YALOVA UNIVERSITY ★ GRADUATE SCHOOL of SCIENCE ENGINEERING and TECHNOLOGY

INVESTIGATION OF ELECTRICAL PROPERTIES OF FLEXIBLE ELECTRICALLY CONDUCTIVE POLYMER COMPOSITES

M.Sc. THESIS

Derya MUTLU

Department of Polymer Engineering

Polymer Engineering Programme

JUNE 2019

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YALOVA ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ESNEK ELEKTRİKSEL İLETKEN POLİMER KOMPOZİTLERİN ELEKTRİKSEL ÖZELLİKLERİNİN İNCELENMESİ

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Derya Mutlu, a **M.Sc.** student of YALOVA **Institute of 165101004**, successfully defended the **thesis** entitled **"INVESTIGATION OF ELECTRICAL PROPERTIES OF FLEXIBLE ELECTRICALLY CONDUCTIVE POLYMER COMPOSITES"**, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Defense : 17 JUNE 2019

To my mother, who has been the meaning of peace, sacrifice and love for me,

FOREWORD

In this thesis, we aimed to produce an electrically conductive, flexible polymer composite and to investigate the piezoresistive behavior of the composite in order to be used as strain sensors.

I would like to thank my advisor, H.Aylin Karahan Toprakçı for giving me the opportunity to work with her. I would like to thank her for her support and patience during my project.
I would like to thank my family for their beliefs, prayers and support.

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Derya MUTLU
Polymer Engineer

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ABBREVIATIONS

e-textiles	**:**Electronic textiles
PMMA	**:**Polymethylmethacrylate
PP	**:**Polypropylene
PVA	**:**Poly (vinyl alcohol)
PE	**:**Polyethylene
PEO	**:**Polyethylene oxide
CNT	**:**Carbon nanotube
CB	**:**Carbon black
SWCNTs	**:**Single walled carbon nanotubes(SWCNTs)
DMF	**:**Dimethyl formamide
MWCNTs	**:**Multi layer carbon nanotubes
HDPE	**:**High density polyethylene
GNPs	**:**Graphene nanoplatelets
PDMS	**:**Polydimethylsiloxane
CNFs	**:**Carbon nanofibres
p-PDMS	**:**Porous-polydimethylsiloxane
dc-PDMS	**:**Dip-coating—polydimethylsiloxane
IPA	**:**Isopropanol
GO	**:**Graphene oxide
SBS	**:**Poly(styrene–butadiene–styrene)
SEBS	**:**Styrene-ethylene/butylene-styrene
CPCs	**:**Manufacture conductive polymer composites
FLG	**:**Low-layer graphene
THF	**:**Tetrahydrofuran

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INVESTIGATION OF ELECTRICAL PROPERTIES OF FLEXIBLE ELECTRICALLY CONDUCTIVE POLYMER COMPOSITES

SUMMARY

Polymers are materials which are generally insulative in terms of electrical conductivity. Some filling materials must be added into the polymer matrix in order to make the polymers electrically conductive. The trend observed in conductive polymer composites, which has been an attractive topic for researchers and industry in recent years, is the production of flexible conductive polymer composites. Flexible conductive polymer composites are highly suitable materials for electrical applications, medical applications, surveillance (civilian and military applications), control systems. Here we have produced commercially feasible, industrially applicable, flexible, and sensitive electrically conductive composites that are compatible with the human body and can be used as strain sensors. The styrene-ethylene-butylene-styrene (SEBS) copolymer, a thermoplastic elastomer, has good elasticity and mechanical strength and is therefore chosen as the binding matrix material. In the class of carbon-based fillers, reduced graphene oxide (rGO) was chosen as the conductive filler due to its excellent electrical properties.To prepare the SEBS/rGO conductive composites, SEBS was dissolved in the appropriate solvent and rGO was added to it, and the composite was coated onto the flexible fabric by solution casting and allowed to dry at room temperature. To investigate the electromechanical behavior and to examine the effects of elongation and test speed on the sensor performance and also to get idea about the long-term use of the sensor samples were tested for 50 cycles at speeds of 20 mm/min and 50 mm/min under elongation of 5, 7.5 and 10%. In the given investigation, rGO were added to the SEBS co-polymer, and tested under different strain percentage(5, 7.5, 10% strain) at different speeds (20mm/min, 50mm/min) to investigate the the electromechanical properties of the stain sensitive coated textile sensor. The results showed that the resistance increased due to the applied strain up to a certain value and strain rate was found significant in terms of sensitivity. Based on these results, the usage range of the sensor is determined. The results of the study showed that flexible, conductive SEBS / rGO composites can be used as stretchable sensor materials. Flexibility of the sensor, its electrical conductivity, ease of use, and its compatibility with the human body make this study to have a major impact on the sensor literature.

