electrical characterization was done to all three CNFs/PDMS sponge composites. The electrical conductivity of S1, S2, S3 were given as 349, 42, 14 S/m, respectively [18].

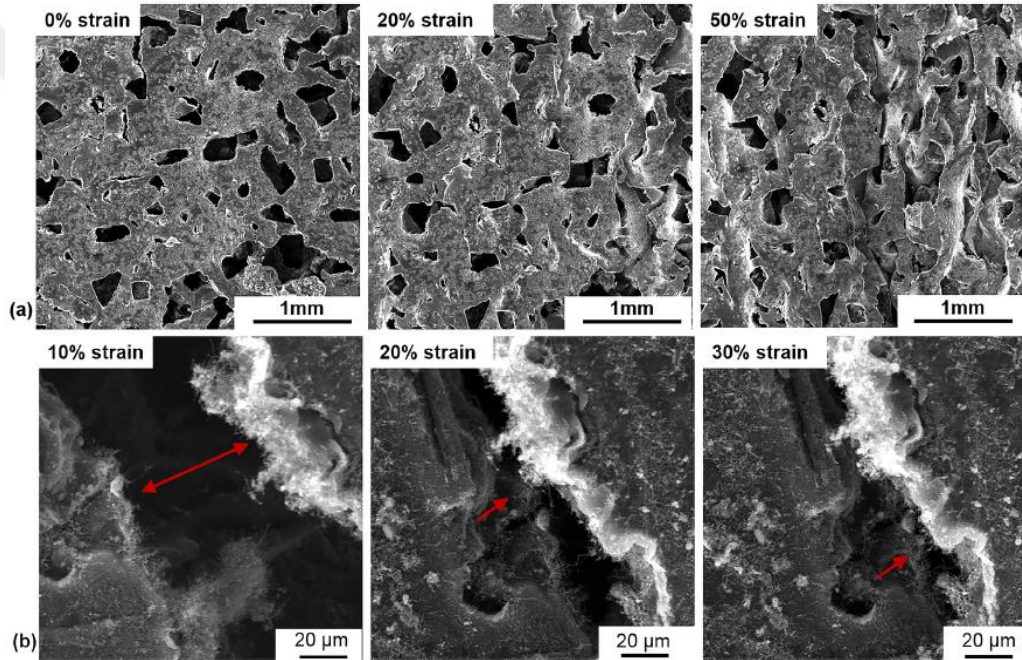


Figure 2.73 Morphology of the macrostructure a) and microstructure, b) of CNFs/PDMS sponge composites under different deformation rates [18]

The morphology of CNFs/PDMS sponge composites under different levels of compression was confirmed by using in-situ micromechanical SEM technique (Figure 2.73). The morphology of macro and micro structures under pressure can be seen from Figure 2.73a-b. As seen from SEM images, CNFs were infiltrated into the pores successfully and when pressure was applied, pores deformed and come close to each other and conductive network formed throughout the pores. When the deformation rate increased the distance between pores decreased and CNFs started to contact with each other. In other words, the gradual increase in deformation leads to the formation of more conductive networks and electrical resistance of composites decreases [18].

$$\Delta R = \frac{(R - R_0)}{R_0} \times 100\% \quad (5)$$

$$GF = \frac{(R - R_0)/R_0}{\varepsilon} \quad (6)$$

The piezoresistive behavior of composites could be characterized by calculation of relative resistance change (**Eq.5**) and gauge factor (GF) (**Eq.6**) that is related to sensitivity of the sensor depending on the deformation rates. Relative resistance change and GF values for all composites were given in Table 2.5 [18].

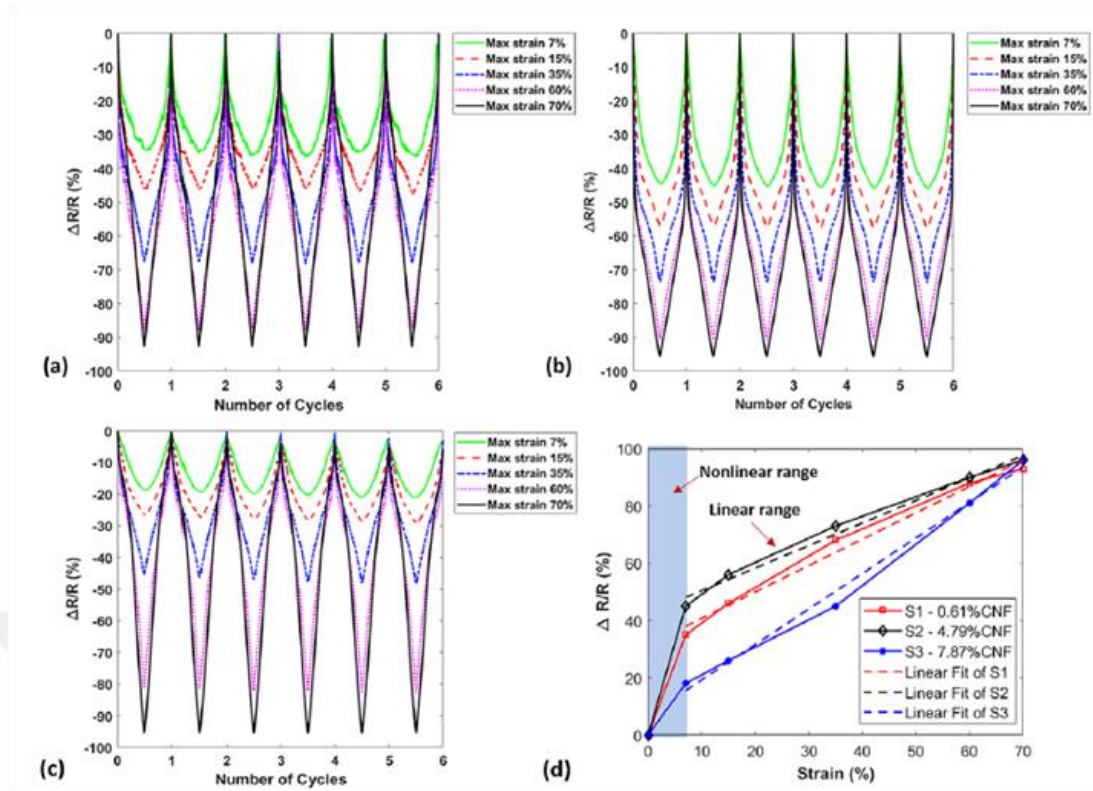


Figure 2.74 a-c) Relative resistance changes of S1, S2 and S3 under different compressive strains, and d) relative resistance change as a function strain for all composites [18]

Table 2.5 : Resistance change for S1, S2 and S3 during cyclic test [18]

Sample type	S1		S2		S3	
	$\Delta R/R$	GF	$\Delta R/R$	GF	$\Delta R/R$	GF
7% Strain	35%	5.0	45%	6.4	18%	2.6
15% Strain	46%	3.1	56%	3.7	26%	1.7
35% Strain	68%	1.9	73%	2.1	45%	1.3
60% Strain	88%	1.5	90%	1.5	81%	1.4
70% Strain	93%	1.2	96%	1.3	96%	1.3

Piezoresistive behavior of all CNFs/PDMS sponge composites (S1, S2, S3) under different deformation rates can be seen from Figure 2.74. Change in relative resistance and GF values were listed in Table 2.5. All composites showed repeatable negative piezoresistive behavior and they showed the highest GF under 7% compression level. GF started to decrease when deformation level is increased up to 70 %. While S2 composite showed the highest sensitivity, S3 composite showed the lowest value. Since S2 showed the highest GF, for further characterizations it was chosen. In Figure 2.75 effect of deformation rate on sensor sensitivity can be seen. As obvious, deformation rate was not found significant in terms of sensor sensitivity. Another significant information that can be concluded from the Figure 2.75 is that there is no hysteresis during cyclic measurements and that makes the S2 composite appropriate for sensing applications [18].

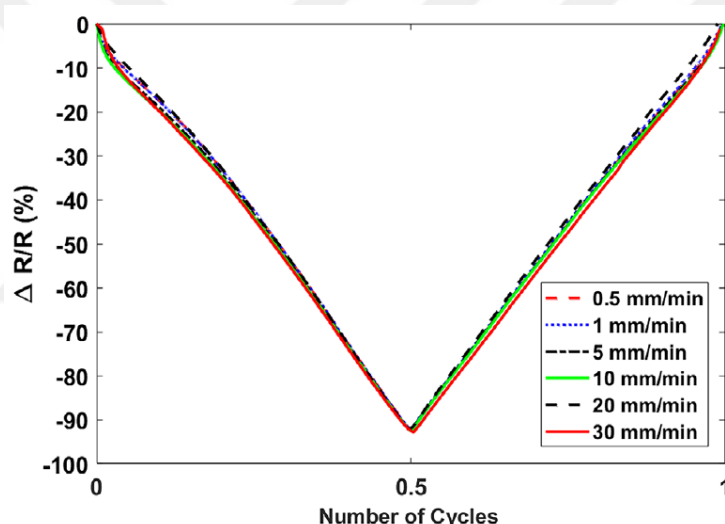


Figure 2.75 $\Delta R/R_0$ of S2 under 70% deformation rate with different test speeds [18]

To summarize, in the study, for the production of electrically conductive, flexible and durable composites brown sugar was used as a template to obtain porous structure. With the infiltration of CNF/THF mixture at different filler concentrations into the PDMS sponges, sensing materials were developed. The electrical and morphological properties were characterized. Piezoresistive response of the samples were characterized under different deformation rates at a constant test speed and depending on the relative resistance changes and GF of composites, the most sensitive one was chosen as an S2. In addition to that, relative resistance of the S2 composite was found independent of the deformation rate and showed very good cyclic stability without any significant hysteresis. One of the most important contributions of the study was

application of in-situ micromechanical SEM technique. By this analysis, morphology of the porous sensing material was investigated under various levels of strain and piezoresistive response was supported by so called SEM images [18].

2.5. Graphene Filled Elastomeric Piezoresistive Pressure Sensors

2.5.1. Graphene

Graphene is a one-dimensional material with a planar morphology that consists of a single layer of carbon atoms with a hexagonal/ honeycomb lattice arrangement [222]. Since it has unique electrical, mechanical, optical and thermal properties, it is used in various applications [223].

The pristine graphene is a two-dimensional (2D) material and the arrangement of carbon atoms in a plane resemble to honeycomb structure. It has four hybrid electrons and three of the electrons create sp^2 σ -bond in-plane and the last electron creates sp^2 π -bond in and out of the surface of graphene. The π -electrons provide the mobility of electrons. With the synthesis of GO many functional groups are created and π -electrons covalently bond with these functional oxygen groups. The covalent bonds limit the mobility of π -electrons and conductivity decreases [223-225].

2.5.2. Production of Graphene and Its Derivatives

There are many methods for the large-scale production of graphene such as mechanical exfoliation, epitaxial growth and chemical vapor deposition (CVD). By using these methods, various types of grapheme with various throughput can be obtained [223]. In this section, most common graphene production methods will be summarized.

2.5.2.1. Mechanical exfoliation of graphite

Mechanical exfoliation of graphite is the first technique for the synthesis of graphene. As known, graphite comprises many monolayers of graphene that are interacted with each other by van der Waals forces. In order to obtain graphene, so called van der Waals forces need to be overcome. The required force for separation of one single layer graphene was reported to be approximately $300 \text{ nN}/\mu\text{m}^2$ [226, 227].

Before improvement of mechanical exfoliation for the production of graphene, plasma etching process was carried out on highly ordered pyrolytic graphite (HOPG) by using AFM tip [228]. By using this process, multilayer graphite was separated to graphene layers with around 200 nm that consists of at least 500-600 graphene monolayers as shown in Figure 2.76 [226].

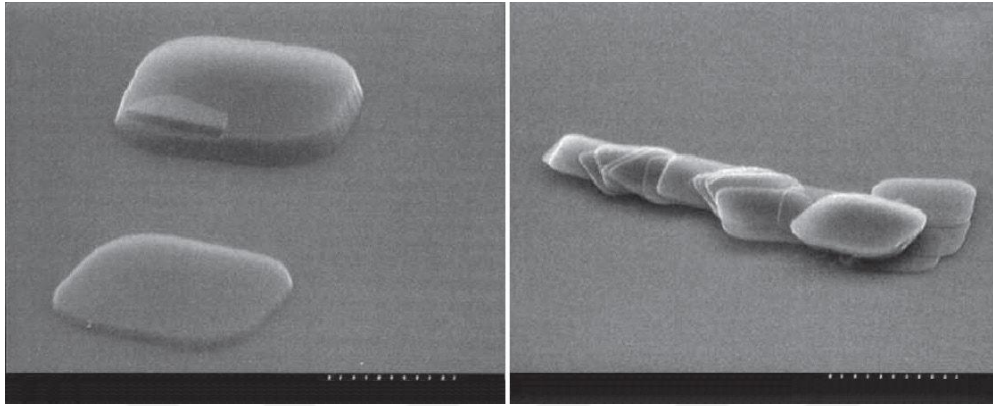


Figure 2.76 SEM images of HOPG after separation of graphene layers by using an AFM tip [222, 228]

To obtain lower number of graphene layers, mechanical cleavage was improved by Novoselov and Geim. The process was based on the peeling of graphene layers from 1 mm thickness HOPG sheet [229, 230]. In detail, by using adhesive tape, HOPG was cleaved recurrently and the obtained particles on tape were deposited onto a substrate such as SiO_2/Si with the approximately 300 nm thickness [231, 232]. With this study, the researchers were awarded with the Nobel Prize in Physics in 2010 for this original invention that leads to improvement of graphene science. In addition, this process has very limited production rate and also not suitable for mass production [231, 233]. Since nanoelectronics require such as less imperfections and high purity, more modifications are needed for mechanically exfoliation method [226, 231].

2.5.2.2. Epitaxial growth of graphene

Epitaxial growth process is another method used for graphene synthesis. In this method, a single layer graphene can be synthesized on a silicon carbide (SiC) substrate. By using this process highly crystalline graphene on the single crystal substrates can be fabricated [226]. Graphene morphology and deposited layer number can be controlled with the pressure and temperature [231].

The product can be classified as homo-epitaxial or hetero-epitaxial depending on the type of the substrate. If the substrate is same as the synthesized material, material is referred as homo-epitaxial; if not, material is called hetero-epitaxial material. With the deposition of graphene or graphite layers on the SiC substrate, hetero-epitaxial layers are produced [226]. Although few layers of graphene can be obtained by using SiC substrate, due to high interactions between graphene and substrate, transfer of the graphene can be problematic. As a substrate carbon also can be used and relatively thick sheets can be obtained [231].

2.5.2.3. Chemical vapor deposition

By decomposition of hydrocarbon gases catalytically on the metal substrates, carbon source is formed. The growth of carbon source occurs at elevated temperatures around 1000°C. With the precipitation of carbon by cooling the substrate, graphene formation is occurred [231, 234]. By controlling the dissolved carbon concentration in the substrate and cooling rate; thickness and crystalline structure of graphene layers can be changed [233].

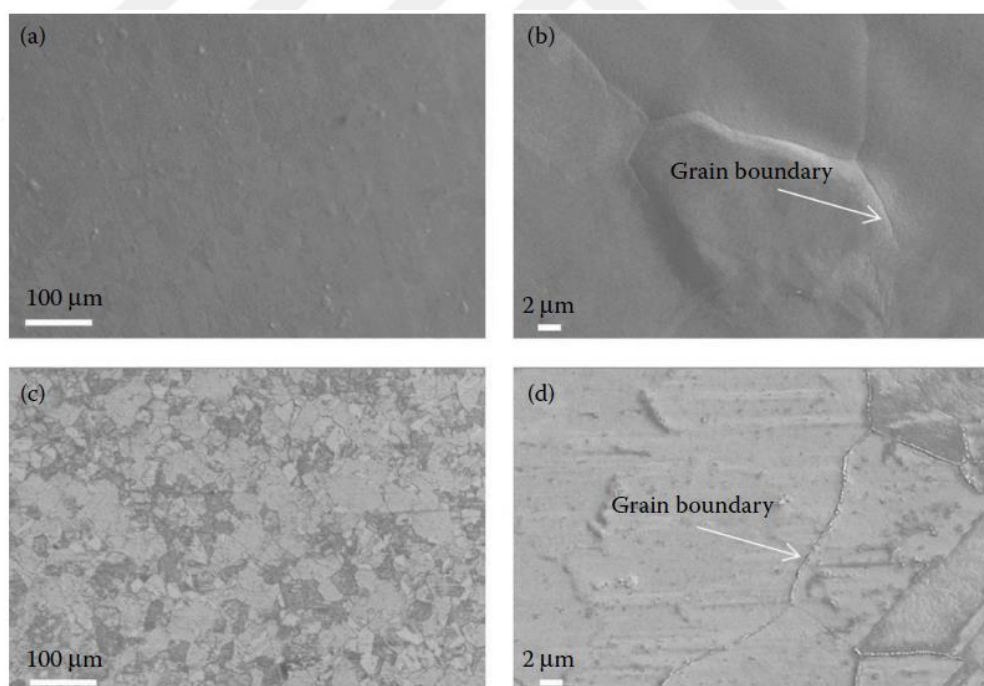


Figure 2.77 FESEM images of graphene synthesis on Cu and Ni substrates. Morphology of the graphene film on Cu substrate a) at low magnification and b) at high magnification. Morphology of the graphene film on Ni substrate c) at low magnification and d) at high magnification [235]

The process is very suitable for large scale manufacturing of high quality, high surface area, graphene. Most commonly used metal substrates are nickel [236] (Figure 2.77c,d) and copper [237-240] (Figure 2.77a,b) and in addition to these gold [241], cobalt [242], platinum [243], rhenium [244], ruthenium [245-247], iron [248, 249], palladium [250], iridium [251] can also be used [231, 233]. After synthesis of graphene, it can be separated from substrate by chemical etching [233].

2.5.3. Graphene Oxide Reduction

Graphene oxide (GO) is one of the derivatives of graphene. It consists of many functionalized groups on the surface, basal plane and also at the edges (Figure 2.78). The oxygen groups locate on the basal plane whereas carbonyl, carboxyl and phenol groups locate at the edges.

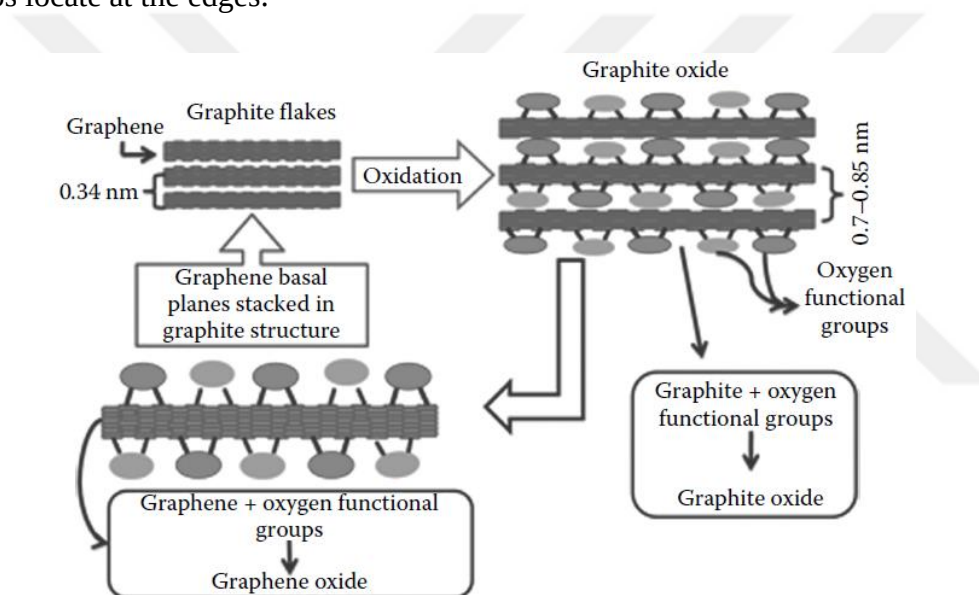


Figure 2.78 Demonstration of GO synthesis [224]

After the oxidation of graphite, the interaction between graphene layers destroyed and therefore graphene layers are separated. In addition, since many functional groups are created with the effect of oxidation (Figure 2.79). As a consequence of that hydrophilic GO is obtained and it can be dispersed in various solvents such as water.

When the functional groups are removed from the oxidized graphene structure, reduced graphene oxide (rGO) is obtained. The rGO contains defects in its structure. With the reduction process, oxygen groups can be removed with the carbon atoms by creating defect in the pristine graphene structure. These defects and the ratio of carbon and oxygen groups change the electrical properties [224].

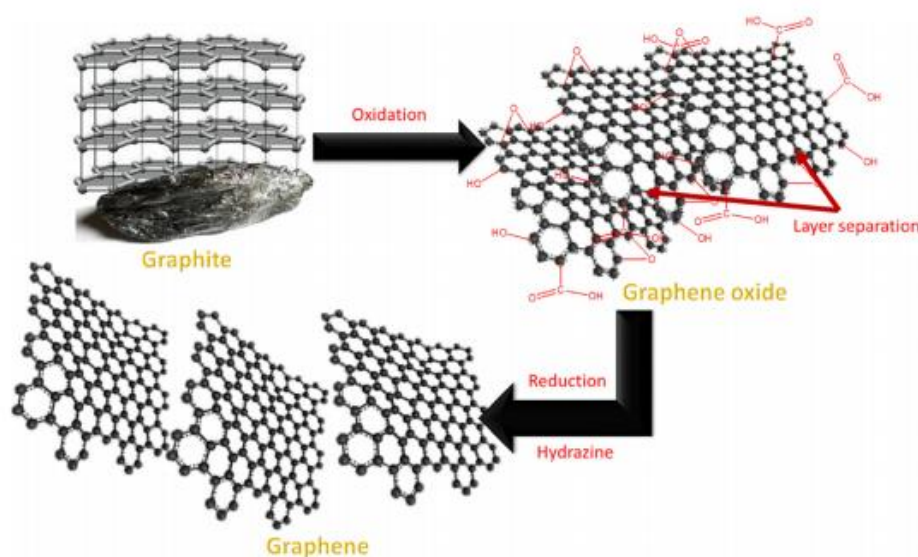


Figure 2.79 Synthesis of graphene by rGO [252]

After oxidation process, the ratio of carbon to oxygen causes to change in the bandgap from 1.7 to 3.6 eV [253, 254]. Therefore, electrical conductivity of graphene decreases with the formation of the functional groups on the surface and at the edges of graphene layers. To enhance the electrical conductivity of GO, reduction methods were developed [224, 255, 256].

2.5.3.1. Synthesis of graphene oxide

For the oxidation of graphite to GO, various methods have been improved as the Brodie method [257], Staudenmaier method [258], Hummers and Offeman method [259], respectively. For the synthesis of GO, these methods have the similar approach but the only differences are the oxidizing agents used for the oxidation of graphite. In detail, NaClO_3 (sodium chlorate) and HNO_3 (nitric acid) mixture is used in Brodie method, H_2SO_4 (sulphuric acid), KClO_3 (potassium chlorate) and HNO_3 mixture is used in Staudenmaier method and H_2SO_4 , KMnO_4 (potassium permanganate) and NaNO_3 (sodium nitrate) mixture is used in Hummers and Offeman method [260].

For the oxidation of graphite according to Hummers method, the oxidizing agents are mixed at high rpm at 0°C. The brownish-gray color change in the suspension is an indication of the starting of the reaction. By using water, the suspension is diluted and H₂O₂ (hydrogen peroxide) is added into the suspension to reduce the residual permanganate and manganese sulfate. After this treatment, the color of the suspension changes to bright yellow. For the separation of residues, filtration is carried out and the mixture is washed with water many times to get GO filter cake in yellow-brownish color. Since GO can disperse in water due to the functional groups (Figure 2.80), GO can be found in the form of suspension in water or it can be dried and can be found in powder form [260].

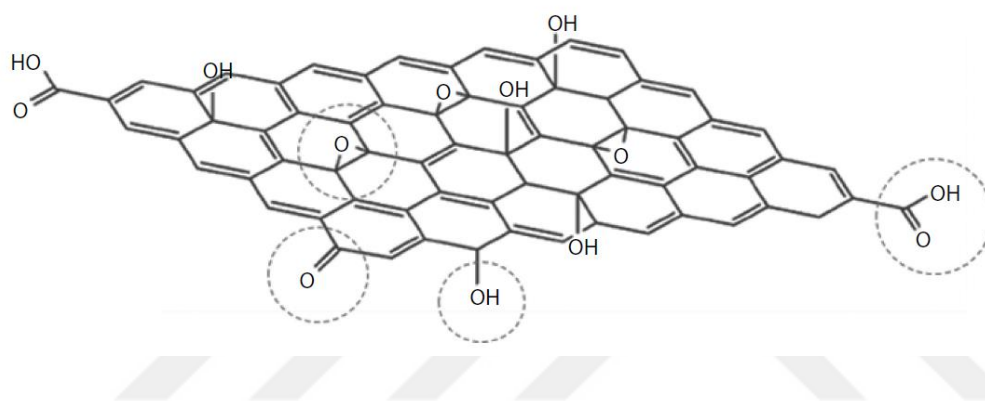


Figure 2.80 Molecular structure of GO that have functional groups on the surface and at the edges [261]

The final GOs, obtained by these three methods mentioned above, have different oxidation degrees and the minimum oxidation degree belongs to GO produced by the Brodie method [262]. In the case of large-scale manufacturing of GO by using these methods, filtration takes long time to remove the residual organic salts and acids. Furthermore, during oxidation processes, toxic gases are formed and these gases can cause to explosions [260].

To overcome these problems, the modified Hummers method was improved [263]. In the process, NaNO_3 was not used and the amount of KMnO_4 was increased and the ratio of H_2SO_4 and H_3PO_4 into the mixture was changed to 9:1 (v/v). Thus, the oxidation ratio increased compared to the Hummers method and more hydrophilic GO structure was obtained. After the reduction of GOs, that were obtained by Hummers method and modified Hummers method, in hydrazine both samples were reported to show similar electrical conductivity values [260]. As reducing agent, hydrazine hydrate, sodium borohydride and dimethylhydrazine can be used [264]. With the modifications in the Hummers method, a feasible and relatively cheap process was developed for the mass production of graphene [224, 260].

2.5.4. Graphene Filled Elastomeric Piezoresistive Pressure Sensors

In this part, previous studies are going to be reviewed. The review contains the elastomeric piezoresistive polymer composites filled with graphene and its derivatives. In these studies, polydimethylsiloxane and polyurethane sponges were used as the polymeric matrixes. In addition, graphene [19], multilayer graphene nanoplatelets [48] and reduced graphene oxide (rGO) [49, 50, 99] were used as conductive fillers.

Rinaldi et al., studied the fabrication and characterization of flexible, low cost and sensitive piezoresistive pressure sensors. In the study, multilayer graphene nanoplatelets (MLG) were used as a conductive filler and PDMS foam was used as a matrix [48].

As shown in Figure 2.81, the composite fabrication process consists of 3 steps. Firstly, colloidal suspension of MLG was prepared in 1-propanol by using ultrasonication. Secondly PDMS foam was prepared. To fabricate the porous PDMS matrix, brown sugar was compressed in a cylindrical mold (Figure 2.82a) and was PDMS infiltrated into the sugar template (Figure 2.82b). After removal of sugar the porous structure was obtained (Figure 2.82c). The last step includes the infiltration of MLG/ 1-propanol mixture into the PDMS foam (Figure 2.82d) [48].

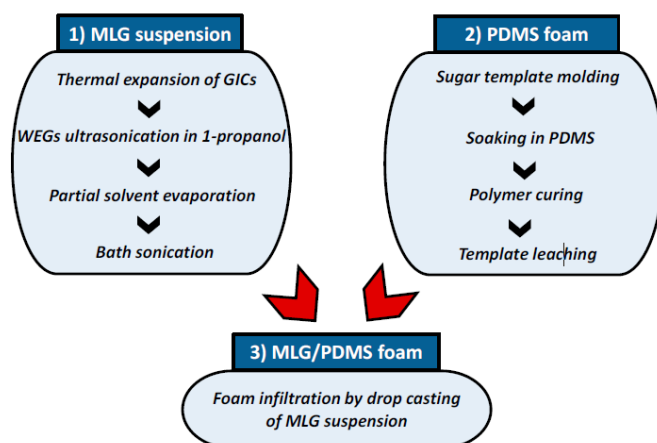


Figure 2.81 Production steps of MLG/PDMS foam composites [48]

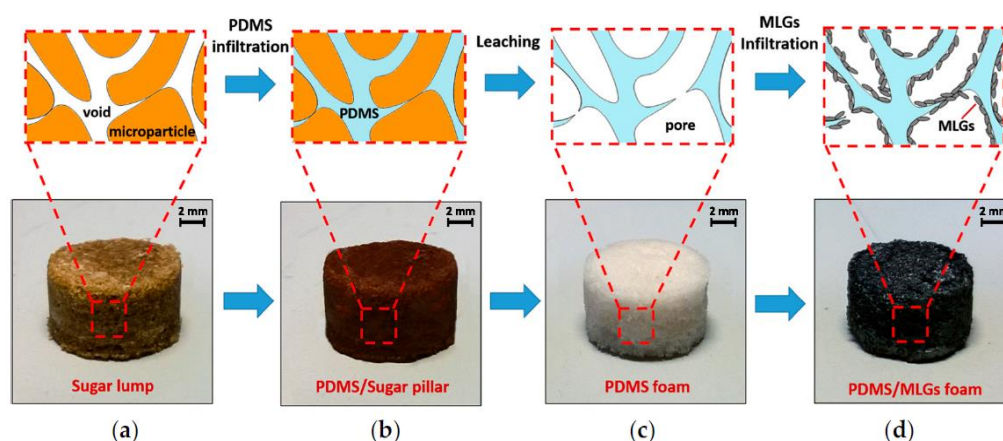


Figure 2.82 Production method for MLG/PDMS foam composite: a) sugar disk, b) infiltrated PDMS into the sugar disk, c) neat PDMS foam after sugar was removed, d) infiltration of MLG into the foam [48]

The morphological properties of open cell structure foam composites were characterized by optical microscope and FESEM. The electrical properties of foam nanocomposites were determined by a current source and voltmeter by two-probe technique. For the characterization of piezoresistive response, a uniaxially tensile testing machine was used [48].

In the study, two different foams were prepared and labeled as F10 and F20. The difference between them was the stoichiometric ratio of prepolymer (PP) to curing agent (CA). The sample F10 and F20 were prepared by using 10:1, 20:1 (PP:CA) respectively. The physical and mechanical properties of the neat PDMS foams were given in Table 2.7. The change in the components was reported to affect the cross-linking density and also flexibility of materials. As expected, F20 foam was more flexible and showed lower elastic modulus when compared with F10 [48].

Table 2.6 : Physical and mechanical properties of neat PDMS foams [48]

Foam Type	ρ_{PDMS} [kg/m ³]	ρ_{foam} [kg/m ³]	Φ [%]	E_{PDMS} [MPa]	E_{foam} [MPa]
F10	1027.8 $\pm$ 5.5	358.0 $\pm$ 13.2	65.2 $\pm$ 1.6	2.69	0.11
F20	1028.7 $\pm$ 9.0	366.8 $\pm$ 18.7	64.3 $\pm$ 1.6	0.74	0.065

During the infiltration of MLG into the PDMS foams, six different MLG concentrations were prepared for both F10 and F20. Totally, 12 samples were prepared as given in Table 2.7 [48].