ESNEK ELEKTRİKSEL İLETKEN POLİMER KOMPOZİTLERİN ELEKTRİKSEL ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Polimerler, elektriksel iletkenlik açısından genellikle yalıtkan olan malzemelerdir. Polimerleri elektriksel olarak iletken hale getirmek için polimer matrisine bazı iletken dolgu maddeleri ilave edilmelidir. Son yıllarda araştırmacılar ve endüstri için çekici bir konu olan iletken polimer kompozitlerde gözlenen eğilim, esnek iletken polimer kompozitlerin üretimidir. Esnek iletken polimer kompozitler elektriksel uygulamalar, mikroelectronik uygulamalar, tıbbi uygulamalar, gözetleme (sivil ve askeri uygulamalar), kontrol sistemleri için son derece uygun malzemelerdir. Bu çalışmada, ticari olarak uygulanabilir, endüstriyel olarak uygulanabilir, esnek, elektriksel olarak iletken, ölçüm aralığı açısından hassas, insan vücuduyla uyumlu ve şekil değiştirme sensörleri olarak kullanılabilen, elektriksel olarak iletken kompozitler ürettik. Termoplastik bir elastomer olan stiren-etilen-butilen-stiren (SEBS) kopolimeri, iyi esnekliğe ve mekanik dayanıma sahiptir ve bu nedenle bağlayıcı matris malzemesi olarak seçilmiştir. Karbon bazlı dolgular sınıfında yer alan indirgenmiş grafen oksit (rGO), mükemmel elektriksel özelliği ve göreceli olarak daha uygun fiyatlı olması nedeniyle iletken dolgu maddesi olarak seçilmiştir. SEBS / rGO iletken kompozitlerini hazırlamak için, SEBS uygun çözücü içinde çözülmüş ve çözeltiye rGO eklenmiştir. Kompozit çözeltisi daha sonra esnek kumaş üzerine çözeltiden döküm yöntemi ile kaplanmıştır ve oda sıcaklığında kurumaya bırakılmıştır. Sensörün elektromekanik davranışını araştırmak için numuneler %5, 7.5 ve 10 uzama altında 20 mm/dk ve 50 mm/dk hızlarda 50 çevrim boyunca test edilmiştir. Sensörün, farklı uzama ve farklı hızlarda test edilmesinin temel nedeni, uzama ve test hızının sensör performansı ve sensörün uzun süreli kullanımı üzerindeki etkilerini incelemektir. Test sonuçları, uygulanan gerilim nedeniyle direnç değerinin belirli bir değere kadar arttığını ve gerilim oranının hassasiyet açısından anlamlı olduğunu göstermiştir. Buna dayanarak,esnek elekteriksel olarak iletken SEBS/rGO kompozitinin, gerilebilir bir sensör maddesi olarak rahatlıkla kullanılabileceği sonucuna varılmıştır. Esnek iletken sensörler özellikle, mikroelektroniklerde, giyilebilir elektroniklerde, esnek gerinim ölçerlerde kullanım için tercih edilen ve üzerine araştırma yapılan konulardandır. Bu bağlamda, sensörün esnekliği, elektriksel iletkenliği, kullanım rahatlığı, insan vücudu ile uyumlu olması göz önünde bulundurulduğunda, bu çalışmanın sensör literatürüne büyük katkılarının olması beklenmektedir.

1. INTRODUCTION

Sensor is a device that measures physical phenomenon and converts the data into a meaningful electrical signal. In other words, it is a convertor with the ability to transform mechanical, optical, chemical, physical stimuli into a measurable electrical signal [1].

In recent years, various studies have been carried out for integrating electronic functionality in fibers and textiles. That led to development of a new field known as electronic textiles or e-textiles [2]. E-textiles are textiles that have aesthetic appearance as classical textiles with electronic functionality. According to their types and applications e-textiles have ability to sense, actuate, storage and or generate energy [3].Electronic textiles sense the fundamental bio-signals that are related to mechanical and physiological activities or stimuli such as pressure, temperature, strain,resistance, velocity, and humidity etc. These bio-signals have significant roles in rehabilitation, control systems and various biomedical applications [2].

Sensors can be classified in many ways, such as according to the distance to the object, contact/noncontact sensors; according to the chosen reference, absolute/relative sensors; according to the external power requirement, active/passive sensors [3]. and depending on the type of measurand (temperature etc.). The basic principle of this grouping is their principle of sensing and functions [4].

The sensor term should not be confused with the transducer. The transducer converts any energy type or property into another energy type or property, while the sensor converts this energy type or feature into a meaningful electrical signal [4]. For example physical sensors convert physical properties into significant electrical signals [5]. Sensors can be used in many applications such as communication and information technologies, sports, medicine (home rehabilitation, health care, disease diagnosis) [6], surveillance (civilian and military applications, emergency rescue units, and law enforcement) entertainment, and protection [7].

Garments and other textile products are prefered as multifunctional platforms because of their unique properties such as being lightweight, flexible and comfortable [8]. When compared with conventional rigid electronics, textile sensors are flexible and stretchable wearable systems that provide direct feedback [9]. Smart fabrics that are mainly composed of one or couple of sensory systems, signal processing and communication networks are described as fabrics that are able to monitor their own health and to perceive environmental conditions [9]. Textile based sensors are comfortable structures

that is basically stem from unique properties of the fabric such as air permeability, moisture absorption [7]. Another important contribution of the textile based sensors is to ensure free dynamic body movement that is the key point in terms of quality of data transfer and service. Although textile based sensors have many potential advantages such as convenient detection interface, easy to use, easy to customize, flexibility and comfort [10] their placement is important [7].

Since wearable sensors are used for various applications including urine, sweat breath [11] and motion detection their locations is of critical in terms of obtaining they should be placed in/onto the best locations to get reliable and sustainable data and undesired slippage or shifting should [12] be prevented either by special fabrics or attachment systems [5]. While sensors are located around chest and heart for breathing analysis, they are located on knee for motion analysis [13]. In addition to location environmental conditions should be considered for the quality of the signal [12]. In other words, textile based sensors should be compatible with human body and environment. In todays word in addition to functionality design, fashion, washability and durability are also important [9].

1.1 Sensing Mechanism

Sensors can be classified in different ways from very simple to complex structures according to the classification purpose and criteria. It is possible to examine all sensors in two types: passive and active [4]. A passive sensor does not require any additional energy source, but can remove energy in their operation. Passive sensors that are known as self-generating systems and electrical output signals are generated without external source (voltage or current). Active sensors need external power [14], called the excitation signal. In addition, when the selected reference is important, the sensors can be classified as absolute and relative [4]. Sensors can be classified as force sensors, pressure sensors, motion sensors, temperature sensors, etc. according to the physical properties they are designed to measure [14].

1.2 Type of Sensors

1.2.1 Capacitive sensors

Capacitive sensors are sensors that electronically measure the capacitance between two or more conductors [15], in dielectric environments [16]. A capacitive sensor consists of a probe and a driver. While probe generates the sensing field, driver is responsible for generation of output signal related with the measurement. An electrical property occurring between two conductors separated by a non-conductive structure is known as capacitance [17]. The capacitance is influenced by the size of the probe and the target surfaces [4], the distance between the probe and the purpose, the type and size of the dielectric material [17]. Capacitive sensors are used in vehicle detection, light switch, proximity

sensing, porsinal detection, and measurement sensors such as flow, pressure, liquid level, thickness etc [16].