Table 2.7 : The amount of suspension for the infiltration of PDMS foam and the amount of MLGs for F10 and F20 foams [48]

Drop-Casted Suspension [mL]		0.75	1	1.5	2	3	4.5
Infiltrated MLGs [wt.%]	MLG-F10	0.29	0.44	0.57	0.85	1.23	1.81
	MLG-F20	0.28	0.39	0.67	0.96	1.17	1.70

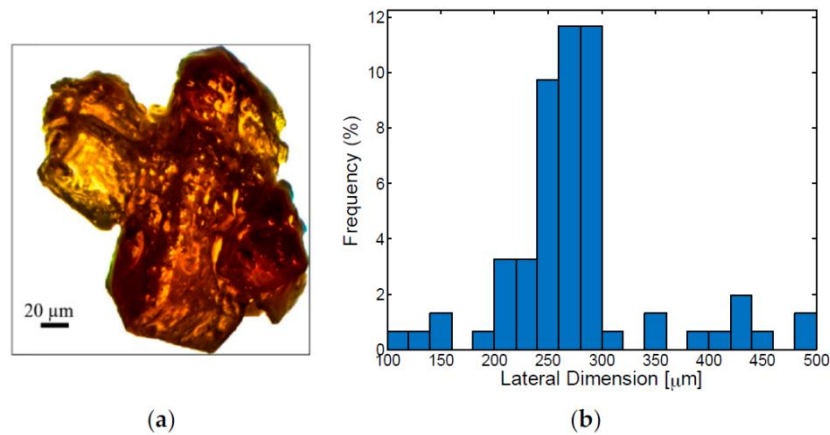


Figure 2.83 a) Optical microscope image of brown sugar porogens and b) size distribution [48]

The structure of brown sugar and size distribution can be seen in Figure 2.83 [48].

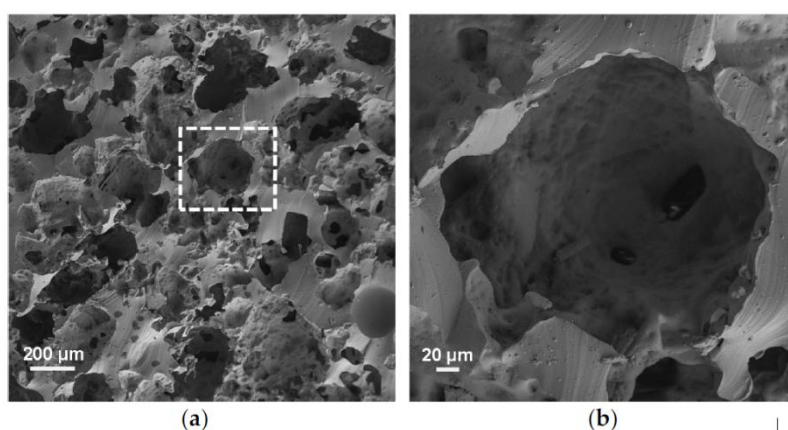


Figure 2.84 a) Cross-sectional image of foam after sugar was removed, b) High magnification image of the highlighted region [48]

The morphology of PDMS and MLG/PDMS foams can be seen in Figure 2.84 and Figure 2.85 respectively. Open cell structure of PDMS and MLGs deposited PDMS foam were showed clearly [48].

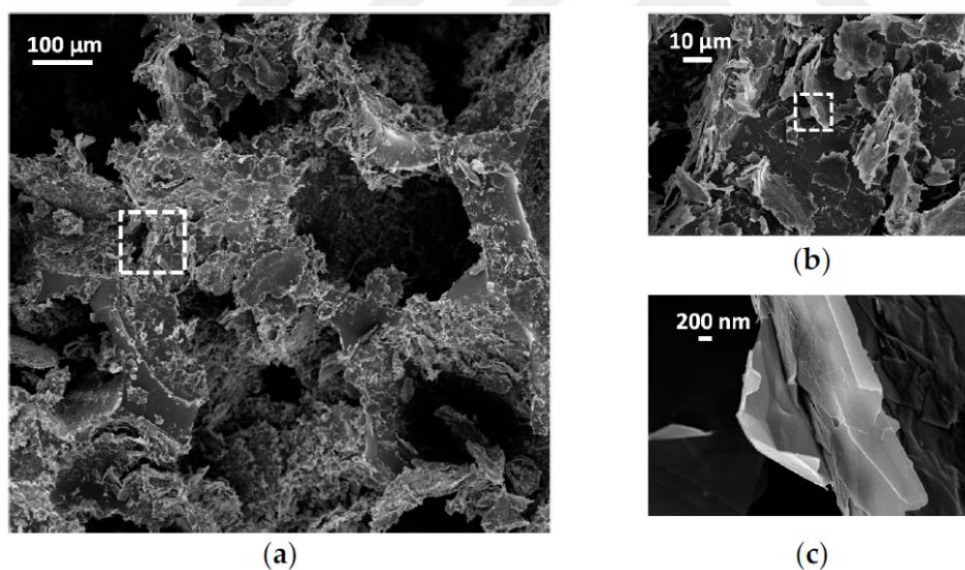


Figure 2.85 a) Morphology of MLG/PDMS foam, b) High magnification of highlighted region in image (a), c) High magnification of highlighted flakes in image (b) [48]

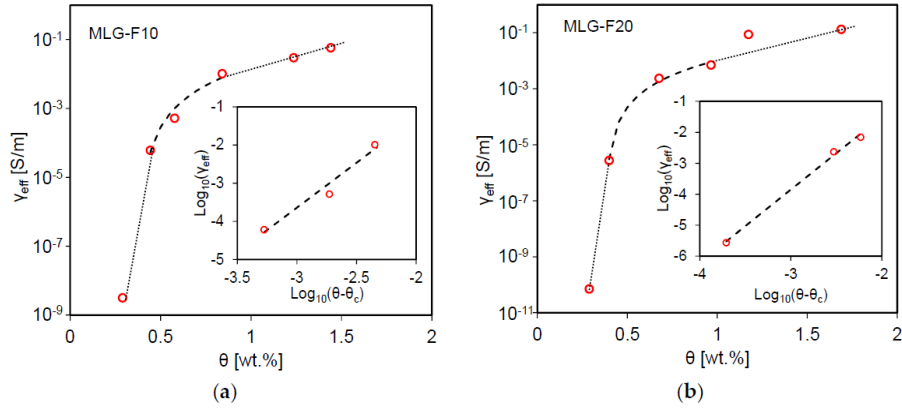


Figure 2.86 Percolation graphs of a) F10, b) F20 MLG/PDMS foam nanocomposites [48]

The percolation threshold graphs F10 and F20 foams were given in Figure 2.86. As anticipated, an increase in filler concentration is eventually led to an increase in conductivity. Especially for both foam types, the significant change in conductivity was observed between 0.3 and 0.4 % wt. MLG. After this region, conductivity changed slightly [48].

Besides the conductivity, the elasticity of a material has an important effect on the piezoresistive behavior. By considering these parameters for piezoresistive characterization, 0.96 wt% MLG/F20-PDMS nanocomposite was chosen [48].

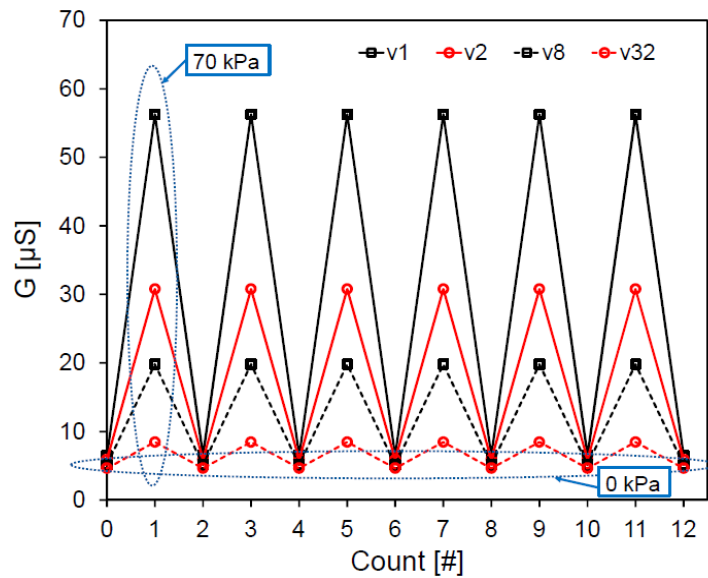


Figure 2.87 Piezoresistive behavior of nanocomposite under pressure at different test speeds (V1= 1 mm/min, V2= 2 mm/min, V8= 8 mm/min, V32= 32 mm/min) [48]

Piezoresistive response of the nanocomposite under pressure with different test speeds can be seen given in Figure 2.87. The conductance (G) values were taken before and after the pressure (in the range of 0 to 70 kPa) was applied under quasi-static conditions. The sample showed negative piezoresistive behavior with good cyclic stability. As seen, test speed affected the piezoresistive behavior and increase in the test speed led to lower sensor sensitivity. This was probably caused by the recoverability of the polymer-based sensor. At higher test speeds, dimensional recoverability of the sensor was reported to be worse [48].

To summarize, this study focused on the piezoresistive properties of MLG/PDMS foam nanocomposites that were produced by infiltration method. To obtain appropriate material properties, two different foam groups, as F10 and F20 were prepared based on their curing agent ratio. For piezoresistive characterization, 0.96 wt% MLG/PDMS foam nanocomposite in the F20 group was chosen due to its mechanical and electrical properties. Piezoresistive behavior of the nanocomposite was studied and test speed was found to be significant in terms of sensor sensitivity [48].

In another study, Luo et al., developed porous pressure sensitive arrays (PSA) with the graphene oxide (GO) and polydimethylsiloxane (PDMS) [49].

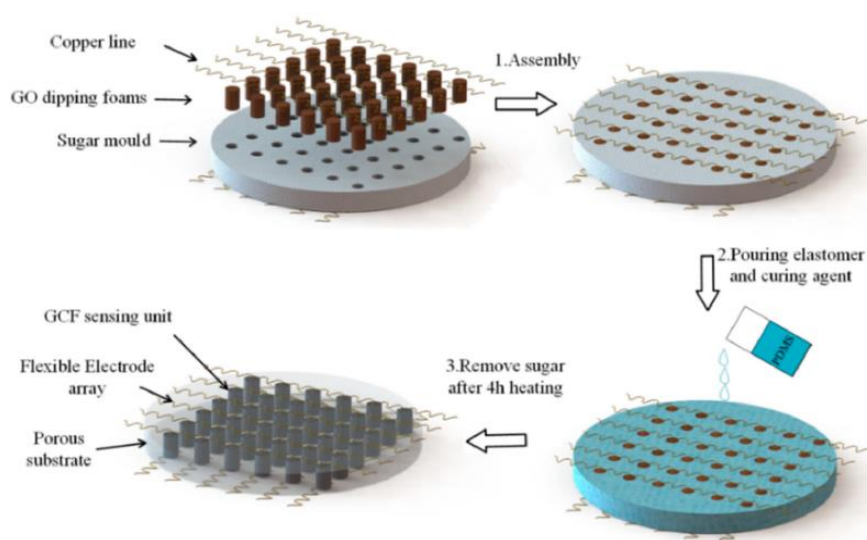


Figure 2.88 The schematic illustration of porous PSA fabrication [49]

The production procedure of PSA that consisted of three steps was given in Figure 2.88. In the initial stage of the process, the sugar template was prepared and cylindrical shaped GO coated PUSs were placed into the template. Then, copper lines were connected to the upper and down surfaces of graphene-coated foams (GCFs) with silver paste. In the further stage of the process, the uncured PDMS solution was poured onto the sugar template. In the last stage of the process, the curing of PDMS and reduction of GO was completed at the elevated temperature and with the dissolution of sugar in water, porous PDMS was obtained. The GCFs were prepared by submerging commercially available PU sponges into the GO suspension. The reduction of GO was completed at elevated temperatures [49].

The electrical conductivity was measured by using two-point probe method. The piezoresistive behavior of PSA was characterized by a tensile test machine and a digital multimeter. The morphological structure was characterized by SEM and the porous structure of GCF was shown in Figure 2.89b. The backbones of PU sponges were covered by graphene sheets as seen from Figure 2.89c-d [49].

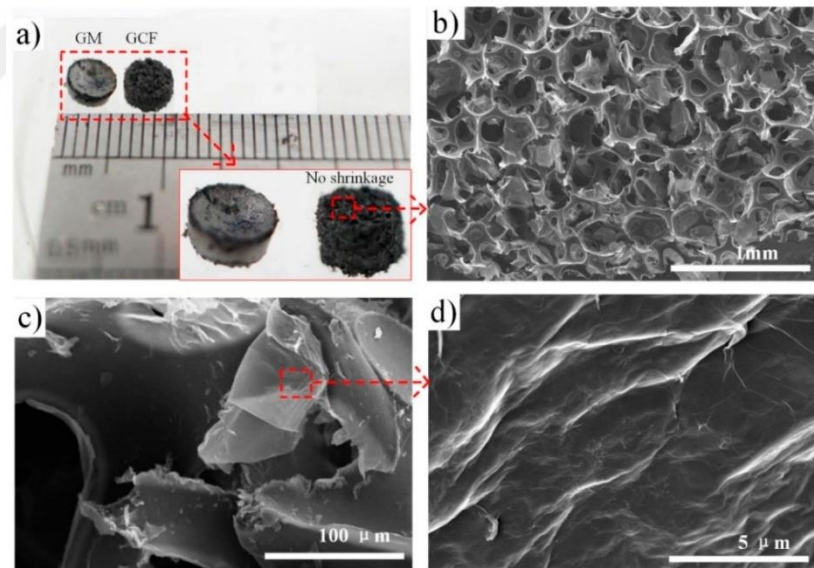


Figure 2.89 a) Appearance of GCF, b- d) Morphology of GCF at different magnifications [49]

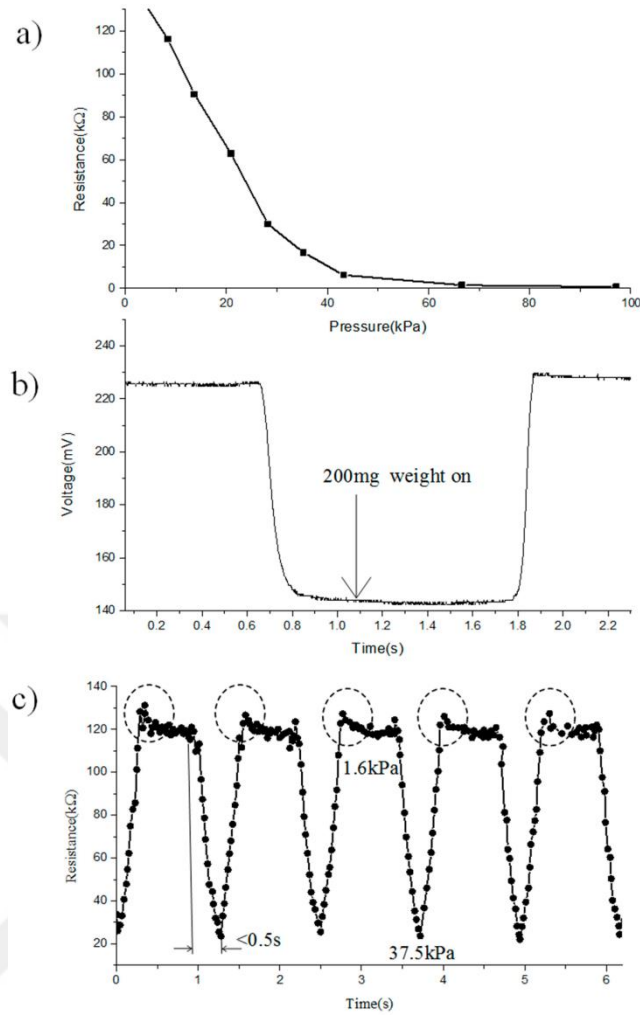


Figure 2.90 a) Resistance change in GCF as a function of pressure, b) Voltage change with time under 200 mg weight on GCF, c) Cyclic piezoresistance response of GCF [49]

The electrical response of PSA under pressure can be seen from Figure 2.90a. PSA has negative piezoresistive behavior until 50 kPa and after this pressure value, resistance shows almost no variation. Voltage change was given as function of time in Figure 2.90b. As seen, when the load was applied (200 mg is applied to 12.56 mm² area that is almost 1.6 kPa) voltage changed that was an indication of sensing ability of the system even under low levels of pressure. The stability of PSA under cyclic loading and unloading from 1.6 kPa to 37.5 kPa was given in Figure 2.90c. The first cycle was used to represent unloading from 37.5 kPa to 1.6 kPa and loading from 1.6 to 37.5 kPa. When the pressure value decreased to 1.6 kPa, PSA showed positive piezoresistance whereas when the pressure value increased to 37.5 kPa, it started to show negative piezoresistive behavior [49].

To summarize, in this study, PSA was fabricated by using conductive reduced graphene oxide coated PU sponges and porous PDMS insulating matrix in one system and aimed to produce a pressure sensitive material. The PSA system was produced by using a sugar template. The produced sensor array can sense very low weight in a short time [49].

Another study was carried out by Zhu et al., in order to produce an epidermal pressure sensor that consists of "asymmetric double-layered structures" by using reduced graphene oxide (rGO) and PDMS [50].

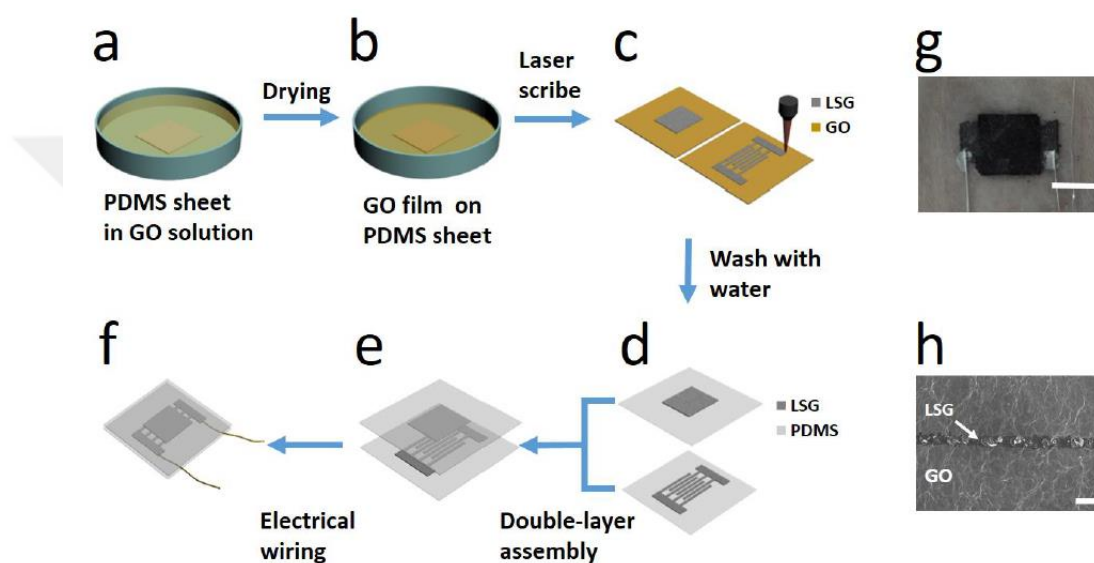


Figure 2.91 a-f) Fabrication of the pressure sensor g) digital image of asensor on the skin. h) SEM image of patterned line by laser on GO. (scale bars, g:0.5 cm, h: 100 μm) [50]

PDMS sheets that contain base polymer and cross-linker were prepared by using the casting method and cured. GO powder was synthesized by modified Hummer's route and GO/water mixture was poured onto the cured PDMS sheets. After the evaporation of water, GO on PDMS films were obtained as seen in Figure 2.91a-b. Reduction of the GO process was done by using laser irradiation technique and different interdigitated patterns were created on the surface of GO/PDMS sheets to produce electrodes. In addition to that a conductive film was also fabricated by using the same method (Figure 2.91c).

Subsequently, the patterned sheets were washed with water to remove residual GO. For completing sensor preparation, electrodes (interdigitated and conductive film) were combined (Figure 2.91d-e) and wires were connected to electrodes (Figure 2.91g-f) [50].

Piezoresistive characterization of the pressure sensors was measured in two systems. For the detection of static low-pressure values, a source meter and an electromagnetic balance for weight measurement, whereas for the dynamic pressure values, a source meter with a computer-controlled stepping motor were used [50].

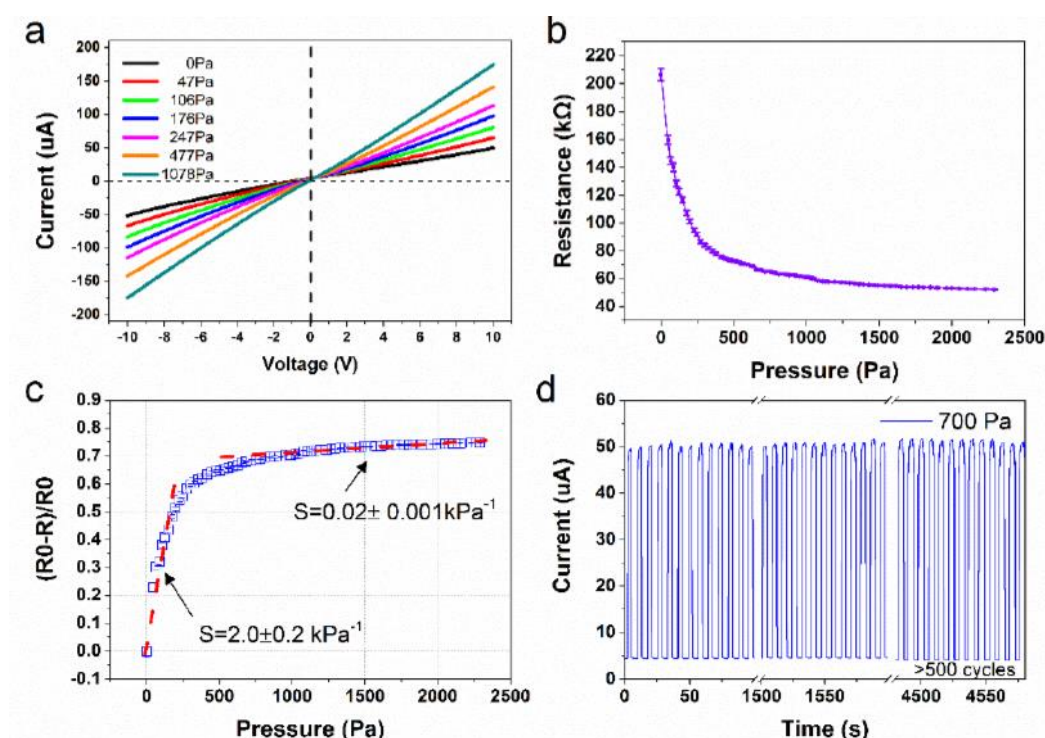


Figure 2.92 Piezoresistive properties of pressure sensor. a) current vs. voltage a function of different pressure values b) resistance changes as a function of pressure c) relative resistance change with applied pressure d) cyclic behavior of the sensor [50]

The piezoresistive properties of the system were measured in two different ways. The first one was for analyzing the effect of static pressure magnitude on the piezoresistive response that was given in Figure 2.92a. The slope of the current-voltage (I/V) graph gives the conductance of the sensor under specific pressure value and as seen in Figure 2.92a, all curves show linear behavior and an increase in applied pressure led to increase in the conductance of the sensor due to the increase of the connections between rGO sheets [50].

The change of the sensor resistance under different pressure values was given in Figure 2.92b. In the range of 0 to 200 Pa, the resistance showed a quick decrease from 210 k Ω to around 100 k Ω that was an indication of higher level of connection between rGO sheets. In the range of 200 to 1600 Pa, the resistance decreased from 100 k Ω to 60 k Ω whereas, after 1600 Pa, the resistance of the system was not significantly affected by the pressure changes and resistance was reported to be around 60 k Ω [50].

As explained above, sensor sensitivity (S) changed depending on the applied pressure as given in Figure 2.92c. When the pressure was less than 200 Pa, S was calculated around $2.0 \pm 0.2 \text{ kPa}^{-1}$. On the other hand, pressure values more than 500 Pa resulted in S value around $0.02 \pm 0.001 \text{ kPa}^{-1}$. An increase in the pressure cause to change in sensitivity of the sensor and sensor was found to be more sensitive to low-pressure values (<200 Pa). The dynamic piezoresistive behavior of the pressure sensor was characterized as given in Figure 2.92d. Almost 500 cycles were completed under 700 Pa and as seen sensor exhibited very stable behavior [50].

In the present study, the reduction of GO was completed by using laser irradiation and "asymmetric double-layered structures" were produced. The static and dynamic piezoresistive properties were studied and pressure sensor was found more sensitive to low-pressure values and showed a very stable response on the cyclic test. The present sensor can be used for monitoring blood pulse and finger touching [50].

For the production of piezoresistive elastomer based nanocomposites, polyurethane can also be used. In the present study, Luo et al., studied with the graphene and polyurethane (PU) materials to produce conductive nanocomposites that are highly elastic and have good piezoresistive behaviors [19].

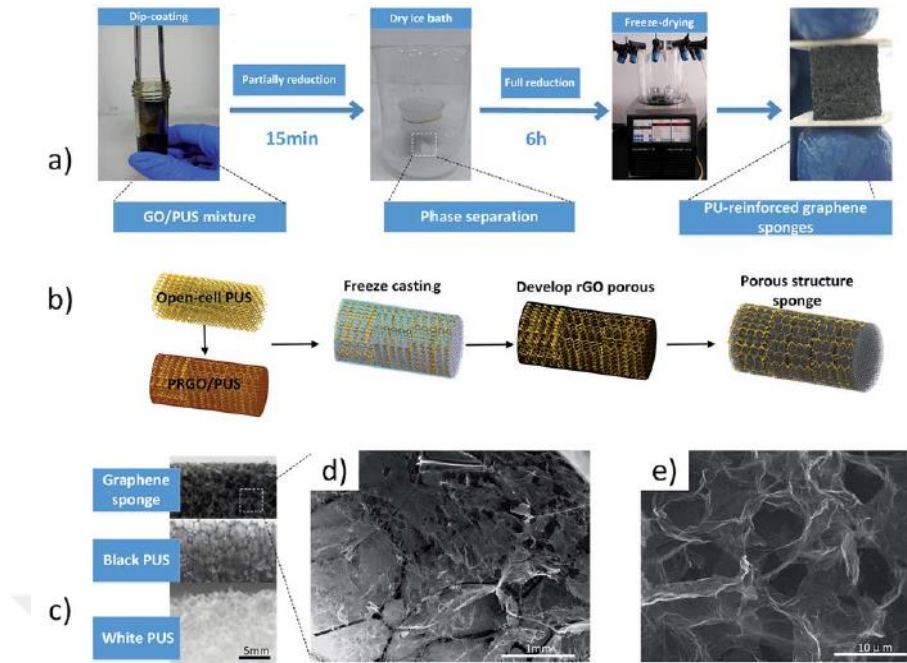


Figure 2.93 a) Fabrication process of graphene/PUS nanocomposites, b) illustration of freeze casting method to create GO/PUS open-cell porous structure, c) Digital images of graphene sponge and PUSs, d-e) SEM images of PUSs [19]

In the production process as given in Figure 2.93a, graphene and PU were used and for the synthesis of graphene oxide, the "modified Hummers method" was used. For the creation of interconnected and 3D structure graphene aerogel, "the freeze casting method" was used by dipping PUSs into the graphene oxide (GO) suspension [19].

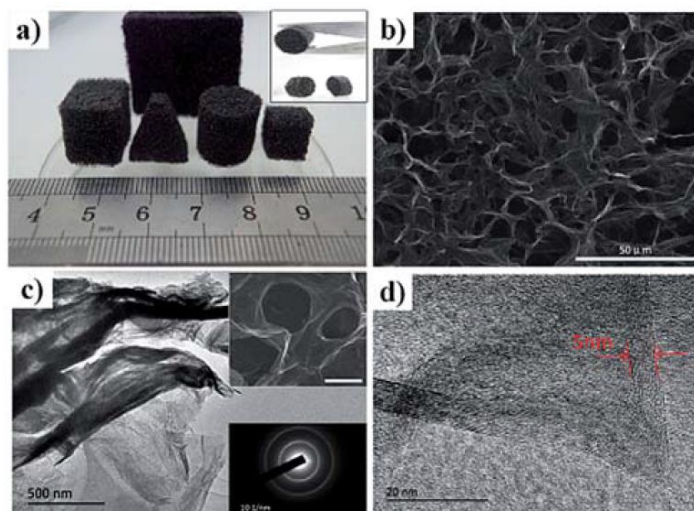


Figure 2.94 a) Appearance of sponge nanocomposites b) A SEM image of porous morphology c) TEM images of graphene at different scales, d) TEM image of graphene at 20 nm scale [19]

After production of polyurethane containing graphene sponges (PGSs), sponges were cut into different shapes (Figure 2.93a). The porous morphology of PGS was given in Figure 2.93b and the average pore size was reported to be around 10 μm . The graphene was characterized by TEM as seen in Figure 2.94c-d. The morphology and microstructure of nanocomposites were characterized by environmental scanning electron microscope (ESEM). The electrical conductivity was measured by "two-point probe method" and tensile testing machine was used for mechanical characterization. In addition to these, for the dynamic piezoresistive characterization, a new device was designed [19].

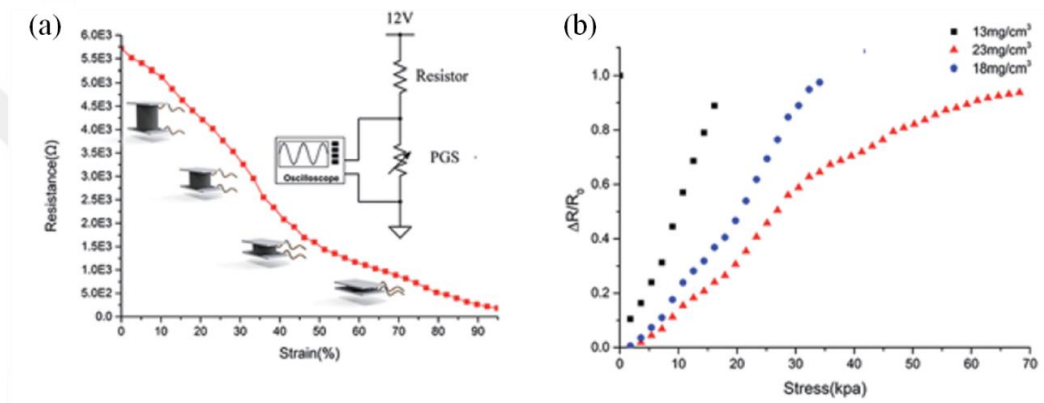


Figure 2.95 a) The resistance of PGS as a function of compressive strain, b) The change in sensitivity of PGS under compression stress for different foam densities [19]

The PGS nanocomposite showed negative piezoresistive behavior with the increase in the compressive strain as seen in Figure 2.95a. That was basically stemmed from the decrease in the distance between the cell edges under applied compressive strain. Various foams were prepared as a function of foam density and rGO content. In Figure 2.95b, sensitivity of PGS nanocomposites at different foam density was given. As expected, all three types nanocomposites show different sensitivity under pressure and an increase in GO concentration causes to decrease the sensitivity of PGS nanocomposites [19].