1.2.2 Inductive sensors

Inductive sensors, are non-contact systems used for the determination of the position of a target that is made form a conductive material [17]. Sensor coil and the ferrite core, the oscillator circuit, the detector circuit and the solid state output circuit are the main parts of the system. Oscillator circuit is reponsible for the generation of the electromagnetic field. If any metal object enters the field, eddy currents are formed on the onbectthat leads to change in signal [18]. Different target materials, such as copper, aluminum, etc., react differently to the sensor. The qualitry of the signals are affected by the size of the probe coil and its target, the distance between the sensor and the target and the target material. Inductive sensors can be used for various applications in order to detect defects, cracks, weld seams and holes in conductive materials [17].

1.2.3 Piezoelectric sensors

Piezoelectric sensors are the active type sensors [3]. Since piezoelectricity is seen only in piezoelectric materials, to fabricate such sensors, material selection is very critical [19]. If an electrical voltage is applied to the material, material will deform based on the magnitude of the external electric field or can produce an electric potential when any mechanical force is applied. This is known as piezoelectric effect. Piezoelectric sensors used to determine pressure, acceleration, force, torque, strain, and acoustic emission [3].

1.2.4 Optical sensors

An optical sensor transforms light rays that come from one or more light beams into meaningful electronic signals. The optical sensor consists of two main parts, the transmission point and receiving part. Transmission point is used to emit the light beam, receving part is used for the determination of the ratio of the received light beam. Optical sensors can be classified as beam, reflector, and retro reflector sensors. When compared with other sensors, optical sensors have several advantages in terms of dynamic range, noise formation, quick response. Optical sensors are used in measurements such as temperature, pressure, liquid flow level, motion, vibration, rotation, magnetic field, acceleration, force, radiation, pH, humidity, strain, velocity, electric field and so on [20].

1.2.5 Chemical sensors

Chemical sensors convert the stimuli from various chemicals into meaningful electrical signals. Stimulants can be either a specific component or a complex chemical structure. These sensors are

designed to determine the presence amount and/or concentration of liquid or gaseous chemical species. Chemical sensors can be independent simple devices or be part of sophisticated systems [4]. Chemical sensors consists of a receptor and a converter. The receptor is not only responsible for the detection of the chemical but also responsible for transformation of information to the transducer [21]. The transducer part the data into meaningful signals. Chemical sensors are used in polymer, food and chemical industry for process and quality control [4].

1.2.6 Piezoresistive sensors

The piezoresistive effect manifests itself in the form of a change in the electrical properties of a semi-conductive material when any stress is applied [22]. Based on this, piezorescence of a semiconductor can be defined as the change in resistance due to applied stress or strain. The semiconductor silicon has a piezoresistive behavior and is still being investigated by researchers. Piezoresistive sensors are used in microelectronics, wearable electronics, flexible sensors and so on [23].

1.2.6.1 Piezoresistive strain sensors

Strain sensors are used in order to determine the amount of the applied strain. For this aim piezoresistive materials are used. As known strain is directly related with the change in dimensions of the material. When force is applied to a piezoresistive material, dimensional changes lead to formation of strain and that causes change in electrical response [24]. If strain is removed, it will react reversibly. To summarize piezoresistive strain sensors are materials that are used for determination of strain by monitoring the change in electrical resistance. Strain sensors can be classified according to their location as surface strain sensors and strain pin sensors. While surface strain sensors are located on the surface of the system, strain pin sensors are located inside system [3].

1.3 Polymer Based Piezoresistive Strain Sensors

Since conventional strain sensors based on semiconductors and metals show various limitations, polymer based strain sensors are noteworthy as alternative materials. Metal and semiconductor strain sensors have various problems related with measurement range, sensitivity, environmental conditions, attachment, cycleability and so on [25]. In that case polymers come into prominence because of their unique properties including flexibility, lightness, easy processability, cost effectiveness and so on [26]. Thermoplastics, thermoset resins, elastomers, thermoplastic elastomers are used as matrix for the piezoresistive strain sensors [25]. As known, random polymers are electrically insulating materials and they can be conductive by the addition of conductive additives such as carbon black [27], graphite, short carbon fibers, graphene and carbon nanotubes [25].

1.3.1 Thermoplastic based piezoresistive strain sensors

Thermoplastics are relatively inexpensive materials used as binders in electrically conductive composites. A conductive filler is added to a polymer matrix to provide durable and flexible materials with high electrical conductivity [28]. In polymer based piezoresistive strain sensors, thermoplastics such as polymethylmethacrylate (PMMA) [6], polypropylene (PP) [28], poly (vinyl alcohol) (PVA) [29], polyethylene (PE) [30], and polyethylene oxide (PEO) [31] are used as polymer matrix. Conductive fillers such as carbon nanotube (CNT) [6, 29, 31] and carbon black (CB) [28, 30] are used to give conductivity to the structure.

1.3.1.1 Polymethylmethacrylate (PMMA) based piezoresistive strain sensors

Kang et al, developed a CNT/PMMA based strain sensors that could be used for structural health monitoring applications [6]. In the carbon nanotube/polymer composites, the polymer improves interfacial adhesion between the phases and creates a stronger bond between the polymer and nanotubes by forming a helical polymer conformation [32]. Polymethyl methacrylate (PMMA) have been used as a matrix material in the carbon nanotube/polymer composites because it is simple to handle and easy to mix with fillers [6]. Since the polymer bond prevents the sensor from slipping, the compound effectively improves the strain transfer across the sensor and exhibits a linear strain response with load [32]. To summarize, PMMA was preferred because of its good binding properties, CNTs were preferred because of their electrical properties. In this study composites were fabricated by solvent casting. SWCNTs were dispersed in dimethyl formamide (DMF) and PMMA was incorporated into that dispersion mixed for 4 h. at 70 ˚C by a high shear mixer. This solution was casted and kept in an oven at 120 C for 12 h.

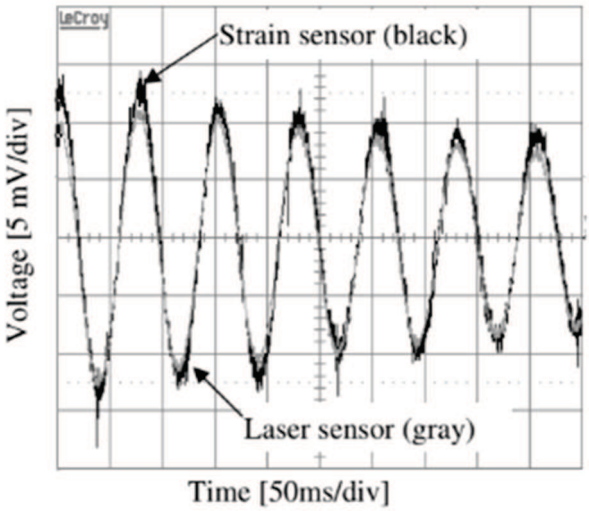

Figure 1.1: Advanced dynamic strain response in a free vibration beam(cutoff frequency 30 Hz 20 dB), response of the SWNT/PMMA 10% strain sensor. [6]

Fig. 1.1 shows the dynamic sensing behavior of the composites in free vibration. The SWNT/PMMA 10% composite sensor was tested with a 20 V driving voltage. The sensor response in Fig. 1.1 was found almost same with the reference sensor (laser displacement sensor). In other words, composite sensor was found successful in terms of measuring the stain [6].

1.3.1.2 Polypropylene (PP) based piezoresistive strain sensors

Zhao et al., prepared the carbon black/polypropylene(CB/PP) and carbon nanotubes/polypropylene (CNTs/PP) composites at various filler concentrations to investigate the percolation and strain sensing behavior of electrically conductive composites. CB and CNTs were used as conductive fillers are used for their different aspect ratios. CB and CNTs were used as conductive fillers are used for their different aspect ratios [28]. Carbon black (CB) is an important nano-scale material that have excellent electrical and thermal properties [27]. Likewise CB, carbon nanotubes (CNTs) are preferred for fabrication of conductive polymer composites due to their high aspect ratio as well as remarkable mechanical, thermal, electrical properties [28]. In order to obtain CB/PP and CNT / PP composites with different filler concentrations, the mixture was stirred for 10 minutes at 190°C in a Haake internal mixer. The mixture was then pressed into the plate mold at 200°C by using a compression molding system. Percolation behavior was determined and following that in order to investigate strain sensing behavior of composites, samples were tested for 10 cycles under maximum strain of 3%.