In addition to determination of the piezoresistance with traditional mechanical testing system actual movements were also analyzed as given in Figure 2.96. The sensor was placed between two electrodes and compressed manually under different compression strain levels. As seen from the Figure 2.96b by increasing the compression level, resistance change increased [19].

As obviously mentioned, the material showed negative piezoresistive response under pressure as given in Figure 2.95. On the other hand, In Figure 2.96a-b, it turns to positive. In Figure 2.96, the y axis was given in term of change in resistance to resistance at given time. The response change is related to the mathematical calculation.

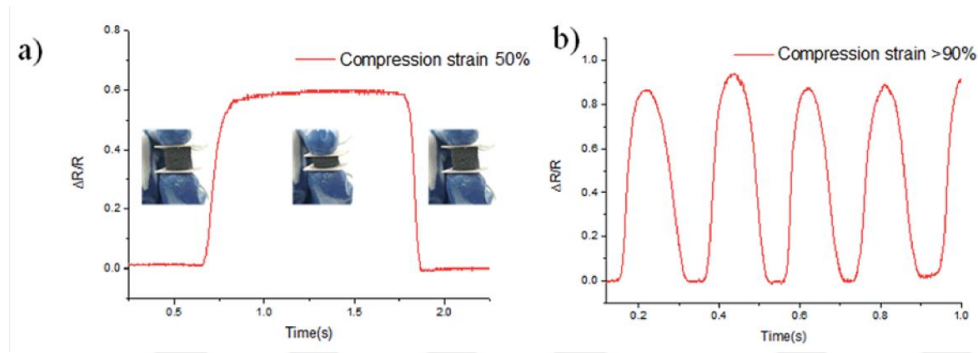


Figure 2.96 a) Change in resistance as a function of time under 50 % compressive strain when compressed manually, b) Change in resistance as a function of time under >90 % compressive strain [19]

Another important contribution of the study is determination of the dynamic piezoresistance by a unique testing system as shown in Figure 2.97. As obvious from the Figure 2.97, the system has a special blade and different levels of pressure can be applied in one cycle. By using this system, the waveform and frequency delay ratio were determined. Under 20-35 Hz loading, delay ratio was reported to decrease from 18 % to 7 % [19].

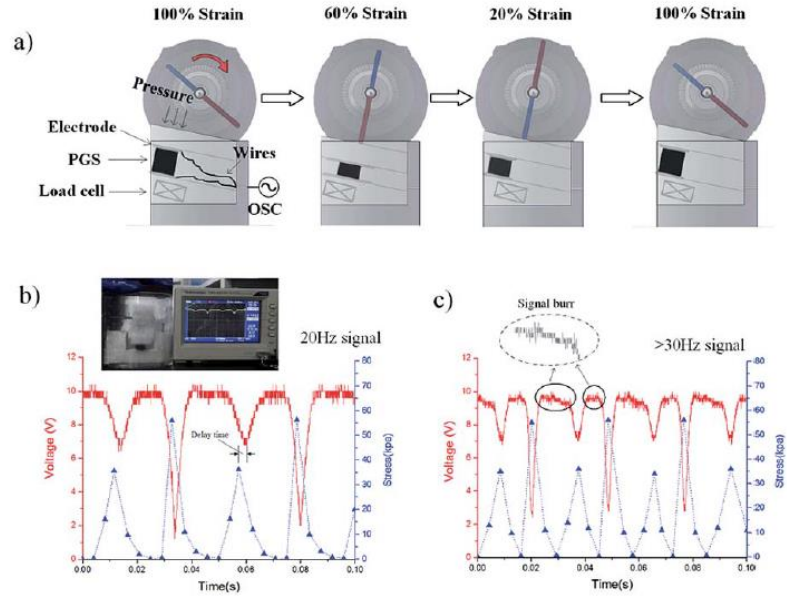


Figure 2.97 a) Special system used for piezoresistance measurements b) response under 20 Hz c) response under >30 Hz [19]

In the study, Yao et al., developed a sponge based pressure sensor. In order to improve the sensitivity of piezoresistive response, microcracks were formed in the structure [99]. In the study, commercially available polyurethane sponge (PUS) and graphene oxide (GO) nanosheet were used. PUS was dipped into the GO suspension and reduced in the hot hydrogen iodide (HI) solution and GO filler coated onto sponge backbones. To create microcracks in the structure, firstly sponge was treated at elevated temperatures, and it was pressed under 95 % compressive strain for 2 h. as given in Figure 2.98a-e [99].

The morphology of rGO/PUS nanocomposite was characterized by SEM as given in Figure 2.98f-i. The 3D open cell structure of untreated rGO/PUS was given in Figure 2.98f, as seen the all networks are connected. In Figure 2.98g, deformed sponge structure can be seen. The inset images (in Figure 2.98f-h) demonstrated that even if the rGO/PUS porous structure was damaged after hydrothermal process (rGO–PU–HT), GO fillers still adhered to the surface of PU and provided electrical conductivity throughout the network. The morphology changes in the presence of pressure were given in Figure 2.98i. When the pressure was applied, the destructed PUS backbones forced to be closer, contact area between backbones increased and new conductive networks were formed [99].

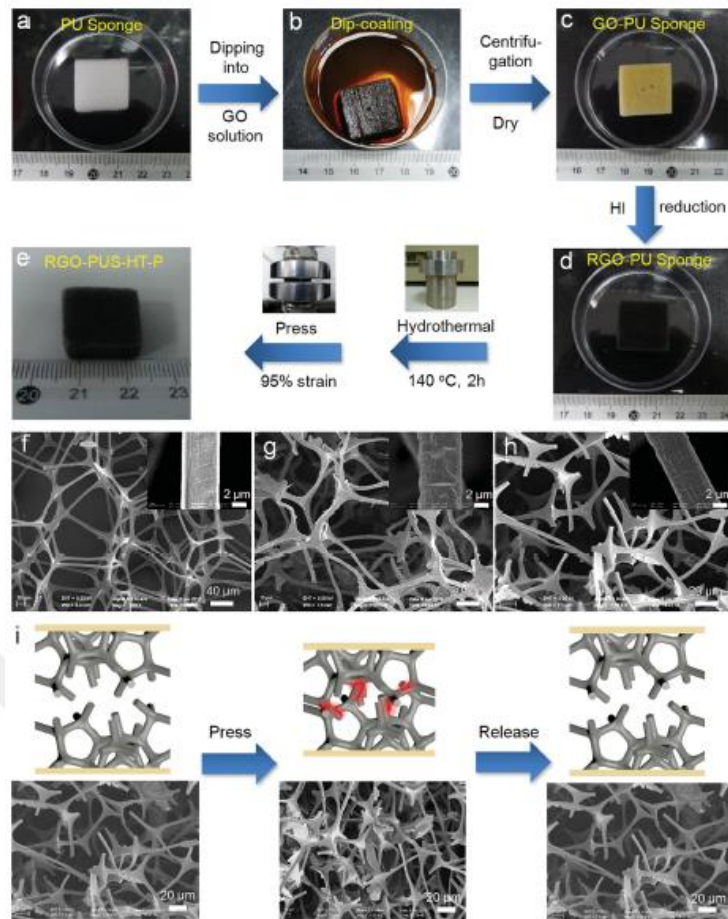


Figure 2.98 a-e) Sensing foam fabrication, SEM images of f) rGO–PU sponge g) rGO–PU–HT, h) the compressed rGO–PU–HT sponge, i) Mechanism of piezoresistance under pressure [99]

Copper electrodes were fixed to two opposite surfaces of the material and copper wires were connected to these electrodes to get electrical data as seen in Figure 2.99a [99].

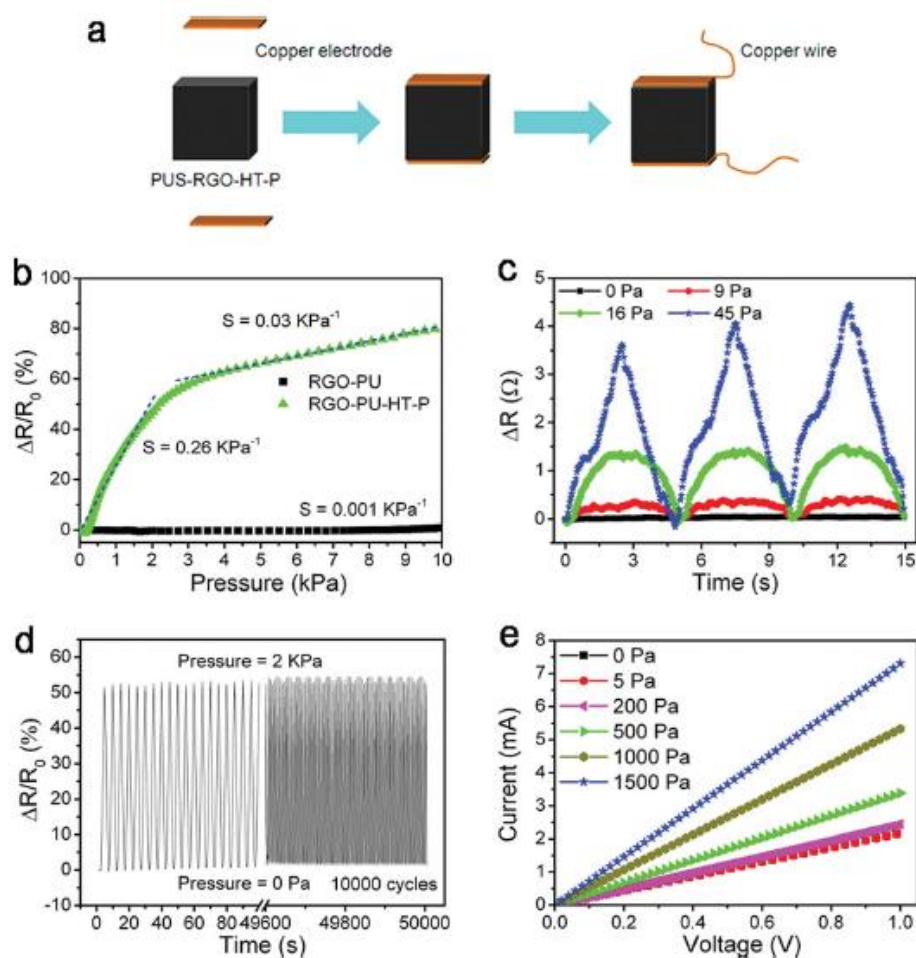


Figure 2.99 Electromechanical characterization of graphene filtrated PUS. a) Illustration of the sensor production, b) change in relative resistance as a function of pressure for both for rGO–PU and rGO–PU–HT–P sponges, c) Cyclic resistance change in the rGO–PU–HT–P sponges under different pressure values as a function time, d) Cyclic relative resistance change as a function of time under 5 kPa, e) Current of the rGO–PU–HT–P sponge as a function of voltage under different pressure values

Piezoresistive behaviors of both untreated rGO/PUS and hydrothermally treated and compressed, rGO–PU–HT–P, nanocomposites were investigated. Two samples were compared in terms of $\Delta R/R_0$ vs. pressure change (Figure 2.99b). Sensitivity of materials, referred to as S , was calculated by the slope of the lines. As obviously seen from the graph, rGO/PUS under pressure is almost zero that means the change in resistance under pressure was very low.

On the other hand, rGO-PU-HT-P nanocomposite showed relatively higher sensitivity. In addition to that, rGO-PU-HT-P nanocomposite was tested under different pressure values (0- 9- 6- 45 Pa) and showed different sensitivity (Figure 2.99c). To generalize, by increasing the pressure, sensitivity of the sensor increased. The increase in pressure caused to increase in the resistance change of nanocomposite and gave more sharp response due to the formation of the conductive network. Also by using different pressure values, the minimum detectable pressure value was obtained [99].

Furthermore, the piezoresistive response of rGO-PU-HT-P nanocomposite was measured under 2 kPa cyclic pressure (Figure 2.99d). The nanocomposite was reported to be highly stable and showed a long working life as a pressure sensor. In Figure 2.9e, the current changes of rGO-PU-HT-P sponge as a function of voltage under different pressure values were examined and in all cases, linear curves were exhibited. As known, the slope of the current vs. voltage graph gives the conductance of material. As shown, higher pressure values led to higher slope values [99].

In summary, to produce electrically conductive, flexible piezoresistive pressure sensors, GO and PUS were used. GO was reduced and rGO was obtained during the process. To increase pressure sensitivity of the nanocomposite, microcracks were formed in the structure by hydrothermal treatment and compression of the treated sample under pressure for 2 hours. The piezoresistive responses of rGO-PU-HT-P sponge were characterized under different pressure values and the minimum working pressure value was determined. The cyclic response of material was studied and it was found highly stable with long working life [99].

3. MATERIALS AND METHODS

3.1. Materials

The linear triblock Poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] copolymer with the S/EB ratio of 20/80 was used. The physical appearance of the SEBS granules and chemical structure of SEBS are given in Figure 3.1 and 3.2 respectively.

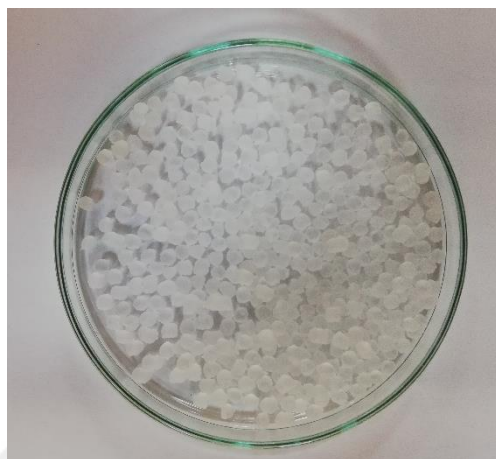


Figure 3.1 SEBS granules

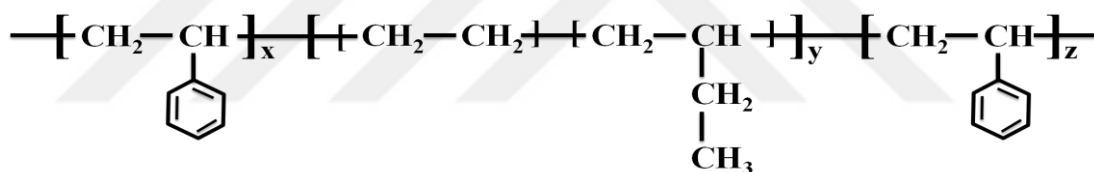


Figure 3.2 SEBS chemical structure

For the preparation of SEBS solution, toluene was used. It was supplied from Merck. The chemical structure of toluene is given in Figure 3.3.

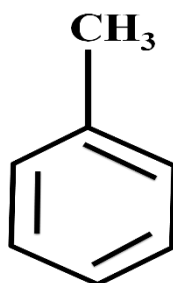


Figure 3.3 Chemical structure of toluene

For the production of pressure sensors, three different conductive filler types were used including carbon black (CB), vapor grown carbon nanofibers (VGCNFs), reduced graphene oxide (rGO).

Carbon Black (CB): In the first set of nanocomposites, carbon black (CB), Super C65, was used. It was purchased from Timical, MTI Corp. CB was synthesized by acetylene black process. The physical appearance of CB is given in Figure 3.4. The morphology of CB was characterized by field emission scanning electron microscope (FESEM) as shown in Figure 3.5. The particle size distribution of CB is given in Figure 3.6. As indicated in the histogram the particle diameter changes between 30-85 nm and the average particle size was calculated as 58 nm.

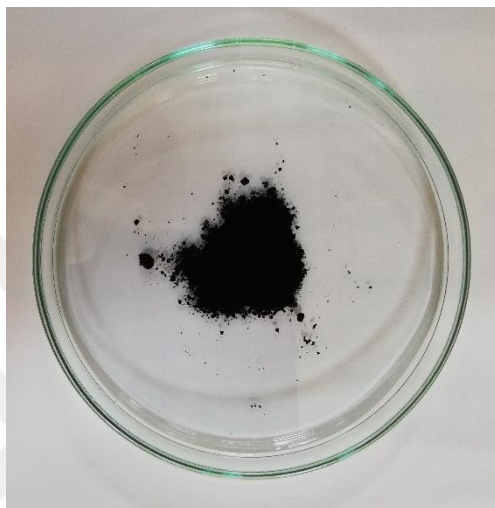


Figure 3.4 Carbon black powder

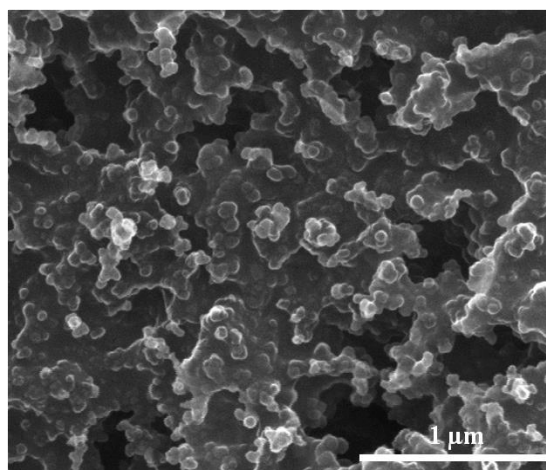


Figure 3.5 SEM image of carbon black powder

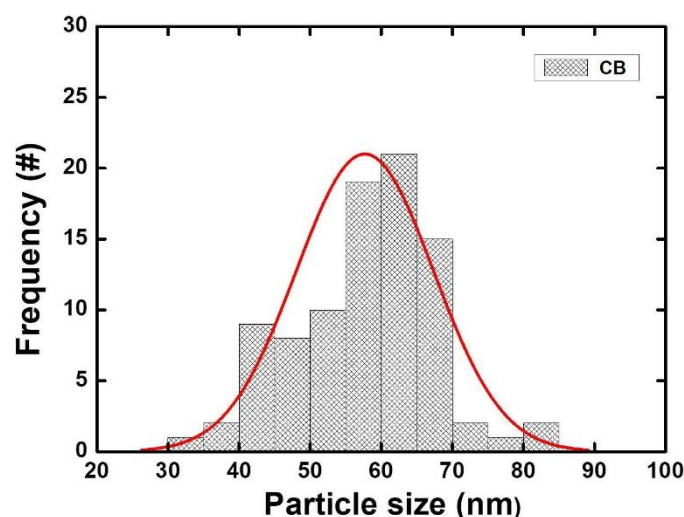


Figure 3.6 Particle size distribution of carbon black powder

Vapor Grown Carbon Nanofibers (VGCNFs): In the second set of nanocomposites, vapor grown carbon nanofibers (VGCNFs) were used. VGCNFs were purchased from Sigma-Aldrich. The physical appearance of VGCNFs is given in Figure 3.7. The morphology of VGCNFs was characterized by FESEM as shown in Figure 3.8. The average fiber diameter distribution of VGCNF is given in Figure 3.9. As shown in the histogram, fiber diameter changes between 40-180 nm and the average fiber diameter was calculated as 125 nm. Since VGCNFs are interconnected fibrous structures, we could not measure the fiber length. According to company information, average fiber length was given between 20–200 μm .

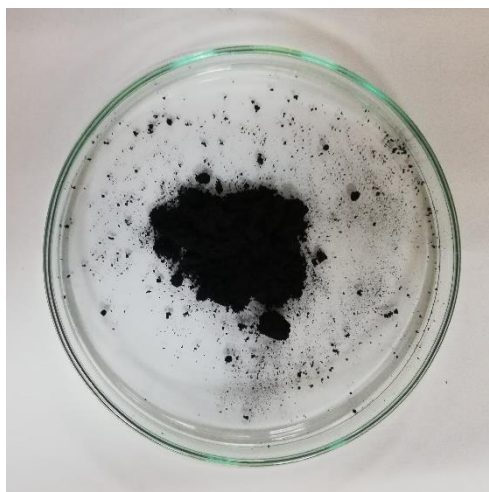


Figure 3.7 Vapor grown carbon nanofibers

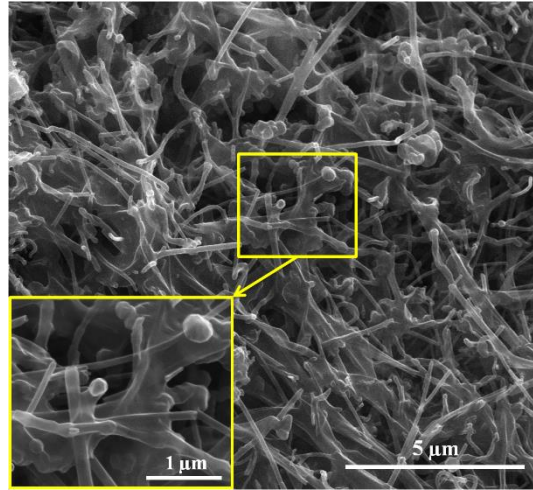


Figure 3.8 SEM image of vapor grown carbon nanofibers

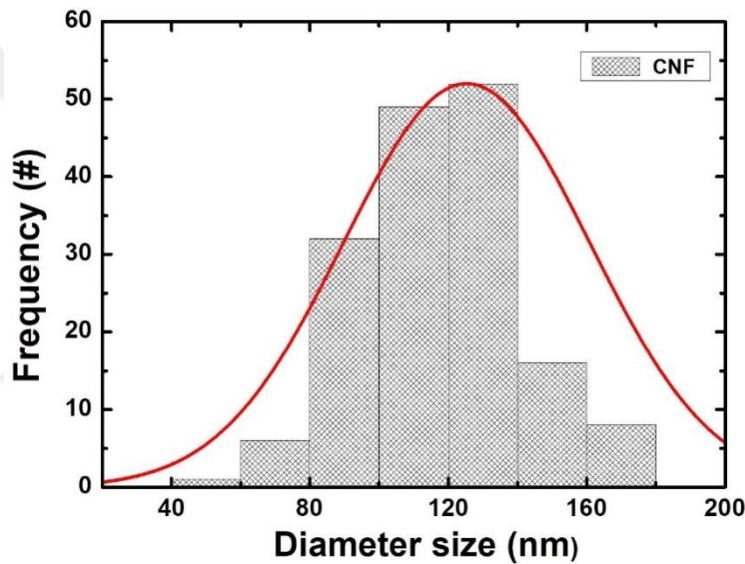


Figure 3.9 Diameter distribution of vapor grown carbon nanofibers

Reduced Graphene Oxide (rGO): In the third set of nanocomposites, reduced graphene oxide (rGO) was used. rGO was synthesized in our laboratory. For the synthesis of rGO, modified Hummers' method was used [263]. Graphite was supplied from Merck. The size of graphite was determined between 5-75 μm and average size was calculated around 50 μm. The physical appearance of rGO is given in Figure 3.10. As shown in Figure 3.11, rGO consists of many graphene layers with wrinkled and folded edges [265].

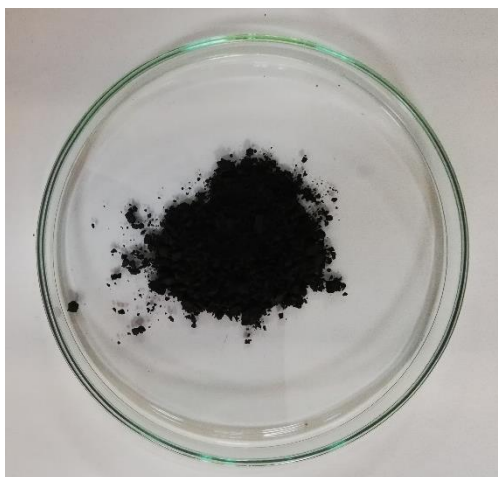


Figure 3.10 Reduced graphene oxide

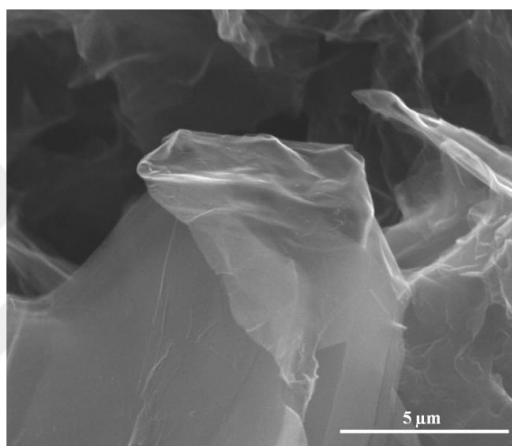


Figure 3.11 SEM image of reduced graphene oxide

Table 3.1 : Equipments and systems used for material production

System Name	Company Name& Model
Analytical balance	Radwag, AS 220.R2
Magnetic stirrer	Daihan MSH 20 D
Hot press (Compression molding system)	Not available (Chinese trade mark)
High shear mixer	Kurabo-Mazerustar, KK250
Thickness gauge	Asimeto

3.2. Methods

In this section, pressure sensor production is going to be explained in two parts. In the first part, preparation procedure of nanocomposites, including SEBS solution, filler/SEBS mixture preparation and nanocomposite film fabrication are going to be described. In the second part, the productions of pressure sensors are going to be given.

3.2.1. Preparation of the Nanocomposites

Nanocomposites were prepared by using solution casting method. In detail, the production of nanocomposites consisted of three main steps. As shown in Figure 3.12, it started with the preparation of SEBS solution. Following this step, filler/SEBS mixtures were prepared. Lastly, nanocomposite films were produced.

Preparation of the SEBS solution: In the initial stage of the process, SEBS thermoplastic elastomer was dissolved in toluene (SEBS: toluene, w:w 1:2) by a magnetic stirrer (Figure 3.13b). Process was carried out for 12 h at ambient temperature until clear solution was obtained. Weight of materials was measured by an analytical balance (Figure 3.13a).

Preparation of the filler/SEBS mixtures: In the second stage of the process, filler/SEBS mixtures were prepared for CB, VGCNFs and rGO.

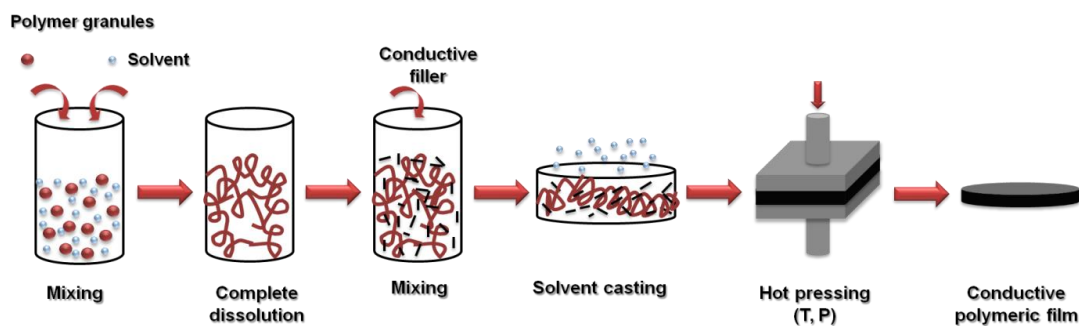


Figure 3.12 Stages for the preparation of filler/ SEBS mixtures and composite film fabrication

Preparation of the CB/SEBS mixtures: CB/SEBS mixtures were prepared by using seven levels of (1-7 wt%) CB. Predetermined wt% CB was added in 10 g of toluene and suspensions were mixed by a planetary high shear mixer at 1600 rpm for 90 s (Figure 3.14). Subsequently, SEBS solution was added into the CB-toluene mixture and mixed by the same system for 90s.

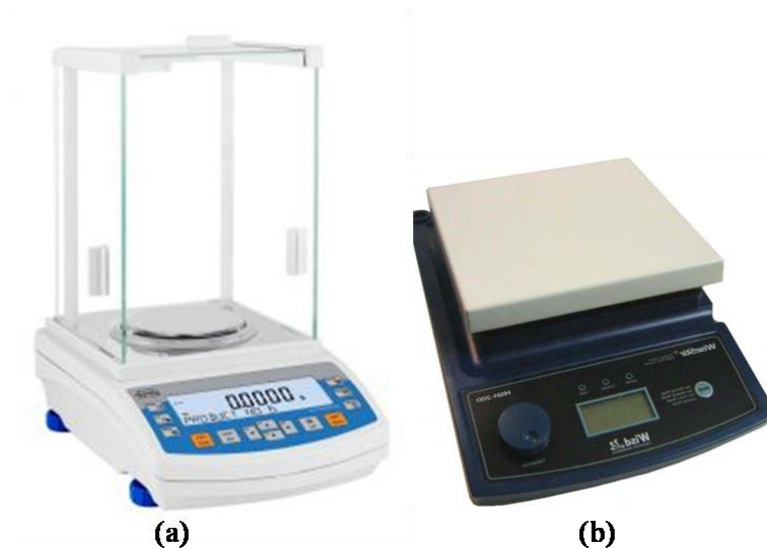


Figure 3.13 a) Analytical balance, b) Magnetic stirrer



Figure 3.14 Planetary high shear mixer

Preparation of the VGCNFs/SEBS mixtures: VGCNFs/SEBS mixtures were produced by using seven levels of (1-7 wt%) VGCNFs. Same mixing procedure mentioned above was used.

Preparation of the rGO/SEBS mixtures: rGO/SEBS mixtures were prepared at different rGO concentrations (1-45 wt. %) and same mixing procedure mentioned above was used.

Preparation of the films: In the second step of the nanocomposite film production, filler/SEBS mixtures were poured into a Petri dish. For the drying process, in order to remove the solvent completely Petri dishes were carefully placed in a vacuum oven at 40 °C for 24 h. Subsequently, the dried nanocomposites were compression molded between Teflon coated parallel plates at 180 °C under 3.5 MPa pressure for 10 min. After this process homogeneous films without any pores were obtained. The thickness of the nanocomposite films were measured by a digital thickness meter (Figure 3.15). At least 10 measurements were obtained and average film thickness was found around 0,7-0,8 mm for all samples regardless of the filler type.



Figure 3.15 Digital thickness meter

Preparation of the pressure sensors: Initially, the nanocomposite films were placed in a cylindrical-shaped mold (10 mm diameter, 10 mm height) as shown in Figure 3.16 and melt- pressed at 180 °C for 15 min. Thereafter, four copper wires were twisted by hand in the form of spring to be used as electrodes. The distance between probes was around 4 mm. These electrodes were embedded into cylindrical shaped nanocomposites and glued with 40 wt % CB containing conductive solvent based adhesive. Before electromechanical characterization, samples were kept for 12 h at ambient atmosphere for obtaining solid electrodes and evaporation of the solvent (Figure 3.17)

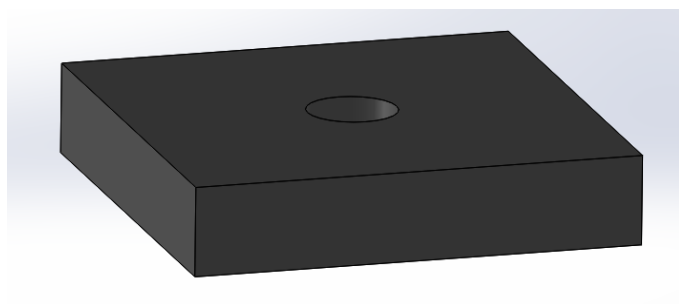


Figure 3.16 Cylindrical-shaped mold (hole dimensions: 10 mm diameter, 10 mm height)

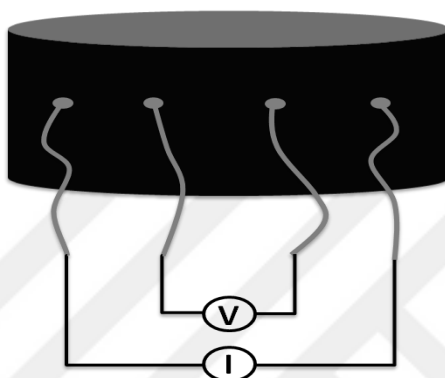


Figure 3.17 Schematic illustration of cylindrical-shaped pressure sensor with solid electrodes

3.2.2. Testing and Characterization

The morphological properties of CB, VGCNFs, rGO and nanocomposites were characterized by Field Emission Scanning Electron Microscope (FESEM) at Middle East Technical University that was operated at 20 kV accelerating voltage. For the cross-sectional characterization of nanocomposites, samples were cryo-fractured in liquid nitrogen. Before the imaging process, sputter coating with gold-palladium alloy (about 3-6 nm thickness) was carried out. The average filler size and distribution were determined from FESEM images by using ImageJ software.

Table 3.2 : Characterization type and system used for pressure sensors

Characterization Type	Company Name& Model
Morphology	FESEM, Quanta 400F
Volume resistivity	Electrometer, Keithley Model 6517B
	Resistivity Chamber, Model 8009
Electrical resistance	Current source, Keithley 6221
	Nanovoltmeter, Keithley 2182A
Dynamic uniaxial compression test	Universal load frame, Devotrans DVT
Morphology	FESEM, Quanta 400F

Before the electromechanical characterization, percolation behaviors of the nanocomposite films were determined. In order to obtain the percolation graphs, volume resistivity of each nanocomposite group was measured in accordance with ASTM D-257 standard by an electrometer and a resistivity chamber (Figure 3.18). For volume resistivity measurement, average thicknesses of all nanocomposites were specified by a digital thickness meter as mentioned above and resistivity values were obtained from the digital screen of the system. At least 5 different measurements were carried out, average values and standard deviation were calculated.



Figure 3.18 An electrometer and a resistivity chamber for the resistivity measurements

The piezoresistive tests were carried out by using a four-point probe system and a uniaxial dynamic load frame (Figure 3.20). Sensors were placed on a load frame with 10 mm gauge length. The test speed and deformation rate values were determined based on the composition of the sensor and given in Table 3.3.



Figure 3.19 Current source and Nanovoltmeter used for resistance measurement

Table 3.3 : Deformation rate and test speed values used during the piezoresistance tests

Sample	Deformation Rate			Test Speed					
	(Compression %)			(mm/min)					
5 wt% CB/SEBS	10	20	-	5	10	20	30	40	50
7 wt% VGCNFs/SEBS	10	20	-	5	10	20	30	40	50
30 wt% rGO/SEBS	-	20	50	-	10	20	30	40	50



Figure 3.20 The uniaxial dynamic compression testing machine

All samples were mounted on the mechanical testing system and subsequently, the pressure was applied at normal direction that caused to deformation and change in thickness. The dynamic resistance testing system was controlled by an automated data acquisition and control system that consists of a current source and a nanovoltmeter under 1 μA input current. The piezoresistive testing system monitored the resistance as a function of time during the cyclic tests. Upon a constant current, variations in resistance of sensors were recorded under applied pressure for 50 cycles. Since the system can store limited number of resistance data, in some cases (such as high deformation rates and low test speeds), 50 cycles could not be completed.

4. RESULTS

4.1. CB/SEBS Piezoresistive Pressure Sensors

4.1.1. Morphological Characterization

In order to analyze the morphology of CB filler in the SEBS matrix, cyro-fractured cross-sectional images were taken by FESEM. For the morphological characterization 4, 5, 6, 7 wt% CB/SEBS nanocomposites were chosen. In the Figure 4.1, the dark grey parts represent the polymeric matrix since it does not conduct the electricity. On the other hand, the light grey parts represent the CB particles because it is electrically conductive.

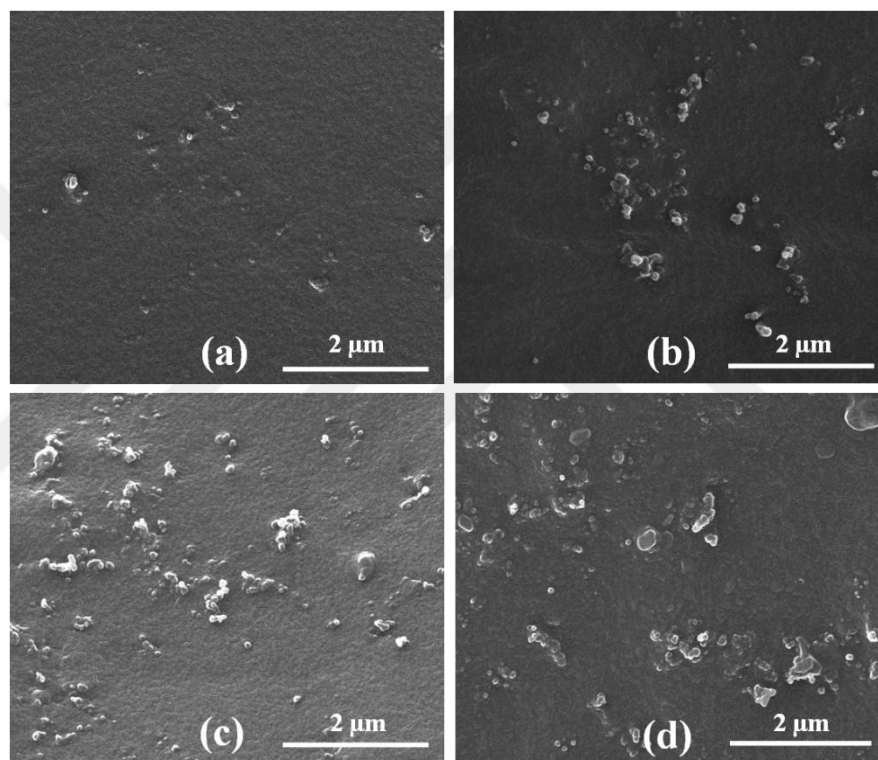


Figure 4.1 SEM images of a) 4 wt%, b) 5 wt% c) 6wt%, d) 7wt% CB/SEBS nanocomposites, scale bar: 2 μm

In Figure 4.1, morphology of 4, 5, 6 and 7wt% CB/SEBS nanocomposites is shown. As seen from the images, CB particles dispersed homogeneously in the polymeric matrix with a good filler-matrix interface. As obvious from the images, with the increase in CB content, the amount of CB in the unit area increases and filler-filler distance decreases. On the other hand, at higher concentrations due to the high interactions between fillers, agglomerate formation is observed.

In terms of morphological characterization, in addition to SEM analysis, AFM images were also used to demonstrate the conductive network formation [53, 100]. The morphological characterization is carried out only few studies in the literature. In parallel with our results, at high CB concentration, composites tend to create agglomerations [101, 150].

4.1.2. Electrical Characterization

4.1.2.1. Resistivity

Percolation behavior of CB filled SEBS nanocomposites were determined by measuring the volume resistivity. The percolation graph is given in terms of volume resistivity as a function of CB content (0-7 wt%) in Table 4.1 and Figure 4.2. The volume resistivity at a given CB concentration indicated by the dots and percolation region is the grey area in Figure 4.2. The increase in CB content, led to decrease the resistivity of the nanocomposites.

Table 4.1 : Changes in volume resistivity as a function CB filler concentration (wt%)

CB Filler Concentration (wt%)	Volume Resistivity (ρ) (ohm.cm)	ρ_0/ρ (ohm.cm)/(ohm.cm)
0	6,13E+17	1,00E+00
1	1,80E+17	3,41E+00
2	1,82E+17	3,37E+00
3	1,43E+16	4,29E+01
4	5,84E+10	1,05E+07
5	9,57E+07	6,41E+09
6	2,39E+06	2,56E+11
7	1,36E+06	4,51E+11

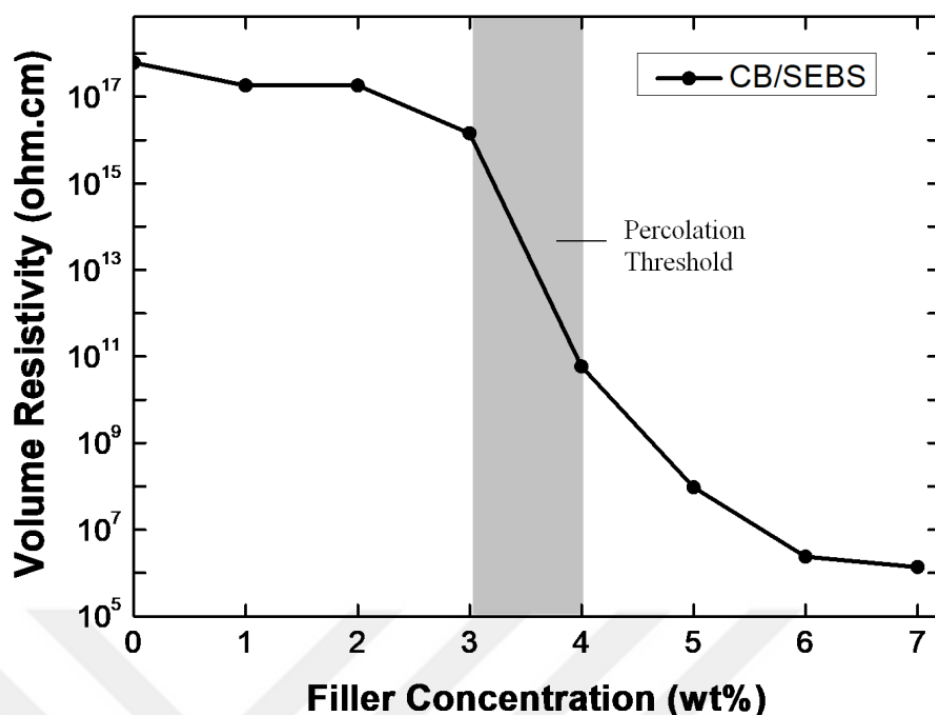


Figure 4.2 Percolation graph of CB/SEBS nanocomposites, volume resistivity vs. filler concentration (wt%)

With the addition of electrically conductive CB in the SEBS matrix, the electrical response of the materials exhibit differences depending on the filler content as given in Figure 4.2. CB/SEBS nanocomposites showed three distinct regions as insulation (0-3 wt%), percolation (3-4 wt%) and saturation (4-7 wt%) regions. The expected response in the insulation region is the stable volume resistivity or observation of a plateau. The volume resistivity of nanocomposites, between 0-2 wt% CB, are in the same orders of magnitude that can also be seen from ρ_0/ρ ratios in Table 4.1. With the increase in filler concentration, the volume resistivity decreased around one order of magnitude at 3 wt% CB but it is still not enough to obtain electrically conductive nanocomposites. The nanocomposites in the insulation region show high resistivity due to the insufficient filler concentration. Fillers are highly separated from each other. With the increase in CB content, the percolation threshold is observed between 3-4 wt% CB. The decrease in volume resistivity is six orders of magnitude as particularly indicated in Figure 4.2. As seen in the SEM images with the dispersion of CB in the matrix, conductive network is formed and current can flow throughout the nanocomposite (Figure 4.1a, c).

The last region that is generally observed as a plateau is the saturation or conductive region. Distinctly from the previous studies in the literature[30, 101], CB/SEBS nanocomposites reached the saturation gradually between 4-7 wt% CB. After a big drop in volume resistivity at the percolation region, insulating structure turned into conductive. When the CB content is increased to 5 wt%, the volume resistivity decreased three orders of magnitude. When the CB content is 6 wt%, the ratio of the decrease in resistivity is around two orders of magnitude. After 6 wt% CB, an increase in filler content did not affect the volume resistivity as given in Table 4.1.

The comparison of the piezoresistive elastomer based conductive polymer composites in the literature and our study in terms of resistivity at percolation threshold is given in Table 4.2.

Table 4.2 : Resistivity change in materials depending on the matrix, filler concentration and production method

Matrix type	Filler concentration	Resistivity at percolation threshold (Ωcm)	Production method	Ref.
NR	10-15 wt%	$\sim 10^7\text{-}10^4$	Solution casting	[148]
NBR	0,6-0,7 phr	$\sim 10^7\text{-}10^3$	Melting (two roll mill)	[149]
SR	22-30 v%	$\sim 10^6\text{-}10^4$	Solution casting	[136]
SR	3-5 wt%	$\sim 10^6\text{-}10^3$	Solution casting	[30]
SEBS	4-6 wt%	$\sim 10^8\text{-}10^3$	Melting (rheometer)	[101]
SEBS	0,02-0,032 v%	$\sim 10^{11}\text{-}10^6$	Melting (internal mixer)	[47]
SEBS	3-4 wt%	$\sim 10^{16}\text{-}10^{10}$	Solution casting	Our study

Despite the given studies, in our study the resistivity in percolation threshold is 10^{16} - $10^{10} \Omega\text{cm}$ at 3-4 wt% CB/SEBS nanocomposites. As seen, depending on the matrix, filler concentration and processing type resistivity values exhibit differences. It is important to reach percolation threshold at very low filler concentration and in our study, we succeeded to reach percolation threshold relatively lower CB concentration.

4.1.2.2. Electromechanical characterization

Depending on our previous studies and experimental trials, 5 wt% CB containing SEBS nanocomposite was chosen for the electromechanical characterization under cyclic pressure. Six different test speeds (5, 10, 20, 30, 40, 50 mm/min) and two different deformation % (10, 20 %) were used for the piezoresistance and resistance was recorded simultaneously for 50 cycles. Change in resistance and normalized resistance (R/R_0) were investigated for the easy analysis of cyclic stability for 50 cycles and single-cycle behavior. In accordance with this purpose, four different graphs are given for 10 and 20 % deformations and all test speeds (5, 10, 20, 30, 40, 50 mm/min). In the first and third graphs (Figure 4.4-4.15 (a-c), 50 cycles are given in order to analyze the cyclic stability and repeatability of the nanocomposite in terms of resistance and normalized resistance. Normalized (relative) resistance is basically R/R_0 (R =Resistance at any time, R_0 = Initial resistance). R/R_0 is significant for comparison of the sensitivity of the systems. In Figure 4.4-4.15 (b-d), first 10 cycles are given in order to understand the piezoresistive response and hysteresis as a function of time in terms of R and R/R_0 .

The effect of test speed on piezoresistive response was determined under 10 % deformation as shown in Figure 4.4-4.9. Regardless of the test speed, 5 wt% CB/SEBS nanocomposite showed the negative piezoresistive response. This behavior is observed due to the arrangement of the CB particles under pressure. As shown in Figure 4.3, interactions between CB particles increased with the pressure and the pressure provided the formation of conductive networks throughout the nanocomposite. This is the reason for the decrease in resistance during the loading cycle. On the other hand, the removal of pressure on nanocomposite caused the destruction of conductive networks and led to increase in resistance during the unloading cycle.

In our study, negative piezoresistive response was observed. This behavior was also seen in CB/NR [148], CB/NBR at low filler concentrations [149], CB/SR [30, 44, 136], CB/SR at a certain pressure value and filler concentration [150], CB/SEBS [47] nanocomposites. With the effect of pressure, resistance of these nanocomposites decreased and formed conductive networks through the nanocomposites.

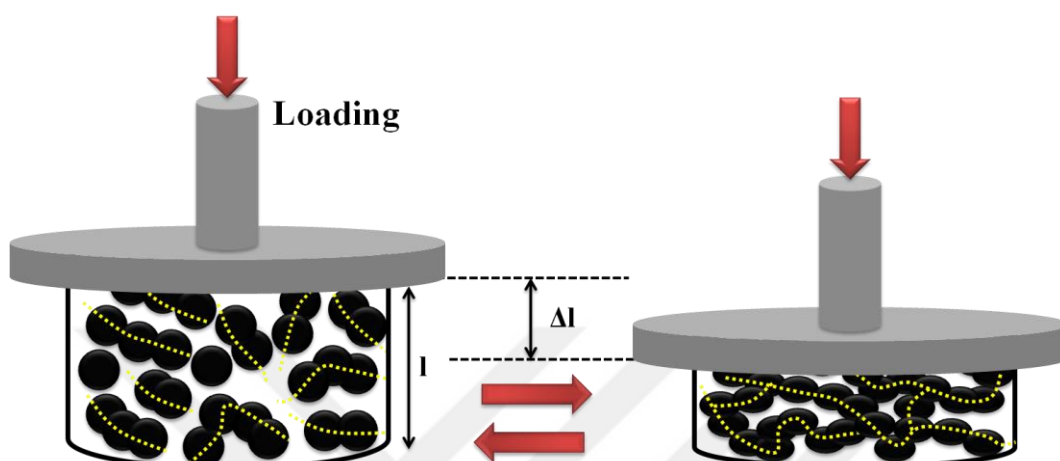


Figure 4.3 Mechanism of negative piezoresistance for CB under cyclic pressure

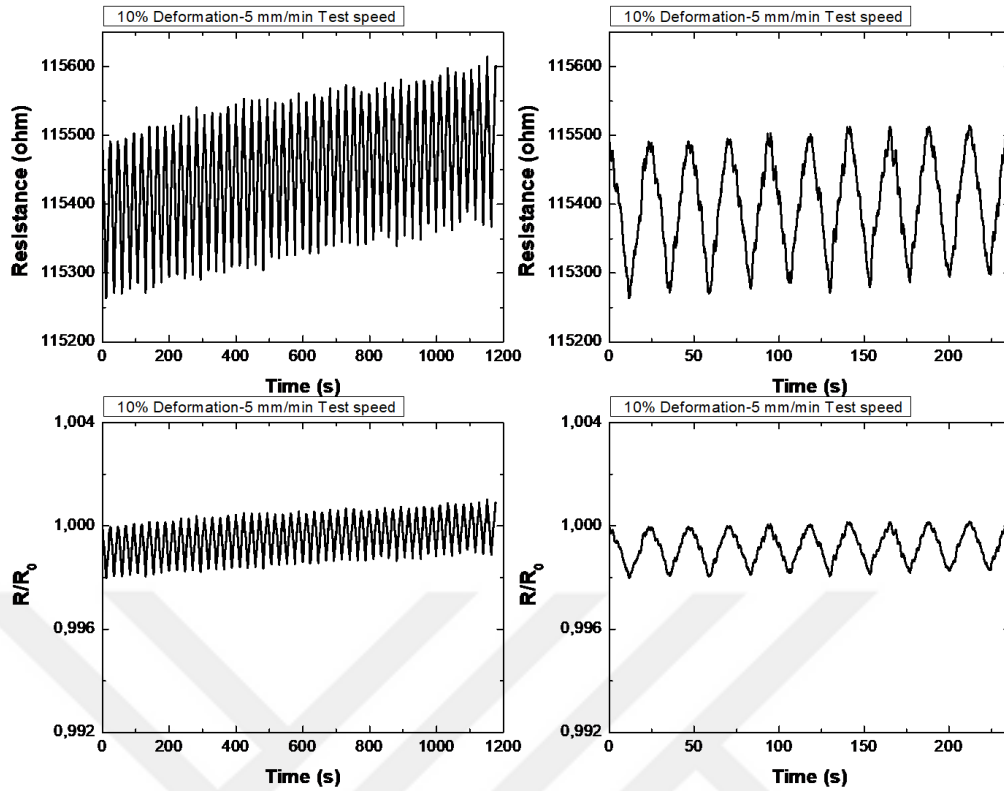


Figure 4.4 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 10 % deformation at 5 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 10 % deformation and 5 mm/min test speed through 50 cycles (Figure 4.4a). However, cycles shifted upwards during 50 cycles. As shown in Figure 4.4b, resistance change is in the range of 115270 to 115620 Ω . The relative resistance change is between 0,998 to 1,001 as shown in Figure 4.4c-d.

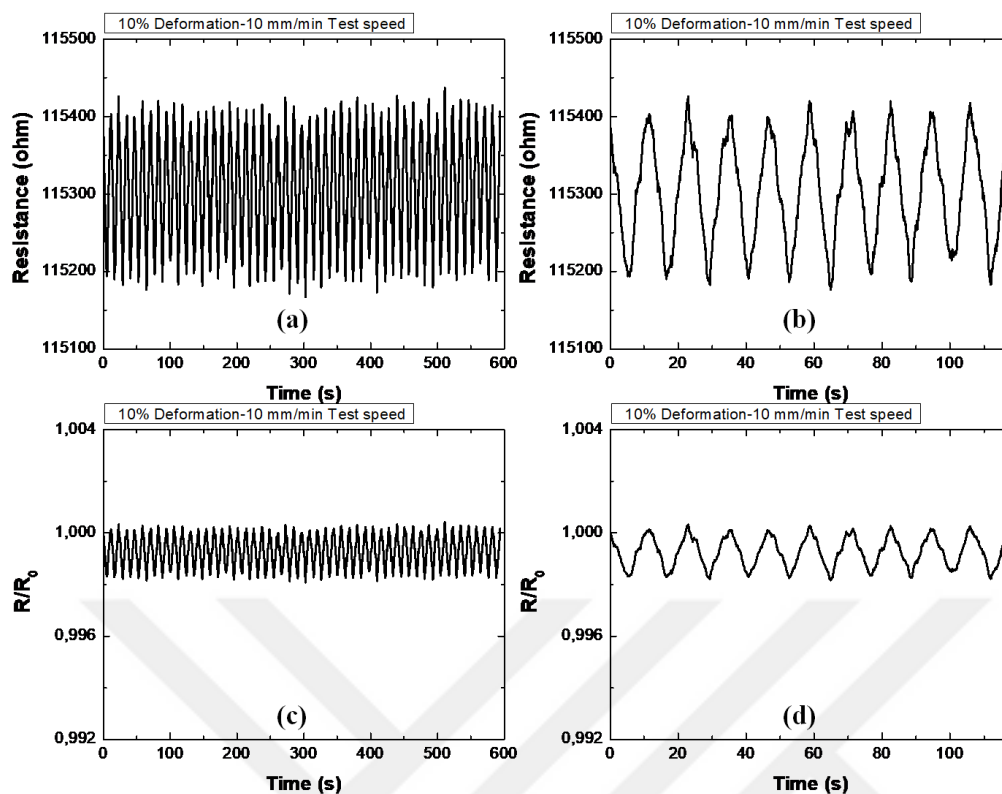


Figure 4.5 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 10 % deformation at 10 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 10 % deformation and 10 mm/min test speed through 50 cycles (Figure 4.5a). As shown in Figure 4.5b, resistance change is in the range of 115170 to 115440 Ω . The relative resistance change is between 0.998 to 1.0004 as shown in Figure 4.5c-d.

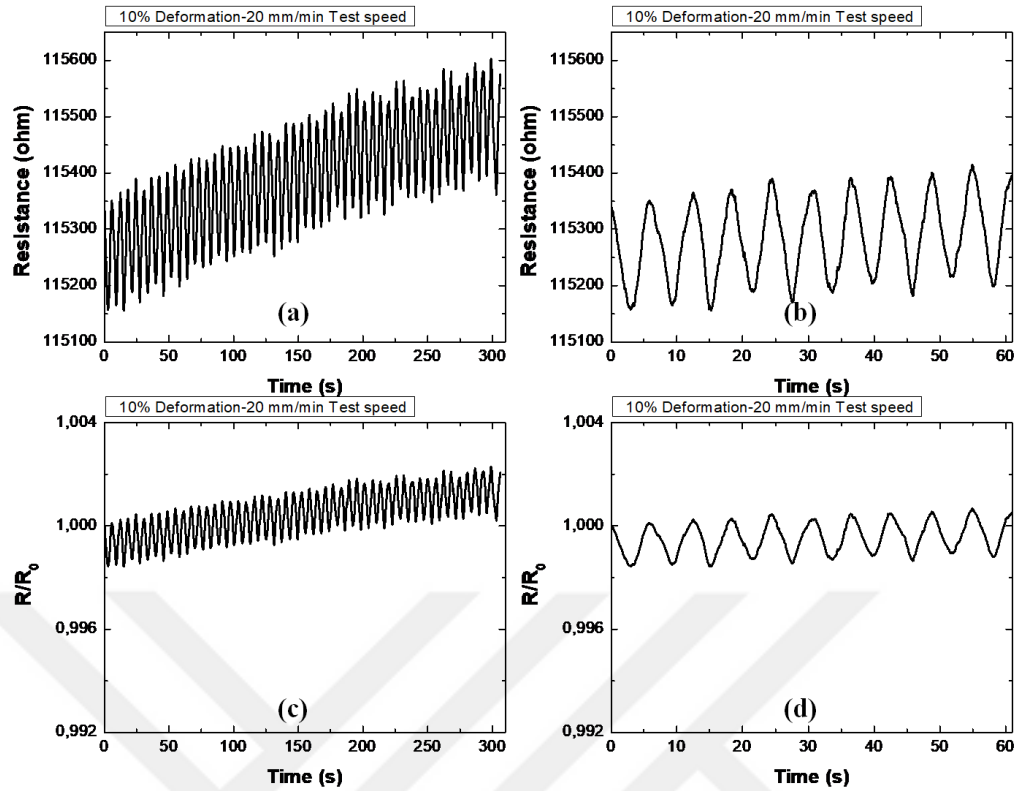


Figure 4.6 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 10 % deformation at 20 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 10 % deformation and 20 mm/min test speed through 50 cycles (Figure 4.6a). However, cycles shifted upwards during 50 cycles. As shown in Figure 4.6b, resistance change is in the range of 115160 to 115600 Ω . The relative resistance change is between 0.998 to 1.0023 as shown in Figure 4.6c-d.

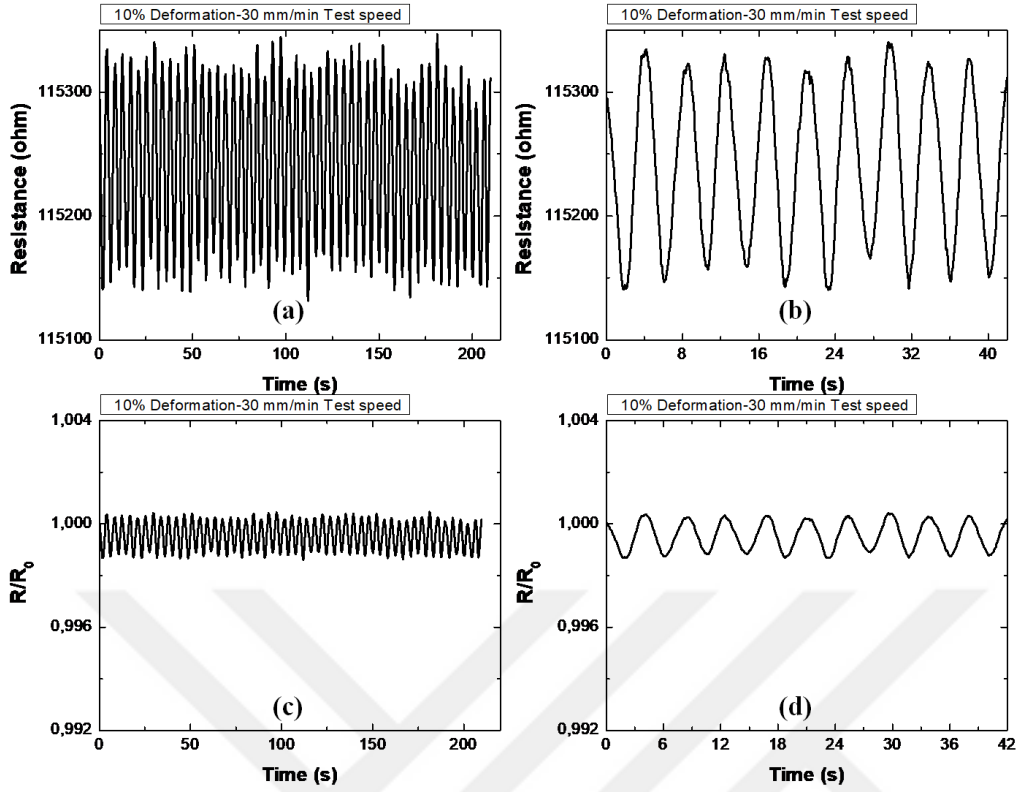


Figure 4.7 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 10 % deformation at 30 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 10 % deformation and 30 mm/min test speed through 50 cycles (Figure 4.7a). As shown in Figure 4.7b, resistance change is in the range of 115140 to 115350 Ω . The relative resistance change is between 0.998 to 1.0005 as shown in Figure 4.7c-d.

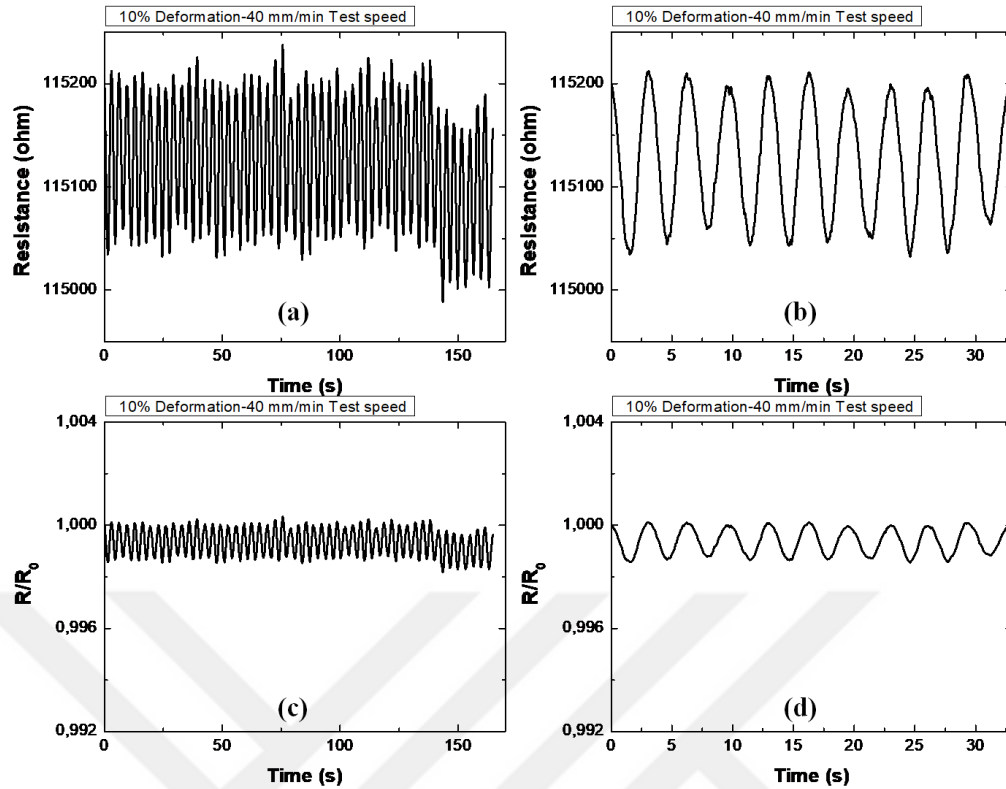


Figure 4.8 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 10 % deformation at 40 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response with variations under 10 % deformation and 40 mm/min test speed through 50 cycles (Figure 4.8a). However, cycles shifted downward during last 6 cycles. As shown in Figure 4.8b, resistance change is in the range of 115000 to 115250 Ω . The relative resistance change is between 0,998 to 1,0003 as shown in Figure 4.8c-d.

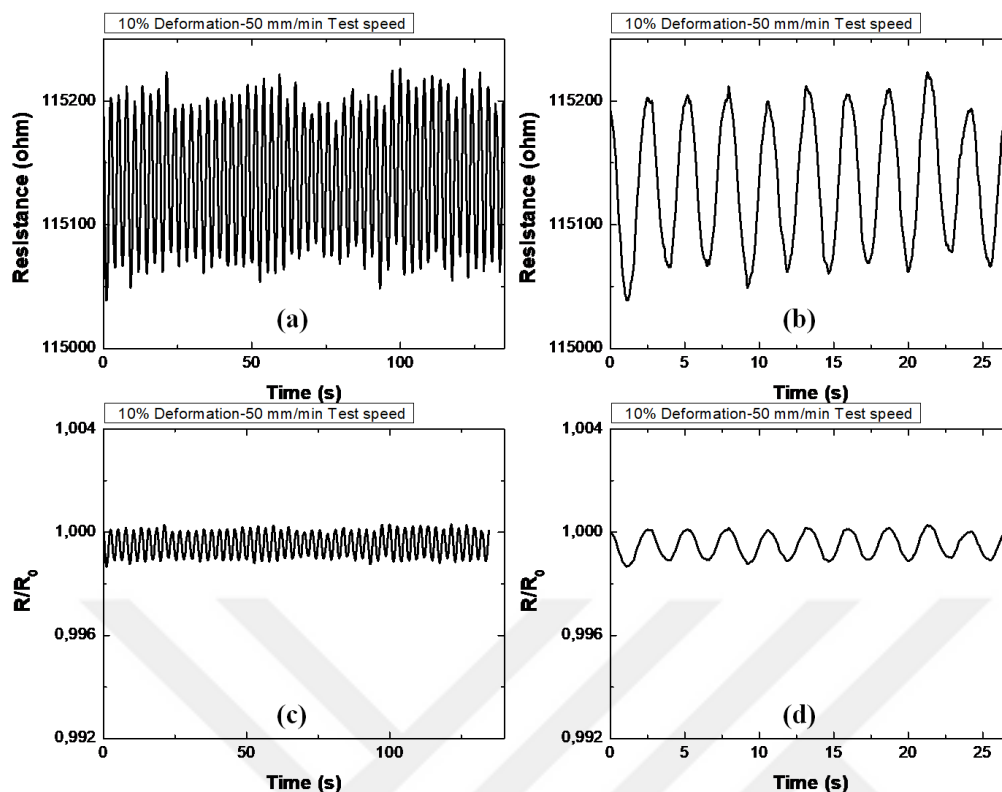


Figure 4.9 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 10 % deformation at 50 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 10 % deformation and 50 mm/min test speed through 50 cycles (Figure 4.9a). As shown in Figure 4.9b, resistance change is in the range of 115100 to 115250 Ω . The relative resistance change is between 0,998 to 1,0003 as shown in Figure 4.9c-d.

Under 10% deformation and at six different test speeds, the relative resistance is between 0,998- 1,002 (Figure 4.4c- 4.9c). At low test speeds, curves exhibit very noisy data with high sharpness. The noisy data is related to the number of recorded data during cycles (Figure 4.4b- 4.9b) and with the increase in test speed, the noise was disappeared. On the other hand, the sharpness shows the ability of CB particles to their initial position when the force is removed.

The effect of test speed on piezoresistive response was determined under 20 % deformation as shown in Figure 4.10-4.15. Regardless of the test speed, 5 wt% CB/SEBS nanocomposite showed negative piezoresistive response as mentioned previously for 10 % deformation.

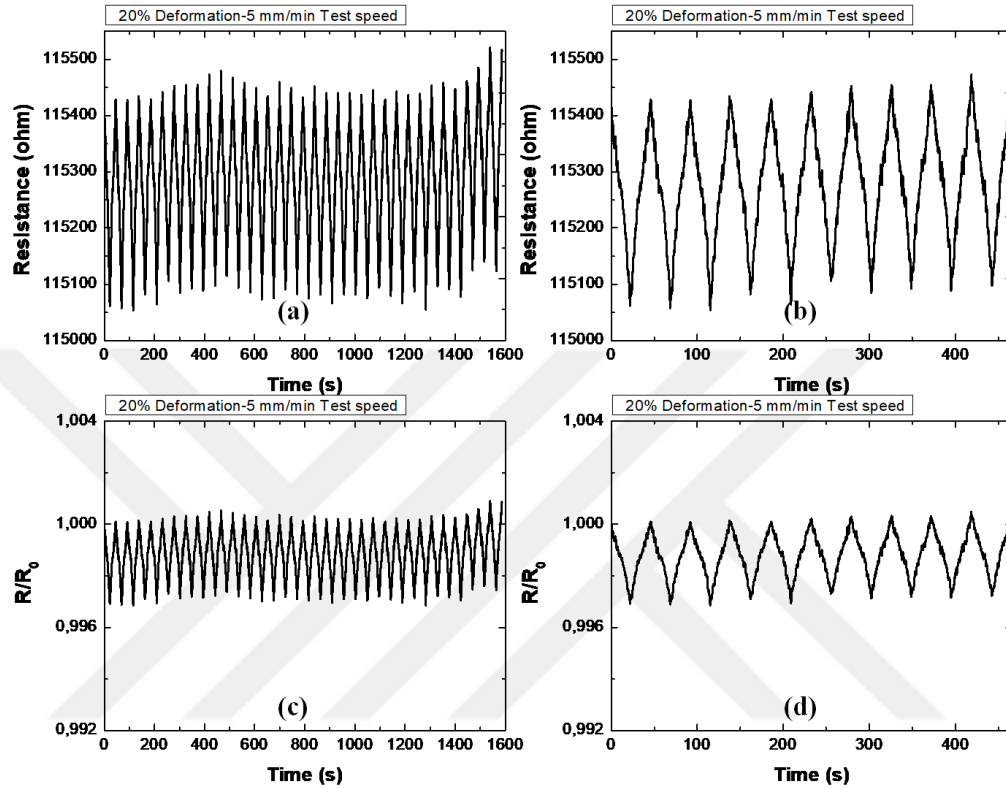


Figure 4.10 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 20 % deformation at 5 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 5 mm/min test speed through 50 cycles (Figure 4.10a). As shown in Figure 4.10b, resistance change is in the range of 115100 to 115600 Ω . The relative resistance change is between 0.997 to 1.001 as shown in Figure 4.10c-d.

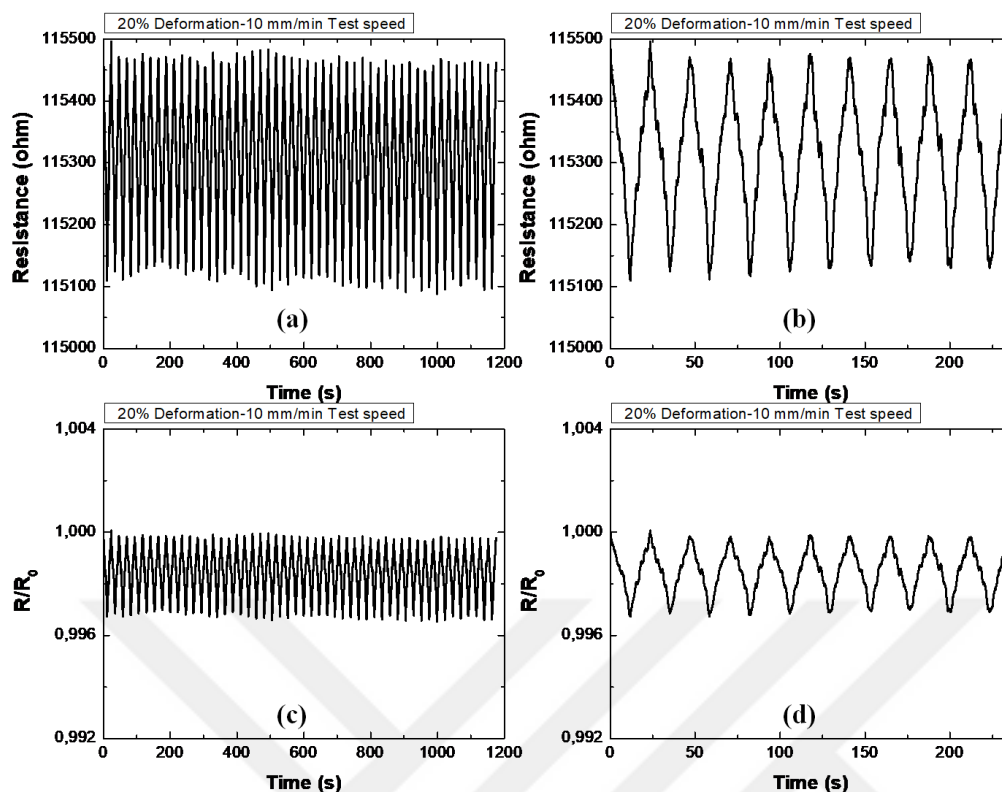


Figure 4.11 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 20 % deformation at 10 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 10 mm/min test speed through 50 cycles (Figure 4.11a). As shown in Figure 4.11b, resistance change is in the range of 115100 to 115500 Ω . The relative resistance change is between 0,997 to 1,0001 as shown in Figure 4.11c-d.

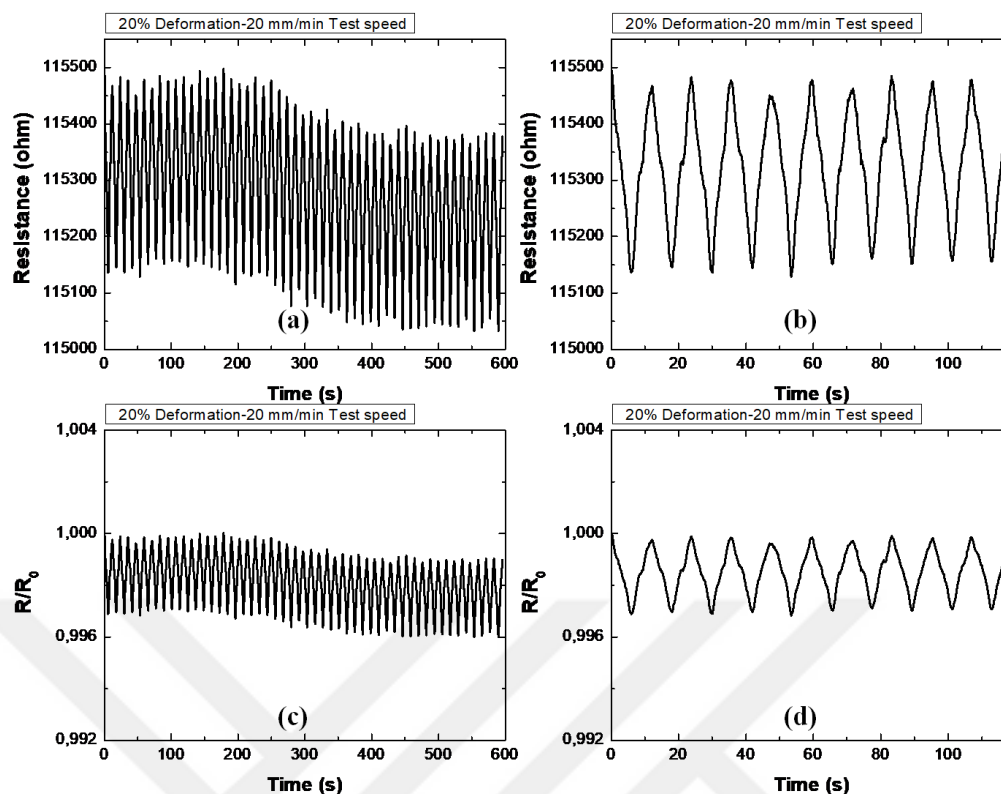


Figure 4.12 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 20 % deformation at 20 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 20 mm/min test speed through 50 cycles (Figure 4.12a). The piezoresistive curves show stable response until the 25th cycle and then the resistance decreased and showed stable response till the last cycle. As shown in Figure 4.12b, resistance change is in the range of 115100 to 115500 Ω . The relative resistance change is between 0.996 to 1.00 as shown in Figure 4.12c-d.

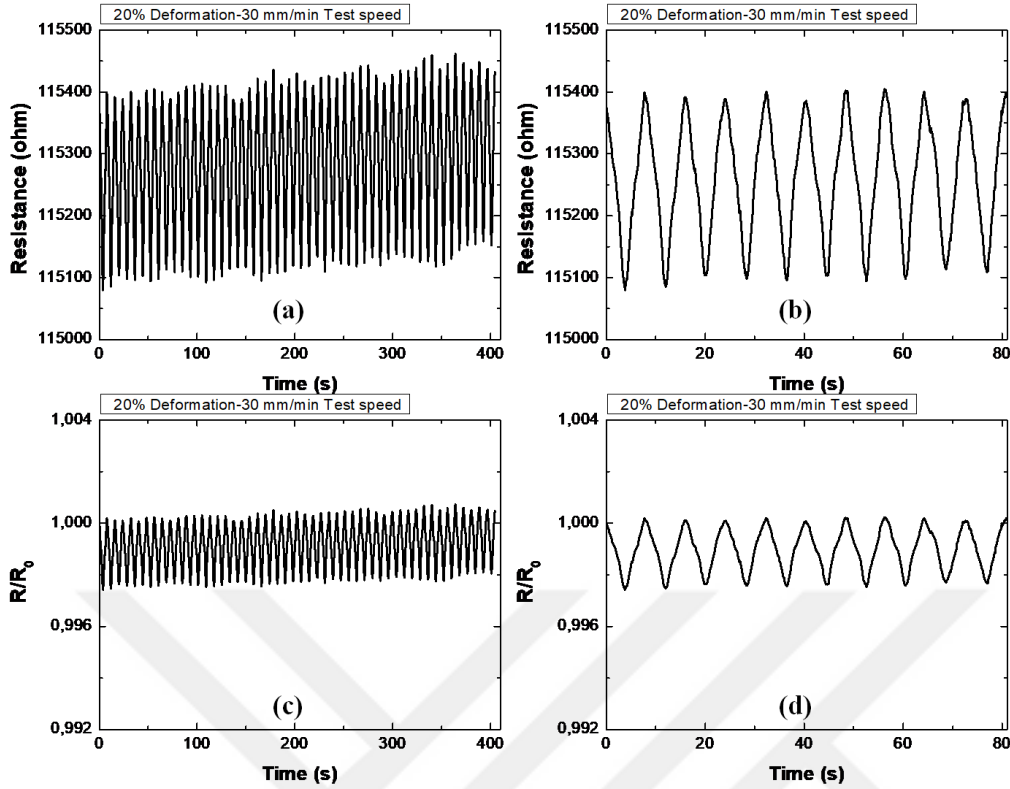


Figure 4.13 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 20 % deformation at 30 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 30 mm/min test speed through 50 cycles (Figure 4.13a). As shown in Figure 4.13b, resistance change is in the range of 115100 to 115500 Ω . The relative resistance change is between 0.997 to 1.001 as shown in Figure 4.13c-d.

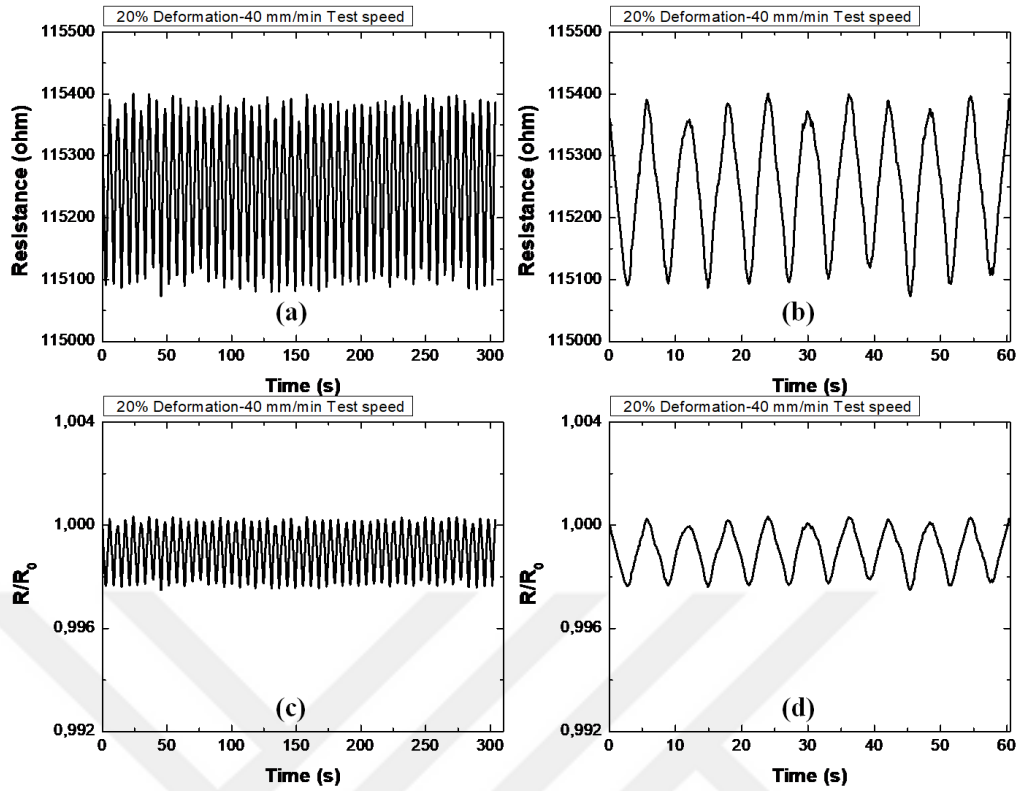


Figure 4.14 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 20 % deformation at 40 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 40 mm/min test speed through 50 cycles (Figure 4.14a). As shown in Figure 4.14b, resistance change is in the range of 115100 to 115400 Ω . The relative resistance change is between 0.997 to 1.0003 as shown in Figure 4.14c-d.

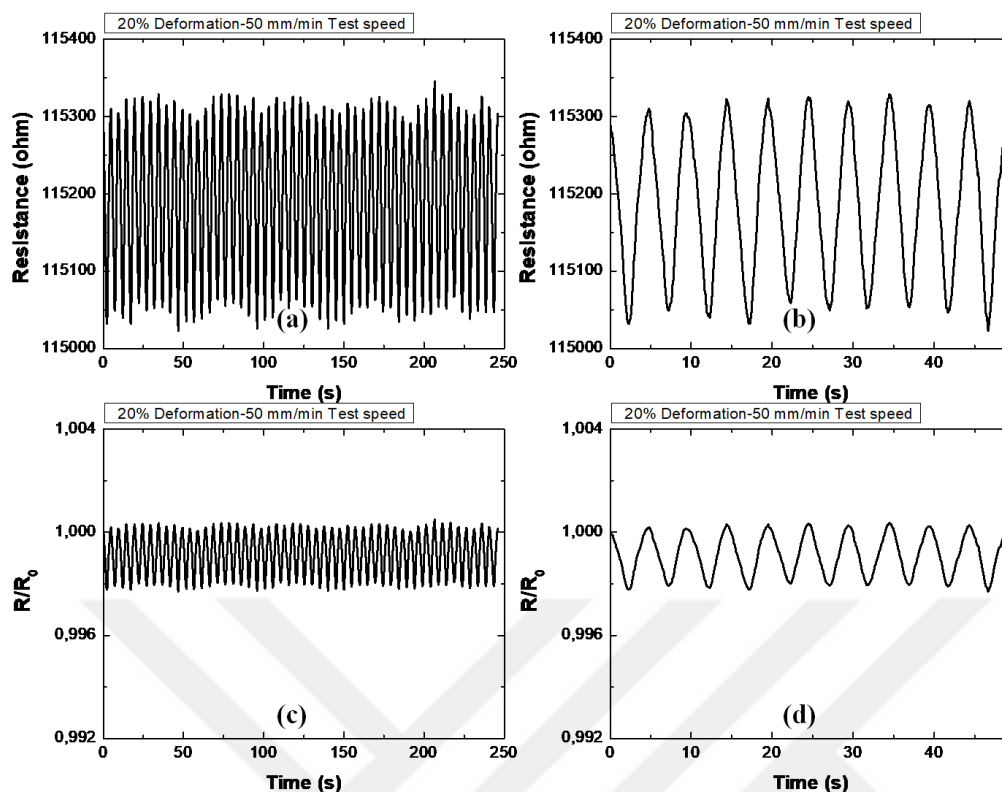


Figure 4.15 Cyclic piezoresistive response of 5 wt% CB/SEBS nanocomposite under 20 % deformation at 50 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 50 mm/min test speed through 50 cycles (Figure 4.15a). As shown in Figure 4.15b, resistance change is in the range of 115100 to 115400 Ω . The relative resistance change is between 0,998 to 1,0005 as shown in Figure 4.15c-d.

The relative resistance under 20 % deformation for all test speeds was around 0,997-1,001(Figure 4.10-4.15 (c-d)). There are very small differences between the relative resistance values. On the other hand, the relative resistance under 10 % deformation was around 0,998-1,002. The relative resistance for 50 cycles is almost the same for each deformation and these results showed that % deformation did not affect the relative resistance (10, 20 %). In addition, under 20 % deformation, test speed also did not affect the relative resistance. Because of this behavior, 5 wt% CB/SEBS nanocomposite returned initial position in all cases.

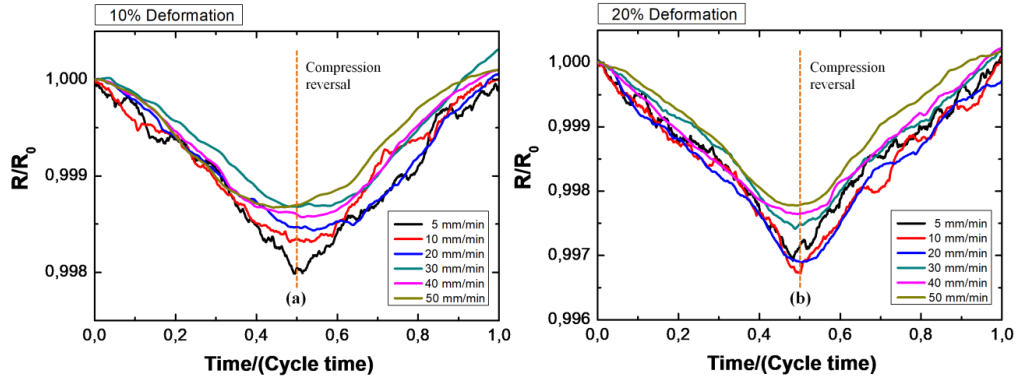


Figure 4.16 Change in relative resistance under a) 10% deformation, b) 20% deformation for all test speeds for a single (loading/unloading) cycle for 5 wt% CB containing SEBS nanocomposite

The comparison of two sets (10 % and 20% deformation) is given in Figure 4.16. The relative resistance for a single cycle for all test speeds (10, 20, 30, 40, 50 mm/min) is given. For easy comparison, the time axis divided into total cycle time for each test speed.

When the sample was deformed 10 %, the relative resistance at compression reversal is roughly between 0,9979-0,9987. On the other hand, under 20 % deformation, the relative resistance at compression reversal is roughly between 0,9967- 0,9978. With the increase in test speed as obviously seen from the Figure 4.16a-b, shape and the noisiness of the curves and sharpness of the peaks decreased. The decrease in the relative resistance change means to decrease in sensitivity of nanocomposite and it is observed in both 10 and 20 % deformation values. The recoverability of polymeric matrix can cause to this response. Also, the smoothness of the curves increased and it is probably related to the testing system. Since at low test speeds, small changes can be measured and the curves show more noisy response. In addition, the increase in test speed also changed the sharpness of the curves.

In terms of piezoresistive response, there are few studies that have dynamic testing system [17, 44] and only one study investigated the effect of deformation % on piezoresistive response [17]. The other studies piezoresistive response was characterized under gradually increased pressure [52, 100, 149, 150] and these testing systems are not good enough to determine the piezoresistive response in terms of cyclic stability and hysteresis in the long term.

4.2. VGCNFs/SEBS Piezoresistive Pressure Sensors

4.2.1. Morphological Characterization

The morphological structure of VGCNFs/SEBS nanocomposites was investigated and cryo-fracture cross-sectional images were taken by FESEM. In Figure 4.17, the SEM images belongs to 2, 4, 6, 7 wt% VGCNFs/SEBS nanocomposites. The VGCNFs are shown in light grey color due to their electrical conductivity whereas electrically insulating SEBS matrix is in dark grey color.

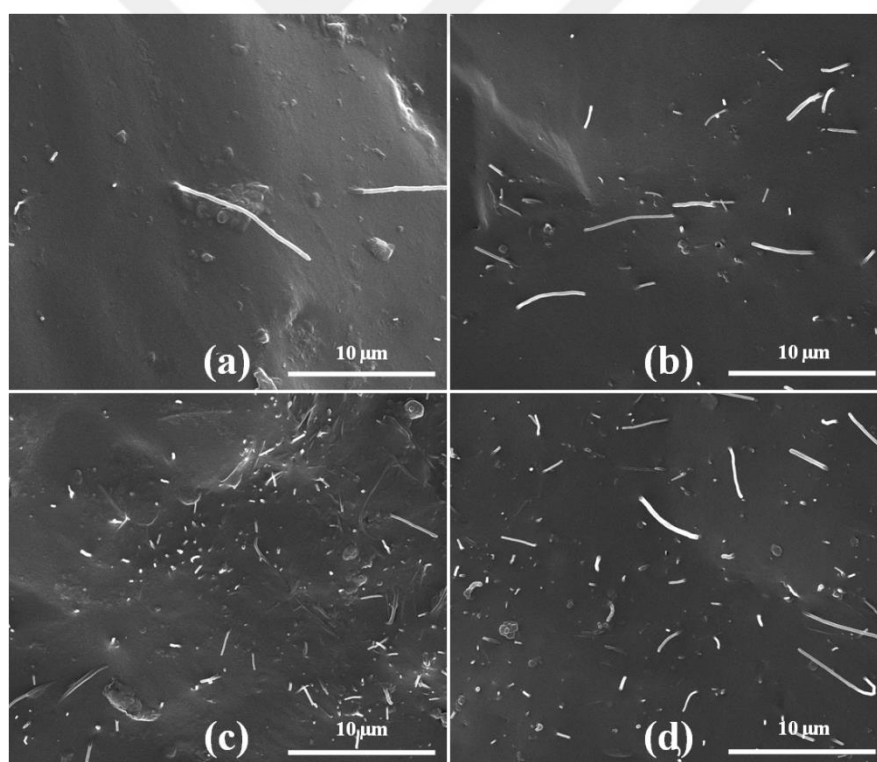


Figure 4.17 SEM images of a) 2 wt%, b) 4 wt% c) 6wt%, d) 7wt% VGCNF/SEBS nanocomposites, scale bar: 10 μm

The SEM images show the dispersion of VGCNFs in the SEBS matrix. VGCNFs are protruded from the cyro-fractured surface. As seen, the VGCNFs are homogeneously dispersed in the matrix and highly interacted with each other. It is also obvious that by increasing the filler ratio, amount of the observed filler increases that is also an indication of homogeneous filler dispersion.

In the literature, in terms of morphological characterization, a new imaging technique was used that is named as in-situ micromechanical SEM technique. With the aid of this technique, macro and micro structures under pressure could be observed [18]. In another study, morphological structure of 8 wt% CNFs/PDMS was characterized and homogenous filler dispersion in the matrix was reported to be obtained [54], that is parallel with our SEM images at both low and high filler concentrations.

4.2.2. Electrical Characterization

4.2.2.1. Resistivity

The electrical properties of VGCNFs/SEBS nanocomposites change depending on the filler concentration in the insulating matrix. The changes in the electrical properties of nanocomposites were investigated in terms of their volume resistivity. The content of VGCNFs in the matrix is ranged from 0 to 7 wt%. In Table 4.3 and Figure 4.18, the volume resistivity of VGCNFs/SEBS nanocomposites as a function of filler concentration is given.

Table 4.3 : Changes in volume resistivity as a function VGCNFs concentration (wt%)

VGCNFs Filler Concentration (wt%)	Volume Resistivity (ρ) (ohm.cm)	ρ_0/ρ (ohm.cm)/(ohm.cm)
0	6,13E+17	1,00E+00
1	3,01E+17	2,03E+00
2	3,30E+10	1,86E+07
3	1,23E+09	4,99E+08
4	5,51E+07	1,11E+10
5	8,34E+06	7,35E+10
6	5,33E+06	1,15E+11
7	2,43E+06	2,53E+11

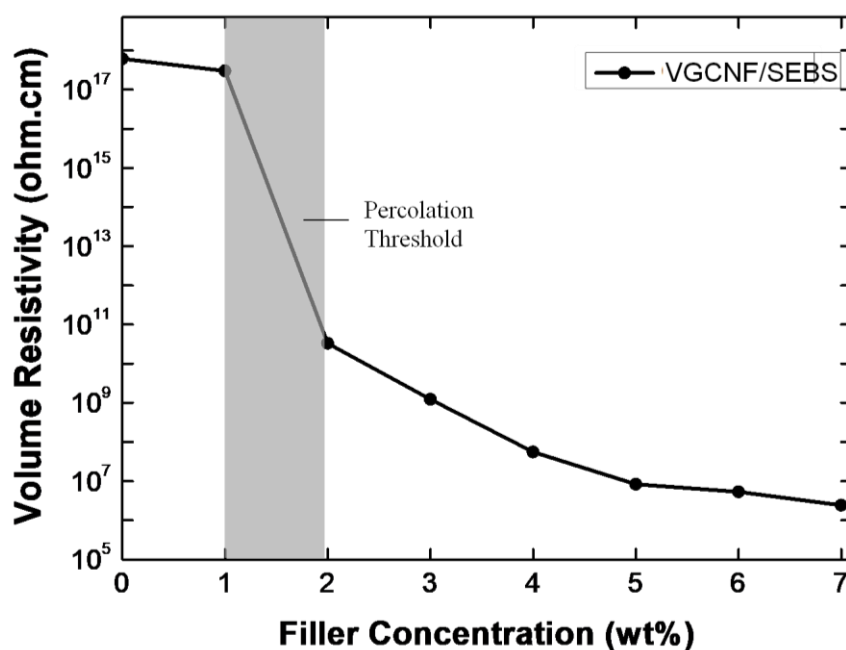


Figure 4.18 Percolation graph of VGCNFs/SEBS nanocomposites, volume resistivity vs. filler concentration (wt%)

As can be seen in Figure 4.18, the VGCNFs/SEBS nanocomposites showed the traditional percolation response [54]. VGCNFs/SEBS nanocomposites display three regions as insulating, percolation and conductive regions. With the increase in VGCNFs concentration, the volume resistivity of nanocomposites exhibits different responses in these regions. The insulating region is in the range of 0-1 wt% VGCNFs content. In this region, the volume resistivity of 1 wt% VGCNFs/SEBS nanocomposite is very close to neat SEBS polymer that can also be seen from ρ_0/ρ ratios in Table 4.3, since the filler-filler distance is very high and cannot form conductive networks. Plateau is observed due to the high resistivity at 1 wt% VGCNFs content. The percolation threshold is observed between 1-2 wt% VGCNFs content. The expected response in the percolation region is the sudden decrease in resistivity with orders of magnitude. The resistivity decreased almost seven orders of magnitude. The decrease is the reflection of the formation of the conductive network as shown in Figure 4.17a. With the dispersion of 2 wt% VGCNFs in the matrix filler-filler distance is decreased and conductivity increased.

The conductive or saturation region is between 4-7 wt% VGCNFs content. This region generally shows plateau and change in resistivity is very small whereas in our study, it reached the plateau gradually. When the filler concentration is increased from 2 to 5 wt%, the volume resistivity decreased almost three orders of magnitude. As shown in Figure 4.17b, the amount of VGCNFs that are connected with each other more compared to Figure 4.17a. This can be attributed to the proceeding of the formation of the conductive network throughout the nanocomposites and resulted in a decrease in resistivity. In the range of 5-7 wt% VGCNFs content, the volume resistivity of nanocomposites is almost constant (Figure 4.17c-d). It also means that VGCNFs/SEBS nanocomposites reached to the maximum conductivity level that will not change even if the filler concentration is increased.

In the literature in terms of percolation threshold, the CNFs/PDMS nanocomposite showed percolation threshold around 1-3 wt% CNFs concentration and the resistivity in this region was in the range of 10^8 - $10^{-3}\Omega\text{cm}$. In our study, the percolation threshold was observed between 1-2 wt% VGCNFs concentrations in the range of 10^{17} - $10^{10}\Omega\text{cm}$. The given resistivity values in the literature study are in saturation region according to our study. As seen, polymeric matrix type and morphology of nanocomposites change the percolation threshold and also resistivity values. Parallel with our study, plateau region was observed in saturation region. On the other hand, the resistivity change in conductive region did not exceed the one order of magnitude whereas distinctly from the literature the resistivity change is almost four orders of magnitude and reached plateau gradually.

4.2.2.2. Electromechanical characterization

For determination of the cyclic performance, 7 wt% VGCNFs/SEBS nanocomposite was chosen depending on our previous studies and experimental know-how. The electromechanical characterization is carried out by using six different test speeds (5, 10, 20, 30, 40, 50 mm/min) at two different deformation % (10, 20%). The resistance of the material was recorded simultaneously for 50 cycles as a function of time. In terms of cyclic stability for 50 cycles and single-cycle behavior, change in resistance and normalized resistance (R/R_0) were investigated. In accordance with this purpose, four different graphs are given for 10 and 20% deformations and all test speeds (5, 10, 20, 30, 40, 50 mm/min). In the first and third graphs (Figure 4.20-4.31 (a-c)), 50 cycles are given in order to analyze the cyclic stability and repeatability of the nanocomposite in terms of resistance and normalized resistance. Normalized (relative) resistance is basically R/R_0 (R =Resistance at any time, R_0 = Initial resistance). R/R_0 is significant for comparison of the sensitivity of the systems. In Figure 4.20-4.31(b-d), first 10 cycles are given in order to understand the piezoresistive response and hysteresis as a function of time in terms of R and R/R_0 .

The effect of test speed on piezoresistive response is carried out and results that belong to 10% deformation are given in Figure 4.20-4.25 and 20% deformation are given in Figure 4.26-4.31. In both % deformation, non-linear negative to positive piezoresistive response is observed regardless of the test speed. This response is observed in the both loading and unloading stages. In the loading stage, with the initiation of the deformation, the randomly oriented VGCNFs started to align and the conductive network is formed. The conductive network formation provides to decrease in resistance and negative piezoresistive response is observed. On the other hand, after a critical deformation value, the aligned VGCNFs started to separate from each other and filler-filler distance increased. This means the destruction of the conductive network and resistance of the material increased. In this part, the material exhibited positive piezoresistance and the loading stage was completed. In the unloading stage, the reverse response is obtained [117]. This was previously observed for VGCNFs filled polymer composites [117].

In parallel with literature, the VGCNFs/SEBS nanocomposites exhibit negative piezoresistive response and this response was also observed in CNFs/PDMS nanocomposites [18, 54]. Distinctly from the literature, VGCNFs/SEBS nanocomposites did not exhibit linear character in all test conditions because of the unstable CNFs response under pressure.

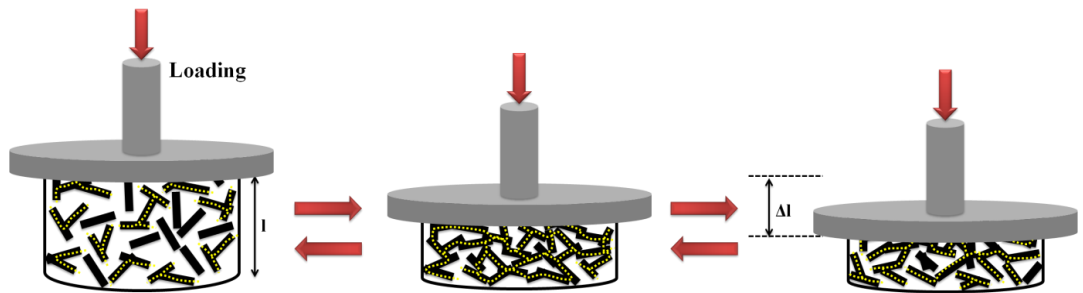


Figure 4.19 Mechanism of negative to positive piezoresistance for VGCNFs under cyclic pressure

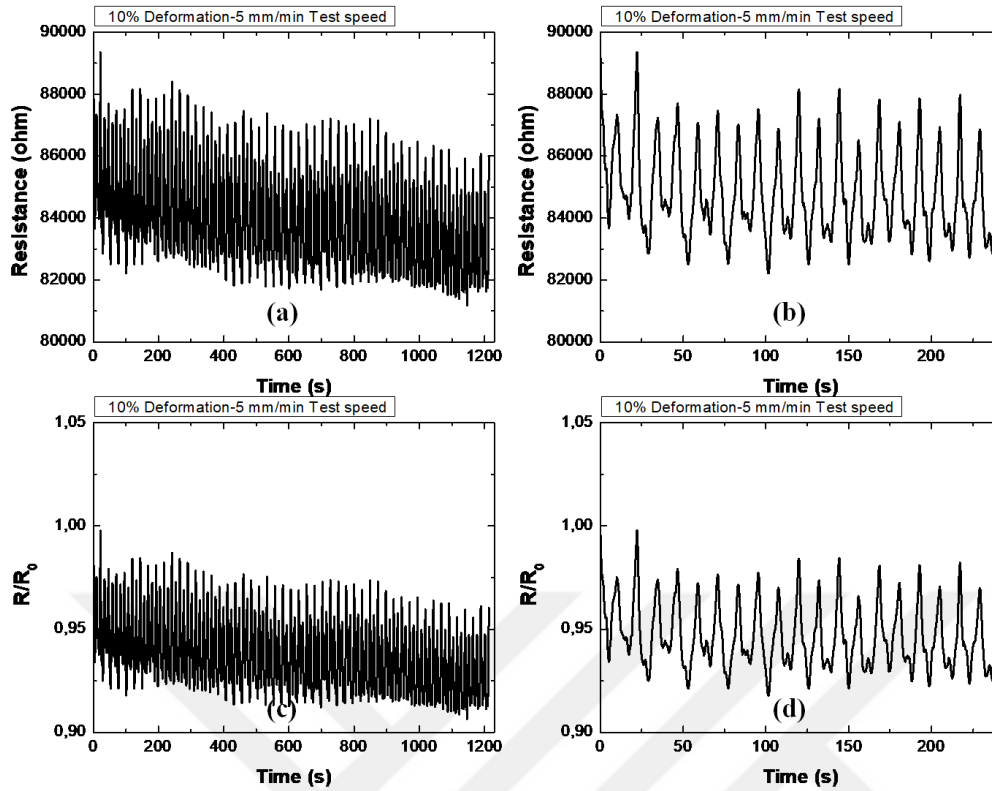


Figure 4.20 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 10% deformation at 5 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 10% deformation and 5 mm/min test speed through 50 cycles (Figure 4.20a). However, cycles showed negligible up and downwards during 50 cycles. As shown in Figure 4.20b, resistance change is in the range of 81200 to 90000 Ω . The relative resistance change is between 0,91 to 1,0 as shown in Figure 4.20c-d.

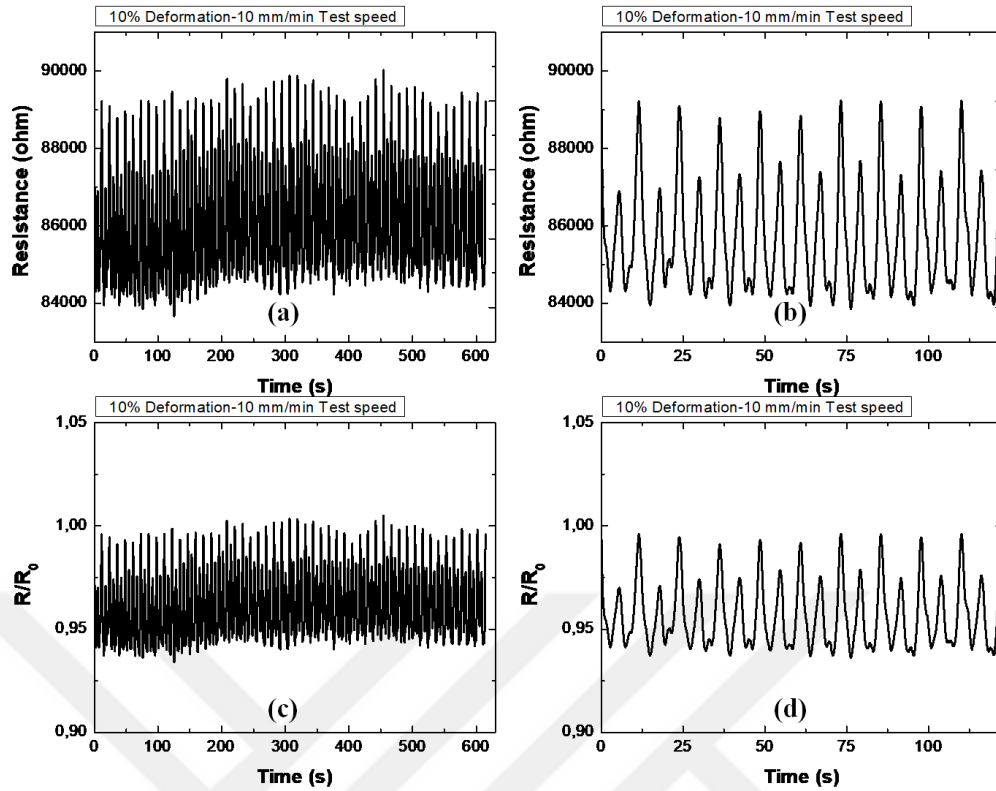


Figure 4.21 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 10% deformation at 10 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 10% deformation and 10 mm/min test speed through 50 cycles (Figure 4.21a). As shown in Figure 4.21b, resistance change is in the range of 84000 to 90100 Ω . The relative resistance change is between 0.93 to 1.005 as shown in Figure 4.21c-d.

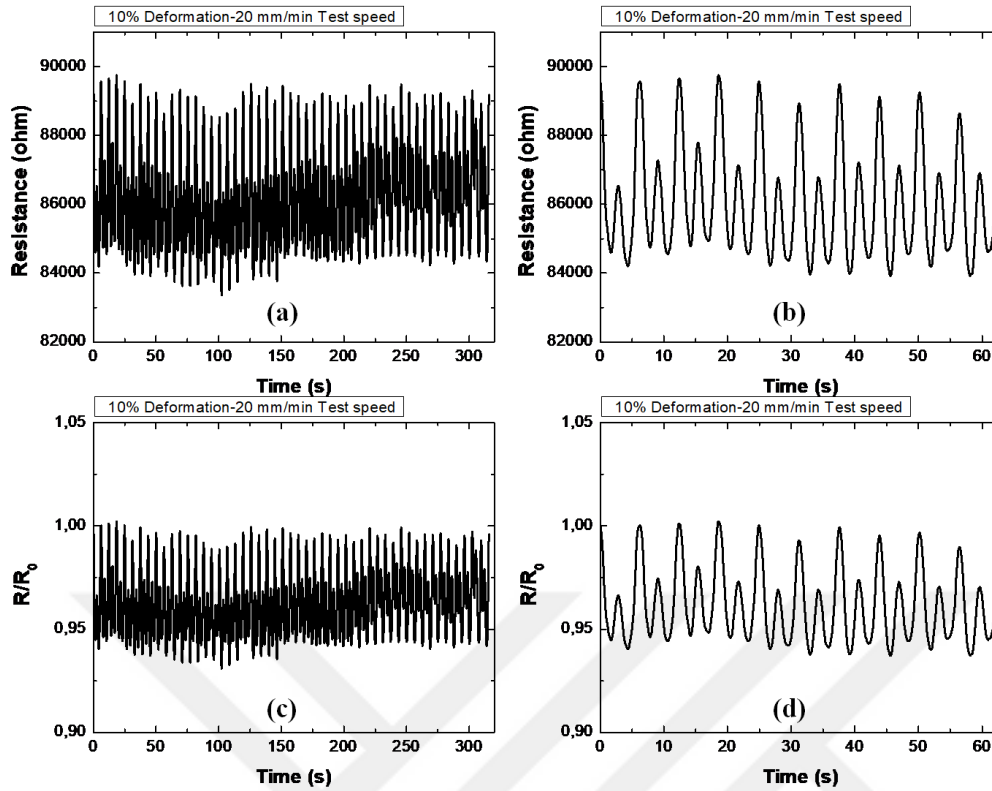


Figure 4.22 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 10% deformation at 20 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 10% deformation and 20 mm/min test speed through 50 cycles (Figure 4.22a). As shown in Figure 4.22b, resistance change is in the range of 83400 to 90000 Ω . The relative resistance change is between 0.93 to 1.002 as shown in Figure 4.22c-d.

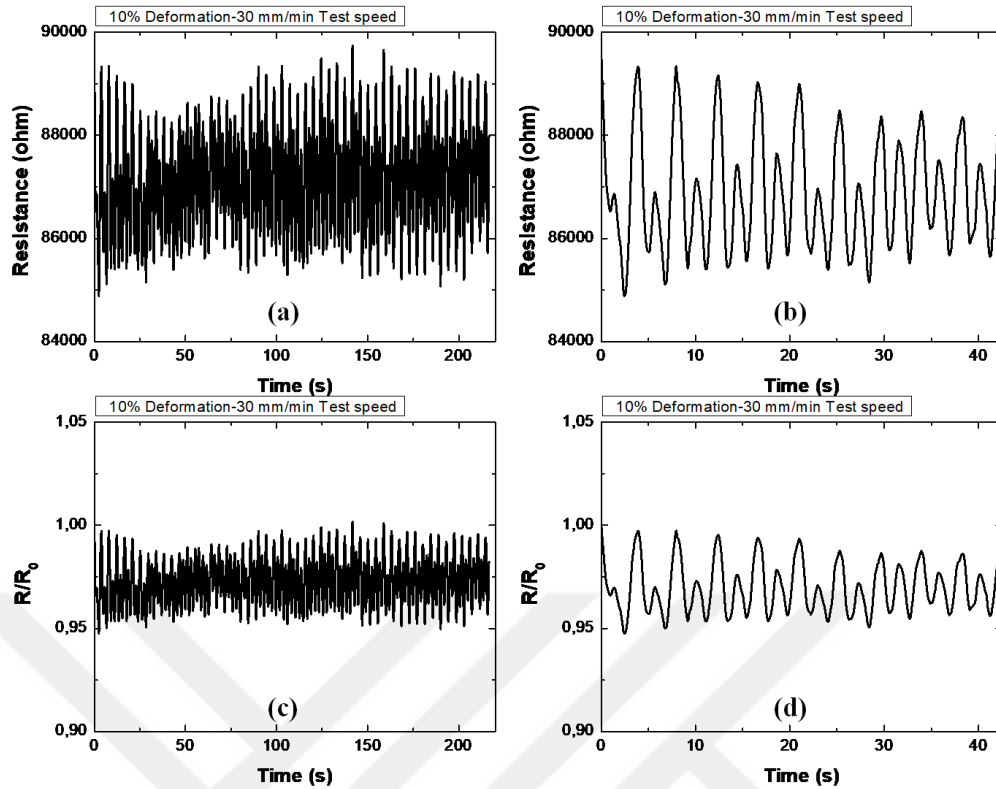


Figure 4.23 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 10% deformation at 30 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 10% deformation and 30 mm/min test speed through 50 cycles (Figure 4.23a). However, cycles showed negligible downwards during 50 cycles. As shown in Figure 4.23b, resistance change is in the range of 85000 to 90000 Ω . The relative resistance change is between 0.95 to 1.002 as shown in Figure 4.23c-d.

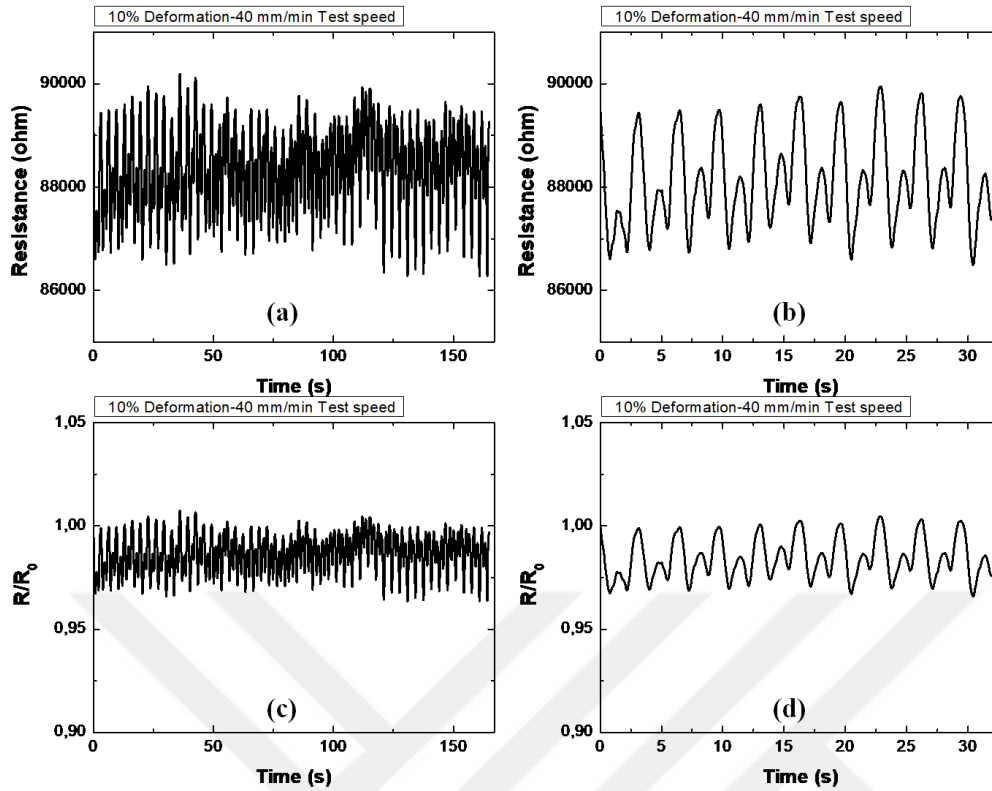


Figure 4.24 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 10% deformation at 40 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 10% deformation and 40 mm/min test speed through 50 cycles (Figure 4.24a). However, cycles showed negligible up and downwards during 50 cycles. As shown in Figure 4.24b, resistance change is in the range of 86300 to 90200 Ω . The relative resistance change is between 0.96 to 1.007 as shown in Figure 4.24c-d.

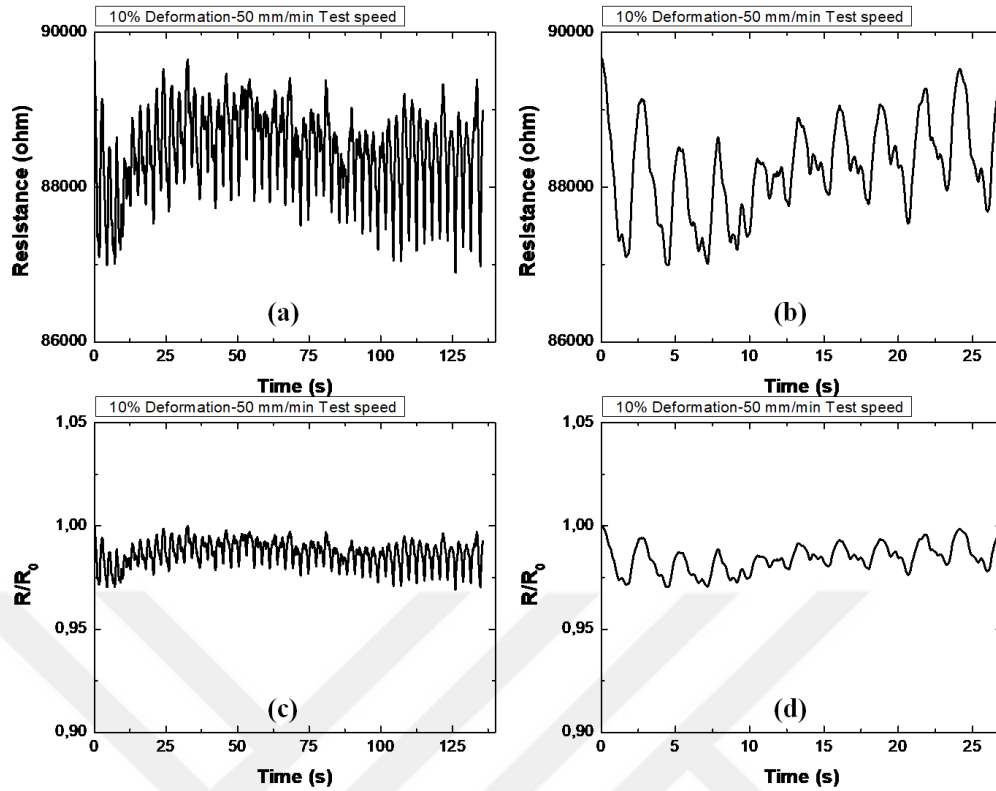


Figure 4.25 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 10% deformation at 50 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 10% deformation and 50 mm/min test speed through 50 cycles (Figure 4.25a). However, cycles showed up and downwards during 50 cycles. As shown in Figure 4.25b, resistance change is in the range of 87000 to 90000 Ω . The relative resistance change is between 0.97 to 1.0 as shown in Figure 4.25c-d.

Under 10% deformation for all test speeds, the maximum relative resistance was almost the same and it was around 1.00 whereas the minimum relative resistance was changed and it increased with the test speed. The minimum relative resistance was between 0.91-0.97 for 5 and 50 mm/min, respectively (Figure 4.20c-4.25c). In terms of resistance, the maximum resistance was relatively 90000 Ω all test speeds. On the other hand, the minimum resistance was in the range of 81200 to 87000 Ω (Figure 4.20a-4.25a). The increase in resistance change and relative resistance resulted in

increase in sensitivity of the nanocomposite. It shows that with the increase in test speed, the VGCNFs cannot find enough time to return to their initial position and cycles started at relatively high resistance values.

The effect of test speed on piezoresistive response was carried out under 20% deformation and the results are given in Figure 4.26-4.31. As mentioned before, non-linear negative to positive piezoresistive response was observed regardless of the test speed.

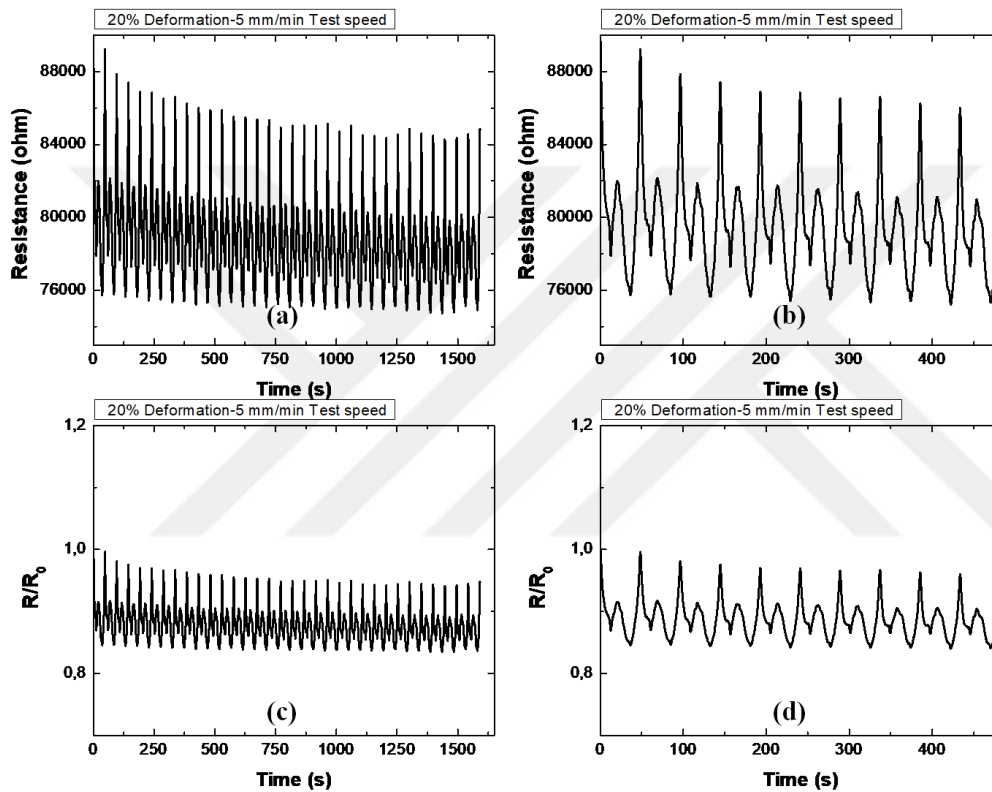


Figure 4.26 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 20% deformation at 5 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 20% deformation and 5 mm/min test speed through 50 cycles (Figure 4.26a). As shown in Figure 4.26b, resistance change is in the range of 75000 to 90000 Ω . The relative resistance change is between 0,83 to 1,001 as shown in Figure 4.26c-d.

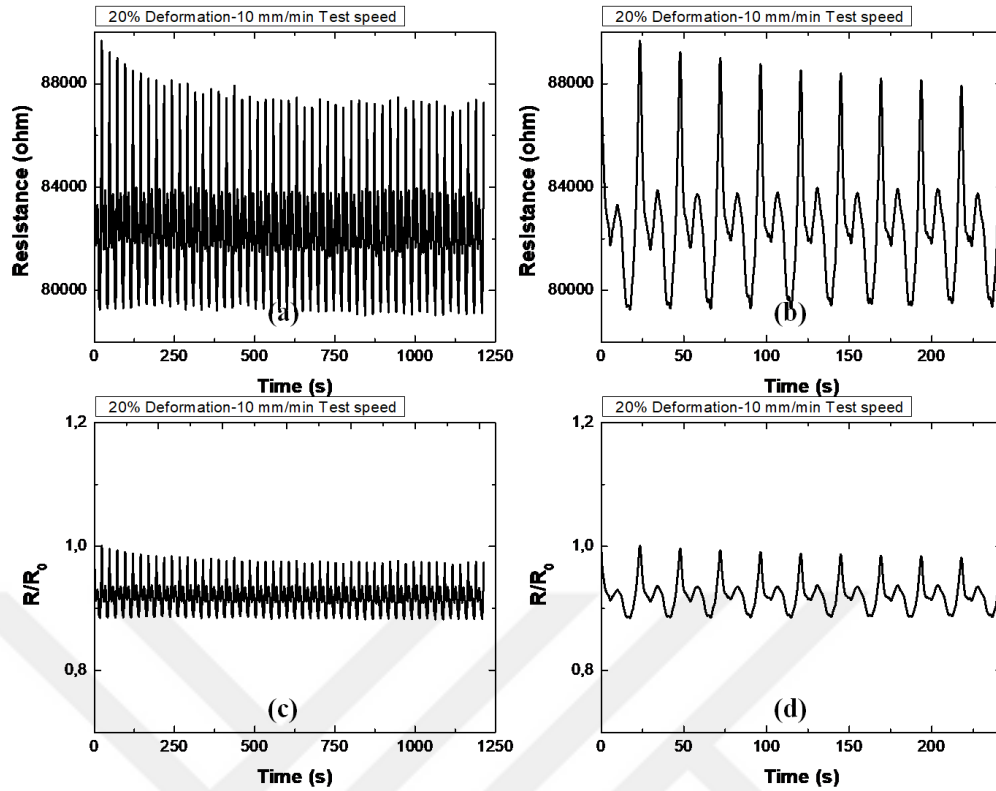


Figure 4.27 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 20% deformation at 10 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 20% deformation and 10 mm/min test speed through 50 cycles (Figure 4.27a). As shown in Fig Figure 4.27b, resistance change is in the range of 79100 to 90000 Ω . The relative resistance change is between 0,88 to 1,001 as shown in Figure 4.27c-d.

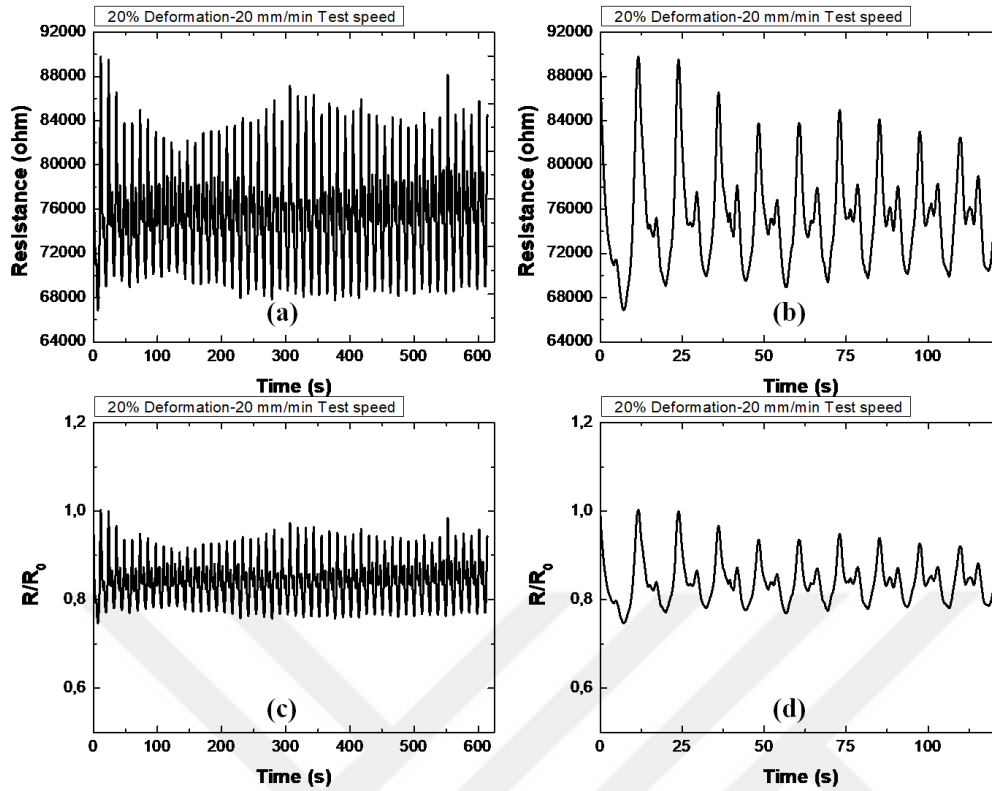


Figure 4.28 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 20% deformation at 20 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 20% deformation and 10 mm/min test speed through 50 cycles (Figure 4.28a). However, cycles showed upwards during 50 cycles. As shown in Figure 4.28b, resistance change is in the range of 67000 to 90000 Ω . The relative resistance change is between 0,75 to 1,002 as shown in Figure 4.28c-d.

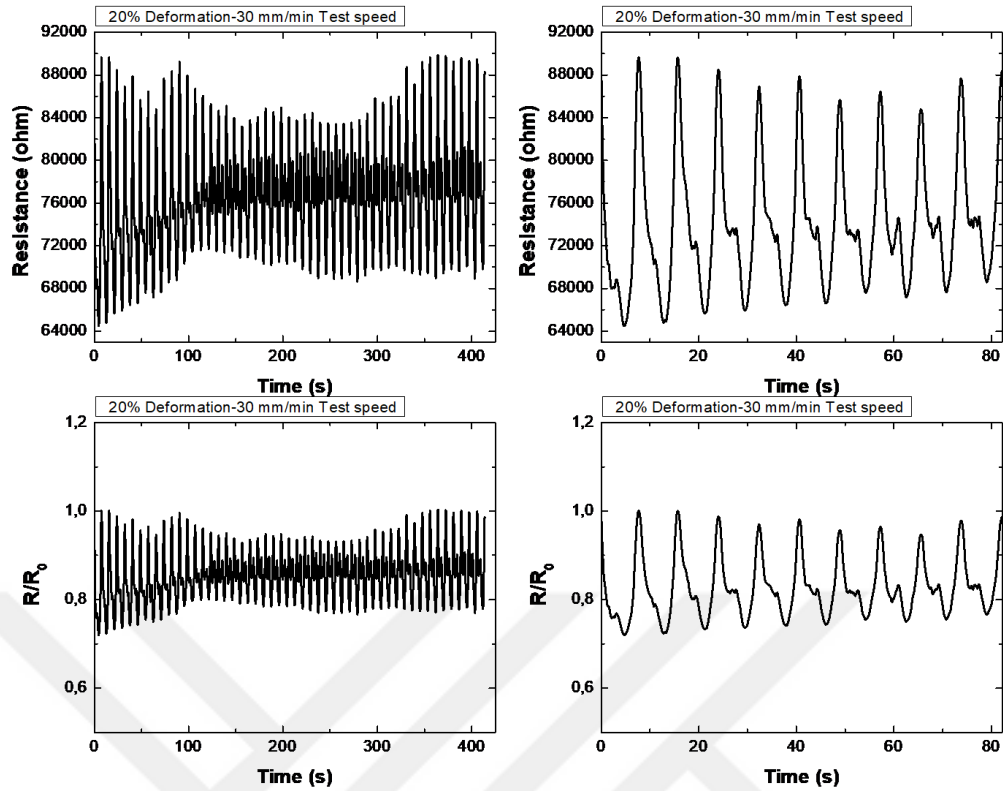


Figure 4.29 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 20% deformation at 30 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 20% deformation and 30 mm/min test speed through 50 cycles (Figure 4.29a). However, cycles showed upwards during 50 cycles. As shown in Figure 4.29b, resistance change is in the range of 65000 to 90000 Ω . The relative resistance change is between 0,72 to 1,003 as shown in Figure 4.29c-d.

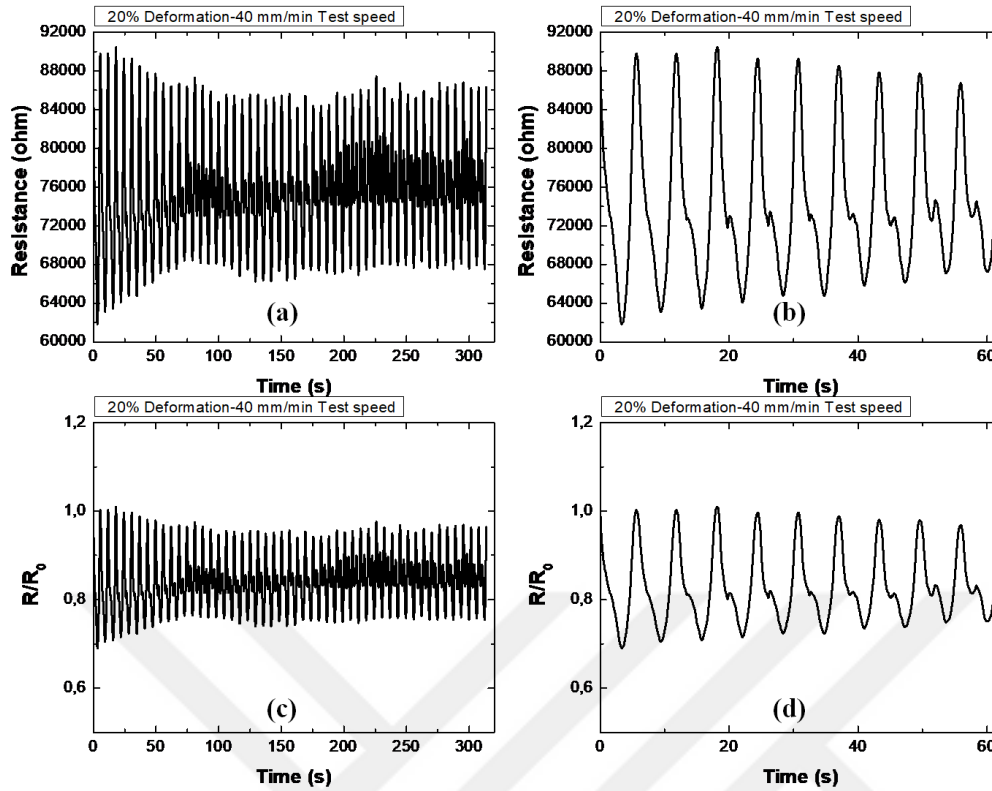


Figure 4.30 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 20% deformation at 40 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response up to a certain level than showed positive piezoresistance under 20% deformation and 40 mm/min test speed through 50 cycles (Figure 4.30a). As shown in Figure 4.30b, resistance change is in the range of 62000 to 91000 Ω . The relative resistance change is between 0,69 to 1,01 as shown in Figure 4.30c-d.

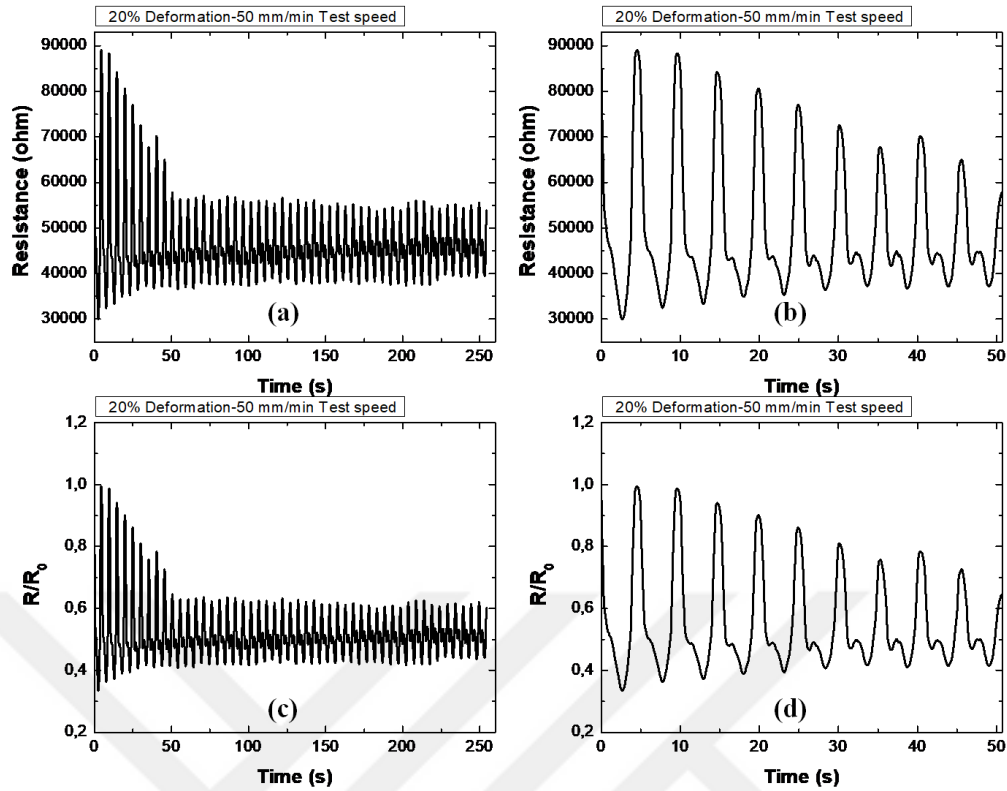


Figure 4.31 Cyclic piezoresistive response of 7 wt% VGCNFs/SEBS nanocomposite under 20% deformation at 50 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed negative piezoresistive response up to a certain level than showed positive piezoresistance response under 20% deformation and 40 mm/min test speed through 50 cycles (Figure 4.31a). However, cycles showed negligible up and downwards during 50 cycles. As shown in Figure 4.31b, resistance change is in the range of 30000 to 90000 Ω . The relative resistance change is between 0,33 to 1,00 as shown in Figure 4.31c-d.

The maximum relative resistance was around 1,00 and it was almost the same under 20% deformation for all test speeds. In terms of the minimum relative resistance, two different cases were observed. In the first case, it increased 0,83 to 0,88 when the test speed is increased from 5 to 10 mm/min and sensitivity of the nanocomposite decreased (Figure 4.26c-4.27c). In the second case, the relative resistance was between 0,88- 0,33 when the test speed was increased from 10 to 50 mm/min and sensitivity increased (Figure 4.27c-4.31c). With the increase in test speed, sensitivity of the curves decreased.

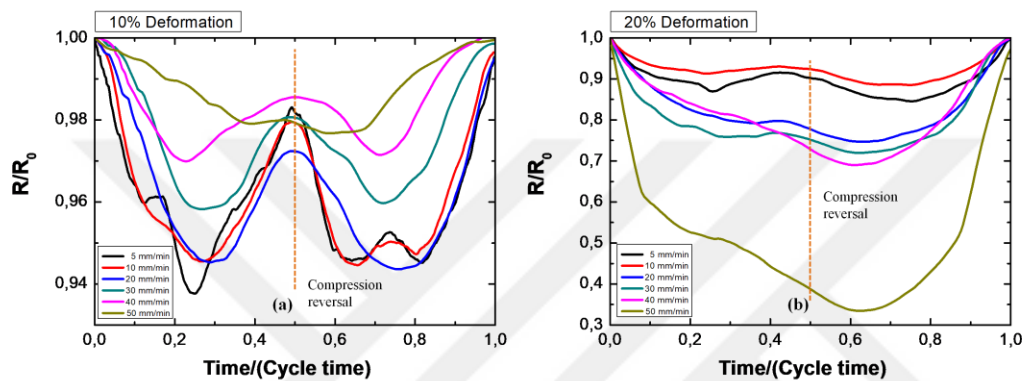


Figure 4.32 Change in relative resistance under a) 10% deformation, b) 20% deformation for all test speeds for a single (loading/unloading) cycle for 7 wt% VGCNFs containing SEBS nanocomposite

Two sets (10% and 20% deformation) were compared in terms of a single cycle response for all test speeds (10, 20, 30, 40, 50 mm/min) as given in Figure 4.32. For easy comparison, the time axis divided into total cycle time for each test speed. When the deformation was 10%, the relative resistance was between 0,91-1,0. Material showed noisy data with sharpest response at low test speeds and with the increase in test speed, the noisiness and sharpness decreased. Under 10%, the test speed also affected the minimum relative resistance values in both loading and unloading stages (Figure 4.32a). As seen the change in relative resistance decreased with increase in test speed and it was resulted with the decrease in sensitivity. When the deformation is 20%, the relative resistance is between 0,33-1,0. The nanocomposite showed more sensitive response under 20% deformation and the most sensitive response is observed at 50 mm/min. This was probably caused by more dominant conductive network formation when the material was deformed at the highest speed. It can be observed after a critical test speed and deformation %. The separated fillers can tend to be

together at high test speed and deformation % and create more conductive networks. Since the deformation % is increased, the minimum relative resistance values in both loading and unloading stages closed to the relative resistance at compression reversal. With the increase in test speed, the response of the material changed as shown in Figure 4.32b.

In terms of piezoresistive response of the studies in the literature, parallel with our testing procedure, piezoresistive response of materials were investigated at different test speeds and deformation % values [18, 54]. With the increase in deformation % under constant test speed exhibit different responses as parallel with our findings, change in relative resistance increases with decreasing sharpness and noisiness of the curves [54]. On the other hand, increase in deformation % under constant test speed can also cause to increase in sharpness [18]. Distinctly from literature, while an increase in test speed caused to decrease in relative resistance, sharpness and noisiness, the relative resistance change was not affected by test speed in the literature studies [18, 54].

4.3. rGO/SEBS Piezoresistive Pressure Sensors

4.3.1. Morphological Characterization

The morphological structure of the rGO/SEBS nanocomposites was investigated by the cryo-fractured cross-section using FESEM. The nanocomposites that contain 10, 17, 23, 35 wt% rGO were used for morphological characterization. The images are given in Figure 4.33 and dark grey parts represent the SEBS insulating matrix while lightly grey parts represent the rGO.

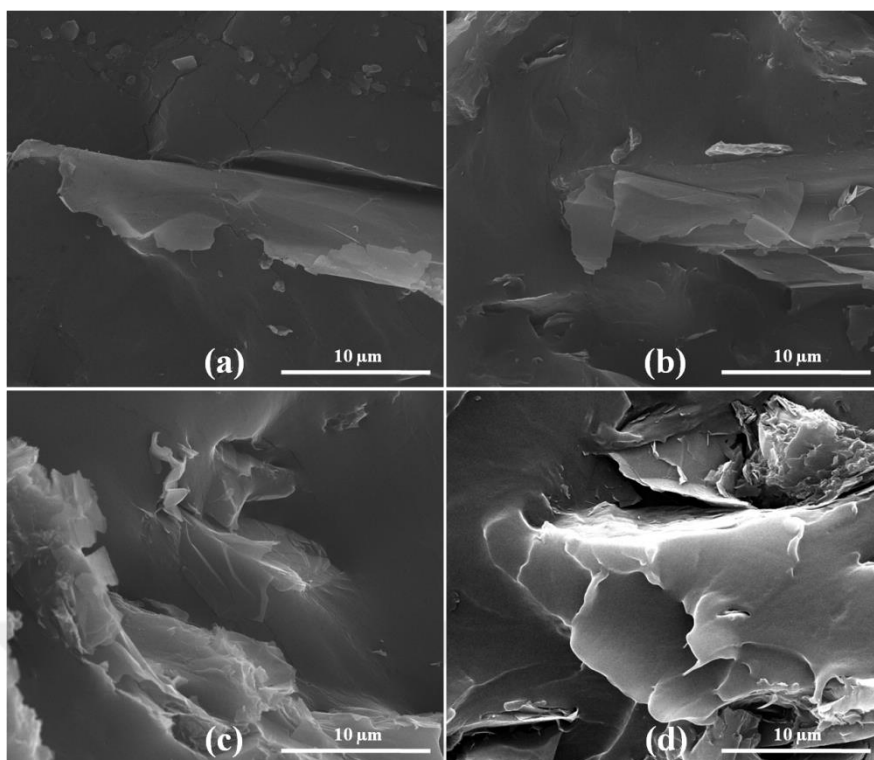


Figure 4.33 SEM images of a)10 wt%, b) 17 wt% c) 23 wt%, d) 35 wt% rGO/SEBS nanocomposites, scale bar: 10 μm

The morphological structure of 10, 17, 23, 35 wt% rGO/SEBS nanocomposites are given in Figure 4.33. The wrapped sheet-like structures represented the rGO filler. With the increase in filler content in the nanocomposite, the rGO in a unit area increased as obviously seen in Figure 4.33. At high concentration with the high interaction between rGO filler, agglomerations can be observed (Figure 4.33d).

In terms of morphological structure, distinctly from our study, the studies in the literature are mostly exhibit porous structure [19, 48, 49, 99]. Dispersion and distribution of graphene was not mentioned.

4.3.2. Electrical Characterization

4.3.2.1. Resistivity

In order to investigate percolation behavior of the rGO filled SEBS nanocomposites, volume resistivity of the samples were determined. The resistivity of rGO/SEBS nanocomposite films as a function of rGO content (0-45 wt%) is given in Table 4.4 and Figure 4.34. The dots represent the volume resistivity at given filler concentrations and the grey field shows the percolation region for rGO/SEBS nanocomposites in Figure 4.34. As can be seen from Table 4.4 and Figure 4.34 with the addition of rGO into SEBS, the resistivity of the system decreased.

Table 4.4 : Changes in volume resistivity as a function rGO filler concentration (wt%)

rGO Filler Concentration (wt%)	Volume Resistivity (ρ) (ohm.cm)	ρ_0/ρ (ohm.cm)/(ohm.cm)
0	9,32E+17	1,00E+00
1	6,35E+17	1,47E+00
3	5,21E+17	1,79E+00
6	4,32E+17	2,16E+00
8	9,84E+16	9,47E+00
10	6,56E+16	1,42E+01
13	7,22E+15	1,29E+02
15	3,37E+15	2,77E+02
17	1,02E+14	9,14E+03
20	8,29E+07	1,12E+10
23	3,58E+07	2,60E+10
27	4,71E+06	1,98E+11
30	4,03E+06	2,31E+11
33	3,83E+06	2,43E+11
35	3,02E+06	3,09E+11
38	2,26E+06	4,12E+11
40	2,09E+06	4,46E+11
45	1,09E+06	8,55E+11

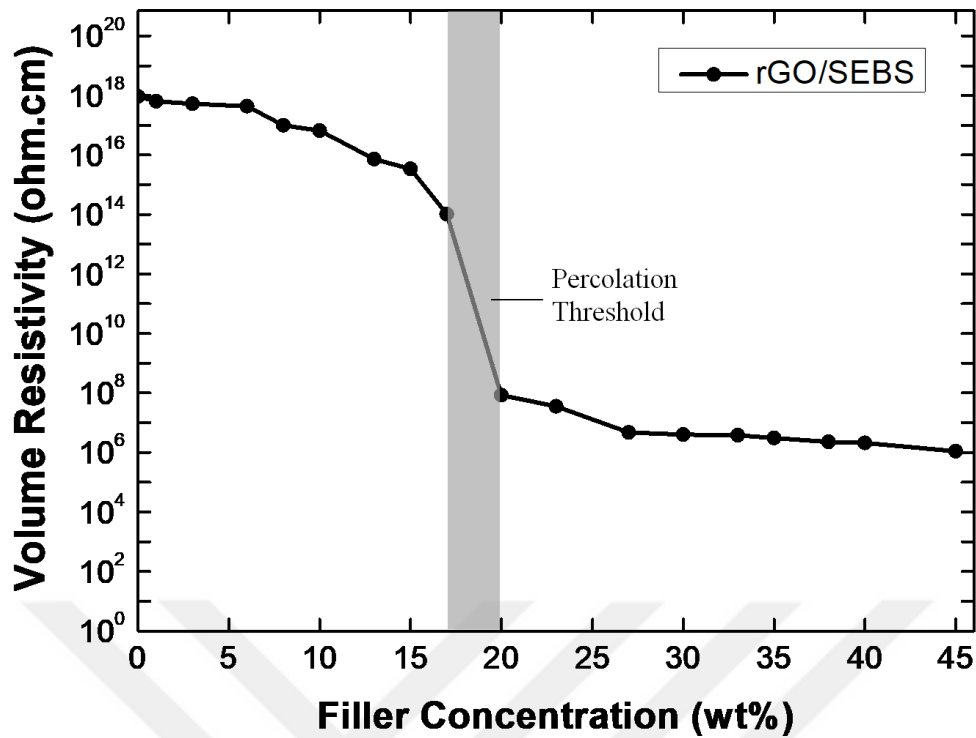


Figure 4.34 Percolation graph of rGO containing SEBS nanocomposites as a function of volume resistivity vs. filler concentration (wt%)

As shown in Figure 4.34, rGO/SEBS composites showed classical transition in terms of percolation behavior. There are three regions in the graph as insulation (0-17 wt%), percolation (17-20 wt%) and saturation (20-45 wt%) regions. Although insulation region is generally observed as a plateau in most of the studies [266-268], in our case insulation region can be evaluated in two parts such as between 0-10 wt% and 10-17 wt%. As can be seen from ρ_0/ρ ratios given in Table 4.4, between 0-10 wt% rGO, the rate of decrease is relatively low even not an order of magnitude. This region is in the plateau form and in this region electrical properties are dominated by the SEBS matrix because of low filler concentration. The consequence of the low filler concentration can be morphologically observed as high level of filler-filler separation as given in Figure 4.33. As seen, fillers are highly separated from each other and there is no conductive network throughout the composite. On the other hand, between 10-17 wt% rGO content (Table 4.4), the drop in resistivity is around one to three orders of magnitude. Although this region is counted as an insulation region, the composites may show higher conductivity when compared with 0-10 wt% region. Although this is not a significant change, it can be attributed to the flock formation as shown in Figure 4.33b. But it should be kept in mind that, in that case both separated fillers and flocks

can be found, they are separated from each other and filler concentration is not enough to establish conducting networks throughout the composite [266-268]. The percolation region can be between 17-20 wt% rGO. The decrease in volume resistivity is almost seven orders of magnitude as highlighted in Figure 4.34. This sudden decrease, around ten orders of magnitude, in volume resistivity is due to the formation of conductive networks throughout the SEBS nanocomposite by the addition of rGO fillers that can also be seen from SEM images (Figure 4.33b)[48, 269-272]. Even the ratio of the filler was increased from 20 wt% to 45 wt% the change in volume resistivity was not found significant. In other words, volume resistivity showed a plateau type saturation region between 27-45 wt% rGO (Table 4.4) As known, after percolation region even if more filler are incorporated into the polymeric matrix, resistivity does not show a drastic drop and this behavior is called saturation (Figure 4.33c-d).

The nanocomposites that contain graphene and derivatives mostly did not characterize in terms of percolation threshold. In the reviewed literature studies, there is only one study and the percolation was observed around 0,3-0,4 wt% multilayer graphene/PDMS nanocomposites. The resistivity was in the range of 10^{11} - $10^6 \Omega\text{cm}$. On the other hand, in our study the percolation threshold was observed at 17-20 wt% rGO concentration in the range of 10^{14} - $10^7 \Omega\text{cm}$. The change can be because of the matrix type and graphene type and morphology.

4.3.2.2. Electromechanical characterization

Piezoresistance can be observed in conductive polymer composites at various levels of sensitivity depending on the filler concentration. Depending on our previous studies and experimental trials, nanocomposite with 30 wt% rGO was determined to be the most suitable sample in terms of its electromechanical properties under cyclic pressure. Piezoresistance was analyzed at five different test speeds (10, 20, 30, 40, 50 mm/min) at two deformation rates (20, 50 %) and resistance was recorded simultaneously for 50 cycles. In other words, effects of test speed and deformation % on dynamic piezoresistance were investigated for 50 cycles.

In order to understand the piezoresistance, change in resistance and normalized resistance (R/R_0) should be investigated in terms of cyclic stability and single cycle behavior. For this aim, four different graphs are given for 20 and 50 % deformation for all test speeds. In the first and third graphs (Figure 4.36-4.45 (a-c)), 50 cycles are given in order to analyze the cyclic stability and repeatability of the nanocomposite in terms of resistance and normalized resistance. Normalized (relative) resistance is basically R/R_0 (R =Resistance at any time, R_0 = Initial resistance). R/R_0 is significant for comparison of the sensitivity of the systems. In Figure 4.36-4.45 (b-d), first 10 cycles are given in order to understand the piezoresistive response and hysteresis as a function of time in terms of R and R/R_0 .

The effect of test speed on piezoresistive response under 20% deformation is shown in Figure 4.36-4.40. As obvious, SEBS nanocomposite showed negative piezoresistance response regardless of the test speed. This could be attributed to change in spatial orientation of fillers. As illustrated in Figure 4.35, contact between rGO sheets increased with the effect of pressure, and new conductive networks formed. As a consequence of that, resistance of the nanocomposite decreased. The increase in resistance during unloading cycle is due to breakdown of the conducting network with the effect of polymeric matrix recovery [19, 48-50].

Parallel with our test results, most of the studies in the literature exhibit negative piezoresistive response under pressure [19, 48-50]. On the other hand, positive piezoresistive response was also found in the literature [99].

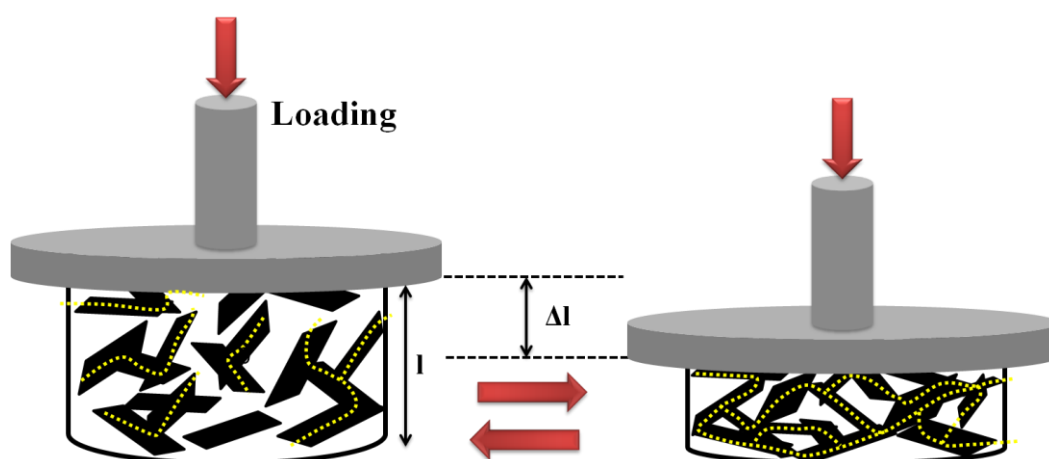


Figure 4.35 Mechanism of negative piezoresistance under cyclic pressure

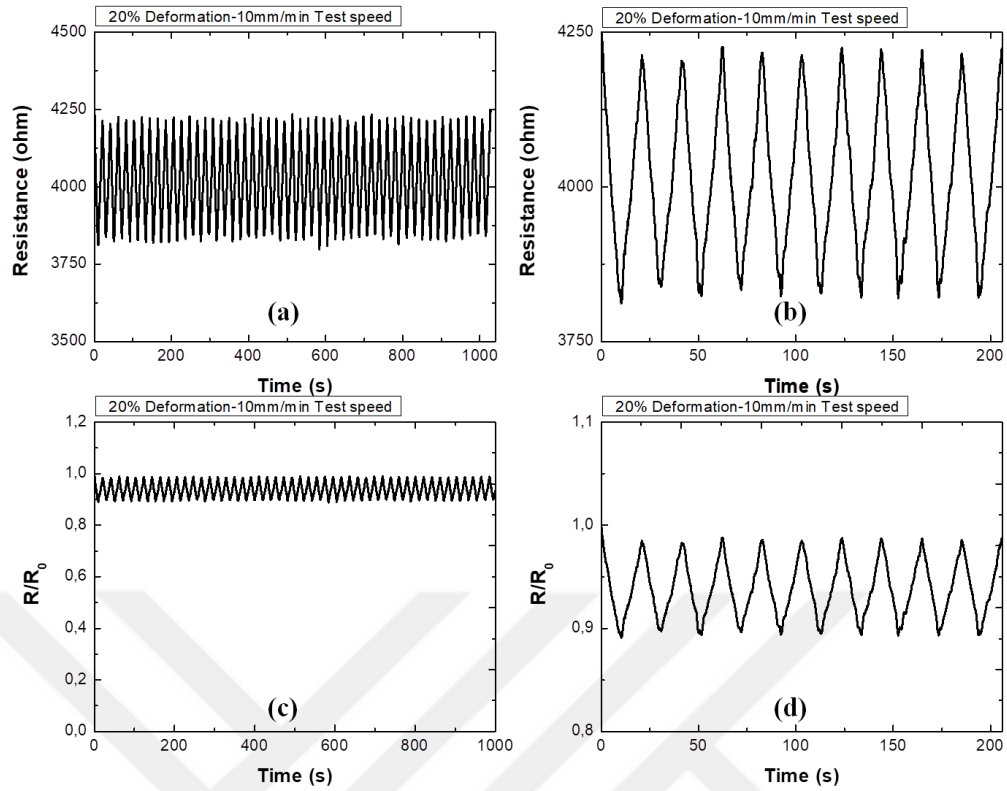


Figure 4.36 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 20 % deformation at 10 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 10 mm/min test speed through 50 cycles (Figure 4.36a). As shown in Figure 4.36b, resistance change is in the range of 3798 to 4277 Ω . The relative resistance change is between 0.89 to 1.0 as shown in Figure 4.36c-d.

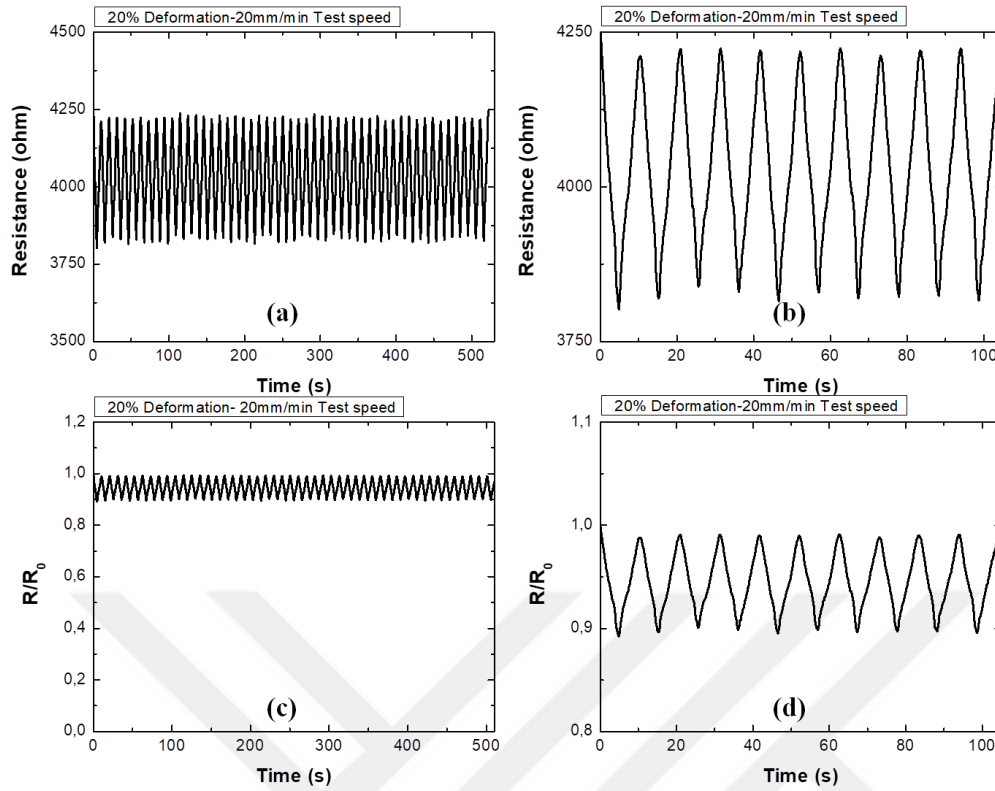


Figure 4.37 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 20 % deformation at 20 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 20 mm/min test speed through 50 cycles (Figure 4.37a). As shown in Figure 4.37b, resistance change is in the range of 3800 to 4260 Ω . The relative resistance change is between 0.89 to 1.0 as shown in Figure 4.37c-d.

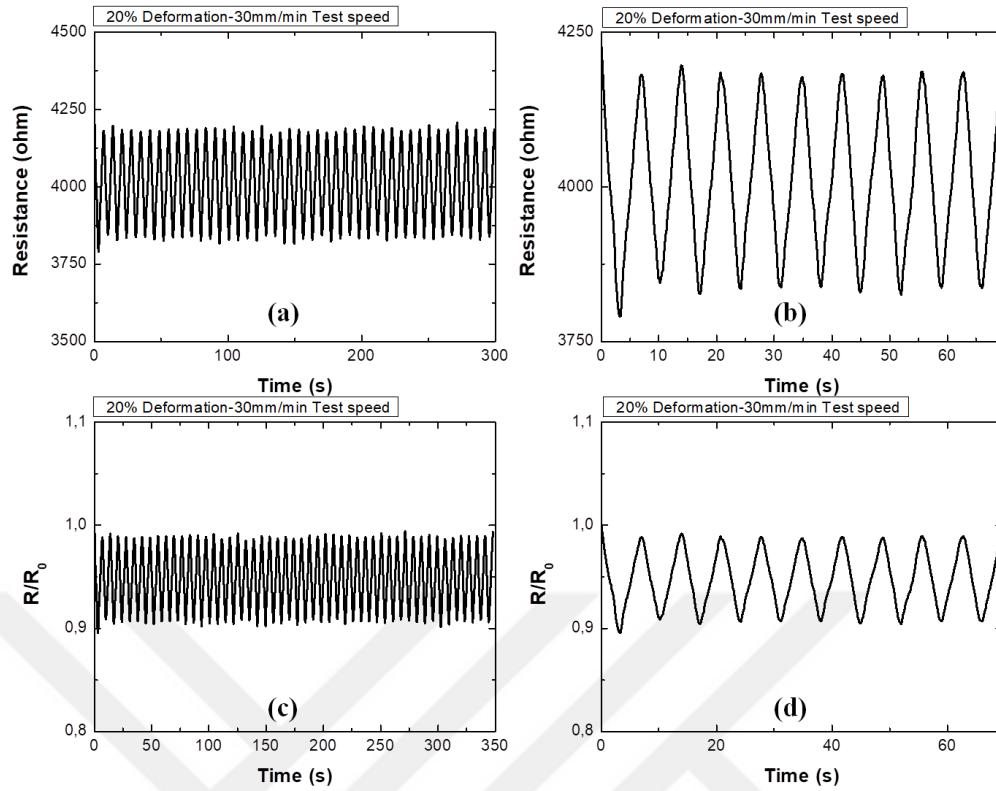


Figure 4.38 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 20 % deformation at 30 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 30 mm/min test speed through 50 cycles (Figure 4.38a). As shown in Figure 4.38b, resistance change is in the range of 3790 to 4230 Ω . The relative resistance change is between 0.9 to 1.0 as shown in Figure 4.38c-d.

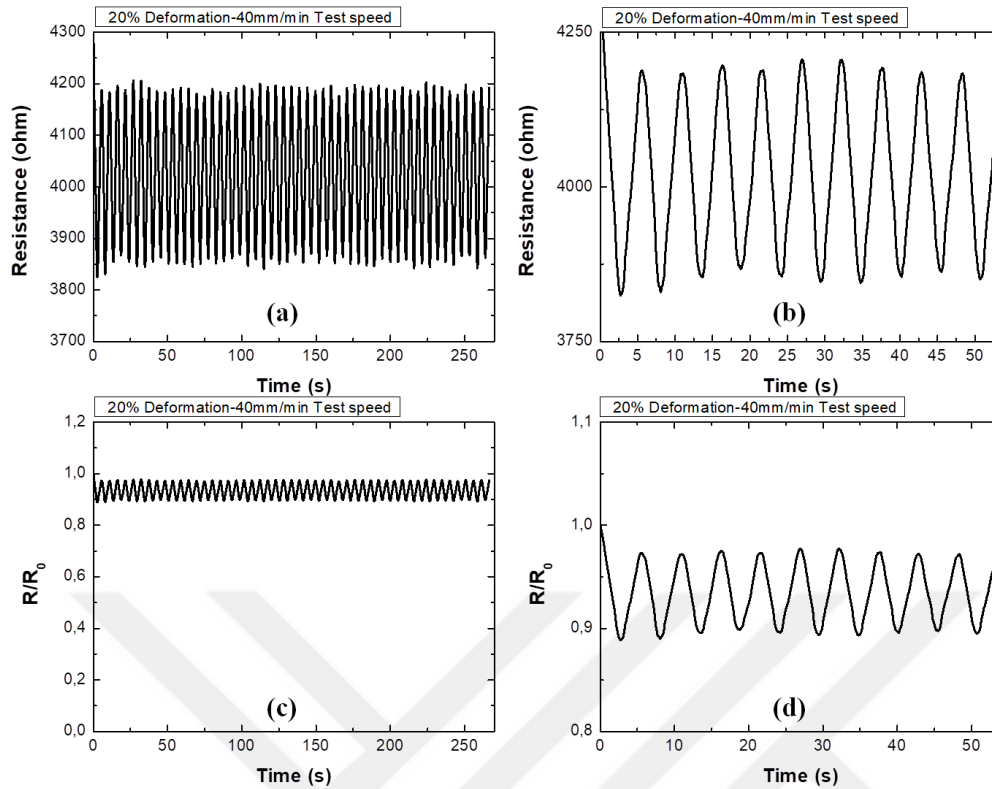


Figure 4.39 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 20 % deformation at 40 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 40 mm/min test speed through 50 cycles (Figure 4.39a). As shown in Figure 4.39b, resistance change is in the range of 3820 to 4300 Ω . The relative resistance change is between 0,89 to 1.0 as shown in Figure 4.39c-d.

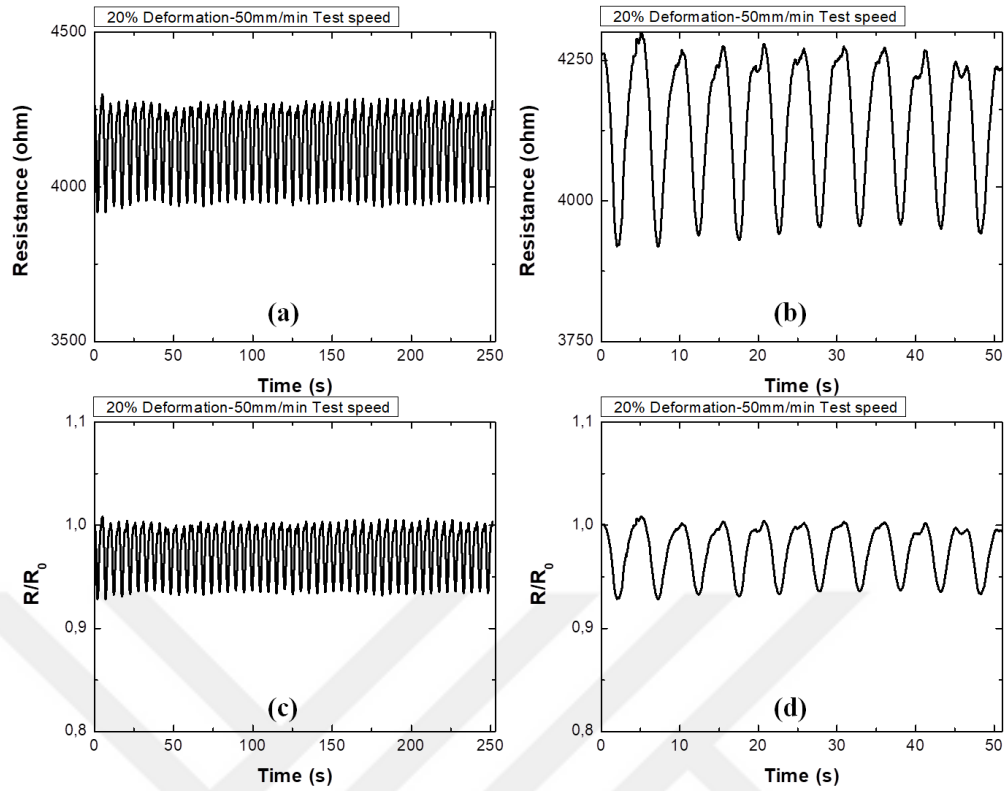


Figure 4.40 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 20 % deformation at 50 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 20 % deformation and 50 mm/min test speed through 50 cycles (Figure 4.40a). As shown in Figure 4.40b, resistance change is in the range of 3920 to 4300 Ω . The relative resistance change is between 0,93 to 1.0 as shown in Figure 4.40c-d.

When carefully controlled, the relative resistance at 10, 20, 30, 40 mm/min test speeds were determined around 0.89-1.0 whereas at 50 mm/min it was around 0.93-1.01 (Figure 4.36c-4.40c). At 10 mm/min test speed, nanocomposite showed highly sharp and linear character (Figure 4.36d). Material could find more time to return to its initial position at low test speeds. On the other hand, with the increase in test speed, sharpness of the curves decreased that is also an indication of lower sensitivity. Another important point is the hysteresis. Although during loading and beginning of the unloading cycle, no significant hysteresis was observed under 50 mm/min test speed, at the end of unloading and at the beginning of loading cycles obvious hysteresis can be seen from Figure 4.40b-d. As obviously seen in Figure 4.40d, after first cycles were completed, the resistance could not reach to the initial resistance value. All these probably caused by lower level of recoverability of the polymeric matrix under this condition. In the case of higher test speeds, less time is given material for recovery [48, 273].

The effect of test speed on piezoresistive response under 50 % deformation is shown in Figure 4.41-4.45. As obvious, SEBS nanocomposites showed negative piezoresistance response regardless of the test speed as mentioned previously for 20 % deformation.

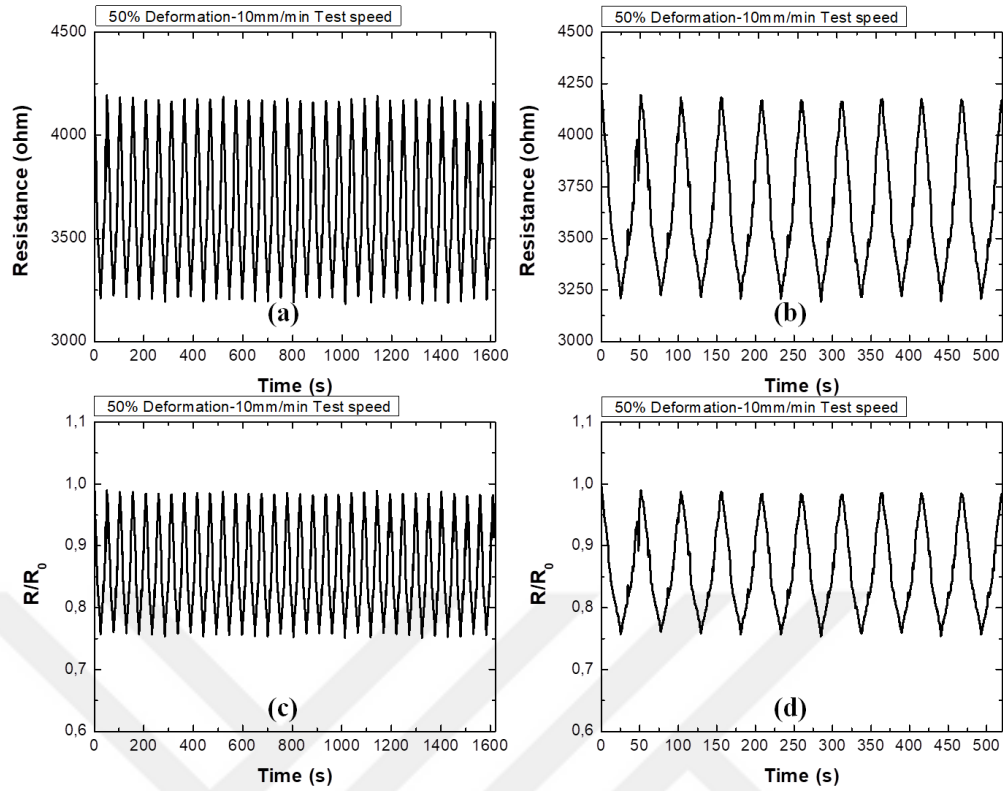


Figure 4.41 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 50 % deformation at 10 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 50 % deformation and 10 mm/min test speed through 50 cycles (Figure 4.41a). As shown in Figure 4.41b, resistance change is in the range of 3180 to 4240 Ω . The relative resistance change is between 0,75 to 1.0 as shown in Figure 4.41c-d.

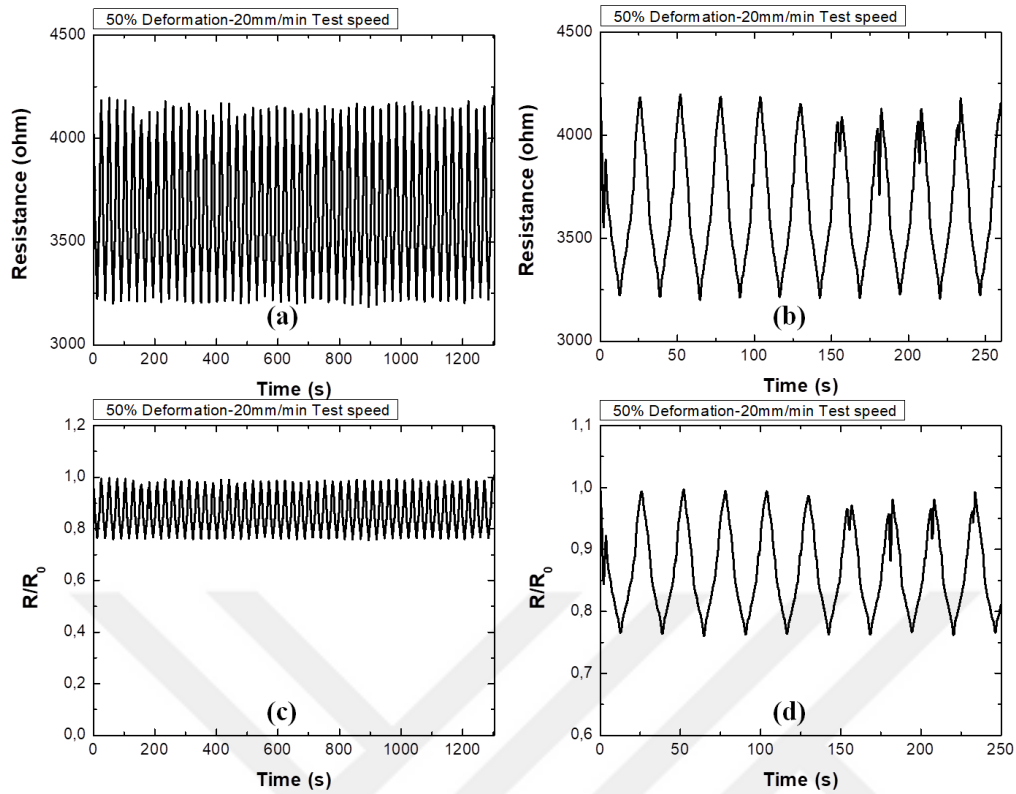


Figure 4.42 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 50 % deformation at 20 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 50 % deformation and 20 mm/min test speed through 50 cycles (Figure 4.42a). As shown in Figure 4.42b, resistance change is in the range of 3180 to 4230 Ω . The relative resistance change is between 0,76 to 1.02 as shown in Figure 4.42c-d.

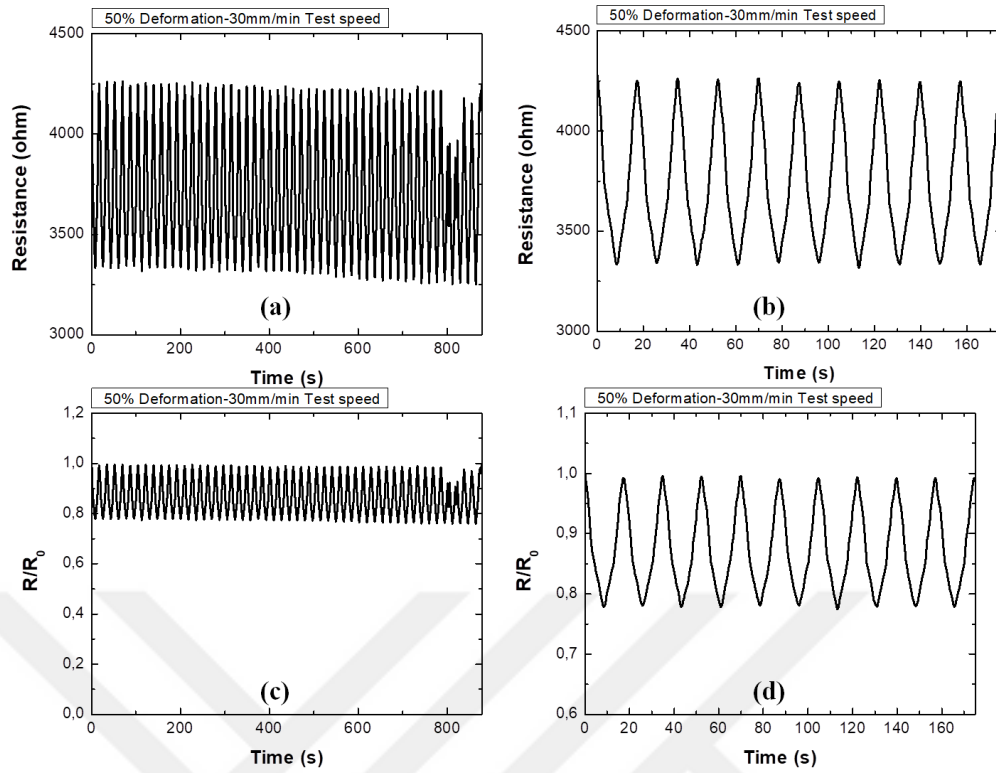


Figure 4.43 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 50 % deformation at 30 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 50 % deformation and 30 mm/min test speed through 50 cycles (Figure 4.43a). As shown in Figure 4.43b, resistance change is in the range of 3250 to 4360 Ω . The relative resistance change is between 0,76 to 1.02 as shown in Figure 4.43c-d.

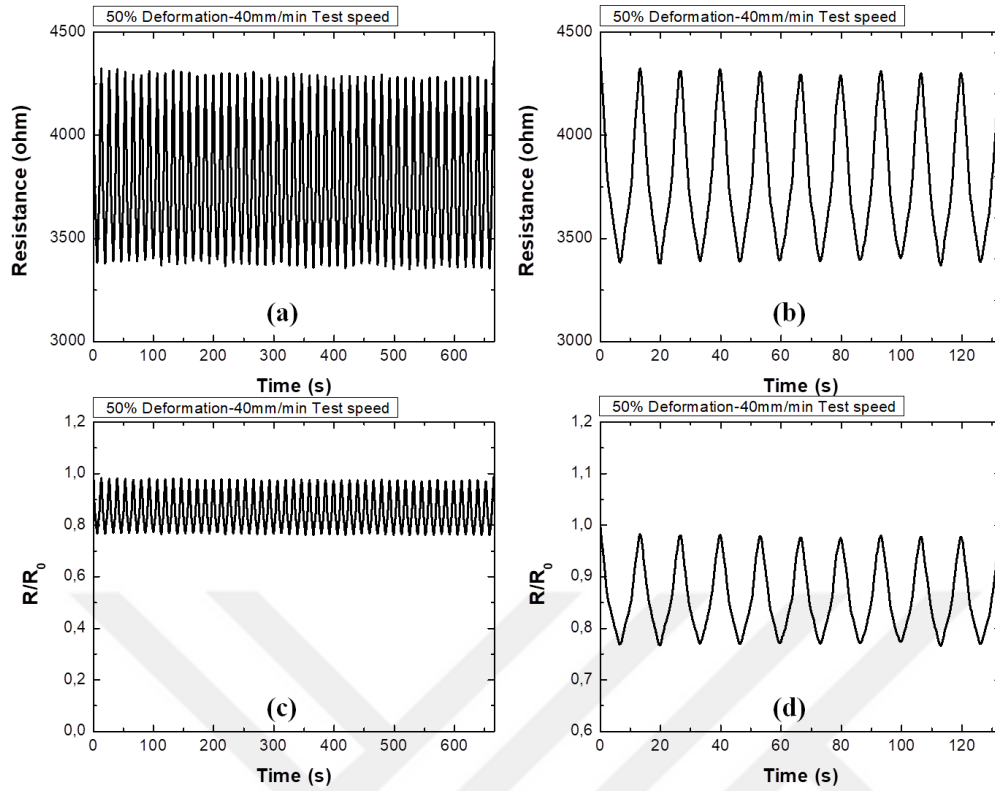


Figure 4.44 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 50 % deformation at 40 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 50 % deformation and 40 mm/min test speed through 50 cycles (Figure 4.44a). As shown in Figure 4.44b, resistance change is in the range of 3350 to 4410 Ω . The relative resistance change is between 0,76 to 1.0 as shown in Figure 4.44c-d.

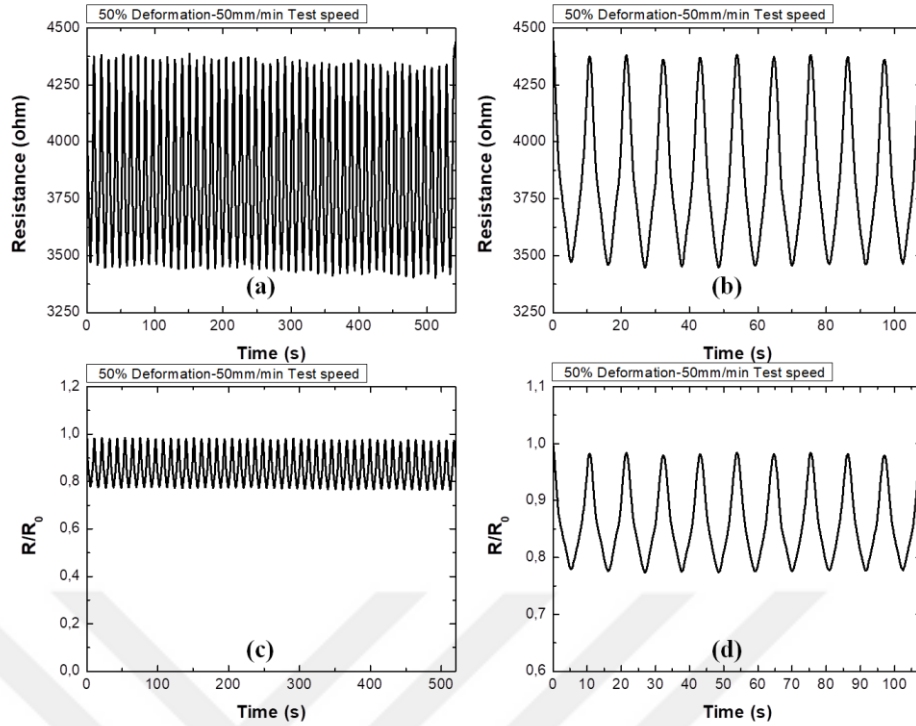


Figure 4.45 Cyclic piezoresistive response of 30 wt% rGO/SEBS nanocomposite under 50 % deformation at 50 mm/min test speed. Change in resistance for a) 50 cycles, b) 10 cycles. Relative resistance (R/R_0) change for c) 50 cycles, d) 10 cycles

The nanocomposite showed stable negative piezoresistive response under 50 % deformation and 50 mm/min test speed through 50 cycles (Figure 4.45a). As shown in Figure 4.45b, resistance change is in the range of 3400 to 4500 Ω . The relative resistance change is between 0.76 to 1.01 as shown in Figure 4.45c-d.

The analysis shows that, the relative resistance for all test speeds under 50 % deformation was around 0.75-1.02 (Figure 4.41(c-d)-4.45 (c-d)). On the other hand, it was around 0.89-1.01 for 20 % deformation (Figure 4.36(c-d)-4.40 (c-d)). The results of this part of the study indicated that compared to 20 % deformation, test speed did not cause significant changes in relative resistance under 50 % deformation. With the increase in deformation, the material could not find enough time to return initial position even if at low test speeds. The resistance values clearly represent the results because the minimum resistance value under 20 % deformation is around 3790 Ω whereas it is around 3200 Ω for 50 %. The relatively higher conductance under 50% deformation is due to the increase the connections and formation of more conductive networks between rGO sheets[49].

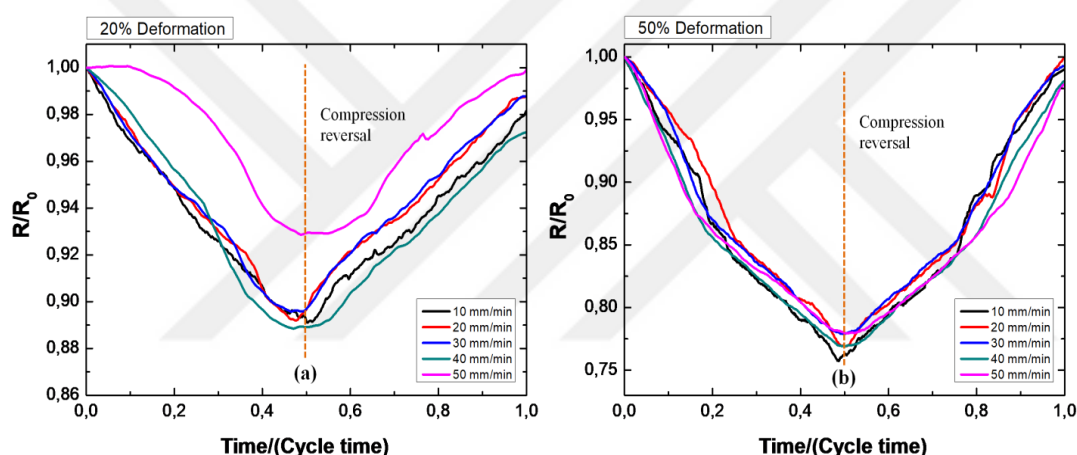


Figure 4.46 Change in relative resistance under a) 20% deformation, b) 50% deformation for all test speeds for a single (loading/unloading) cycle for 30 wt% rGO containing SEBS nanocomposite

Figure 4.46 is given in order to compare two sets (20 % and 50 % deformation). R/R_0 values of 30 wt% rGO containing SEBS nanocomposite under two different deformations (20, 50 %), are given for all test speeds (10, 20, 30, 40, 50 mm/min) for a single cycle. For easy comparison, the time axis was divided into total cycle time for each test speed.

In the case of 20 % deformation, (Figure 4.46a) the minimum relative resistance under 20 % deformation is approximately 0.89 for 10, 20, 30, 40 mm/min test speeds because these test conditions led rGO sheets to return to their initial positions. Under 20 % deformation between 10-40 mm/min, test speed did not affect the relative resistance of the material. On the other hand, at 50 mm/min test speed, minimum relative resistance is found nearly 0.93. As seen, the sensitivity of material decreased. As previously mentioned, this was probably caused by recoverability of the matrix. At high speeds same had less time for recovery.

In addition to that, with the increase in test speed, smoothness of the curves increased. This is probably related with the measurement system. At low test speeds, the small changes in resistance can be measured but at high test speeds, the measured data in a given time decreased and smother curves were obtained. The sharpest peak in relative resistance was obtained at 10 mm/min (Figure 4.46b) and with the increase in test speed the intensity and shape of the curves and sharpness of the peaks decreased. At 50 mm/min test speed, hysteresis was observed and character of curve changed. The hysteresis is observed due to viscoelastic behavior of polymers. While material is deformed (loading) rGO sheets changed their positions into matrix and when the force was removed (unloading) rGO started to turn back to initial position but they cannot turn back to in a cycle time and hysteresis occurred [274].

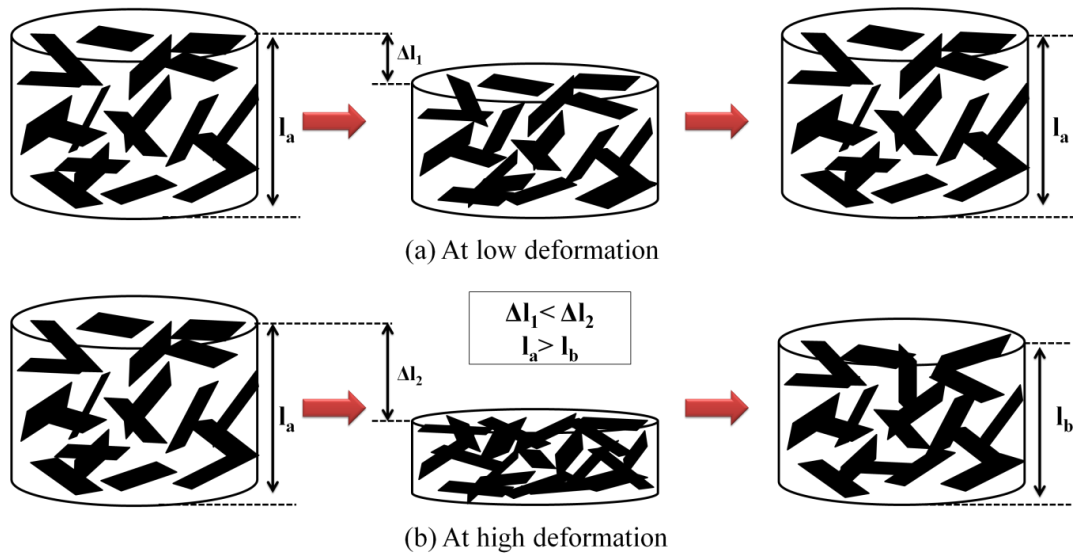


Figure 4.47 Mechanism of the effect of deformation on R/R₀ value, a) at low deformation, b) at high deformation

In the case of 50 % deformation (Figure 4.46b), relative resistance is approximately 0,75 and it was not affected by the test speed. When compared with 20% deformation, the relative resistance decreased. With the increase in % deformation, in loading stage, connections and contact area between rGO sheets increase and material became more conductive whereas in unloading stage, the distance between rGO sheets increased and conductance decreased. In addition to that, dimension of material could be changed with the effect of high deformation as illustrated in Figure 4.47b.

In terms of piezoresistive response, distinctly from our study, the increase in deformation % caused to increase relative resistance change and more sensitive materials were obtained [19, 99]. On the other hand, according to our results, with the increase in deformation % relative resistance of the material decreased and sensitivity decreased. The differences in piezoresistive response could be attributed to different sensor morphology because the tested sensors mostly exhibit foam structure.

5. CONCLUSIONS AND FUTURE SUGGESTIONS

In the study, for the design and fabrication of pressure sensors by using a TPE based matrix SEBS and CB, VGCNFs and rGO conductive fillers were used. The morphological, electrical and electromechanical properties of nanocomposites were investigated. For the production of nanocomposites combination of solution casting and compression molding methods were used. In all filler types, homogeneous dispersion was obtained due to high shear mixing. With the compression molding, fillers were wetted by matrix more efficiently. In terms of electrical characterization, all three filler types exhibited different conductivity values and percolation threshold values. The electromechanical characterization was completed with dynamic cyclic tests. To observe the effect of test speed and deformation %, materials were tested under different test conditions. Regardless of the filler type, test speed and deformation %, all nanocomposites showed negative piezoresistive response. It is observed that piezoresistive response of the materials was affected by test speed and deformation %. As a conclusion, it is proved that these nanocomposites are sensitive to pressure. Electrically conductive polymer nanocomposites are appropriate to be used as pressure sensors in the field of medical applications such as health monitoring, controlling systems and pressure mapping.



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