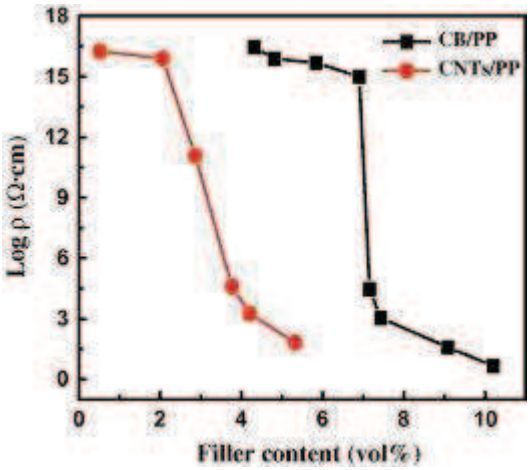

Figure 1.2: Change in volume resistance versus CB and CNT content for CB/PP and CNT/PP composites [28]

As seen from the Fig. 1.2 percolation values for CB and CNT filled composites were found different. CNT showed a lower percolation value that is caused by high aspect ratio. Since CB is a cylindirical shaped filled, its aspect ratio is relatively lower than that of CNTs. After determination of the percolation behavior samples were tested in terms of their electro mechanical behavior.

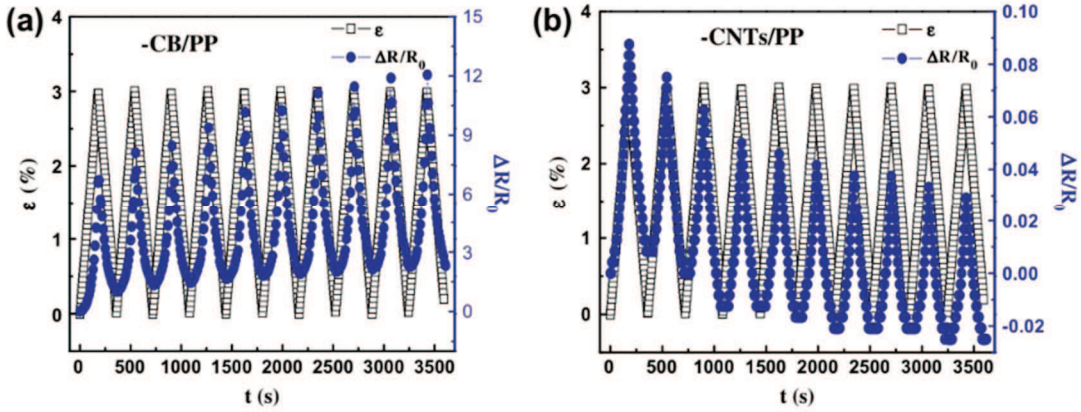

Figure 1.3: The relationship between strain and $\Delta R/R_0$ versus time of (a) CB (7.16 vol.%)/PP and (b) CNTs (3.41 vol.%)/PP composites during 10 cycles. [28]

Fig.1.3(A) shows CB/PP composite Fig.1.3(B) shows CNT/PP composite. As seen from the graphs of Fig.1.3, the $\Delta R/R_0$ and strain values were given for two conductive polymer composites. When stress is applied, $\Delta R/R_0$ value increases and when strain is removed it decreases. When the strain is applied, the conductive particles move and separate from each others and conductive network starts to break-down. In the case of removal of strain the relative resistance of the samples decreased because of the reversible formation of the conductive network.

As a function of stress, the change of conductive polymer composites about stress and $\Delta R/R_0$ is examined. For CB / PP composite, $\Delta R/R_0$ value was found to be increased exponentially due to strain and explained by tunneling mechanism. However, for CNT/PP composite R/Ro increased linearly. These two tendencies are based on differences in the microscopic morphology of CB and CNT, and it is suggested that this causes in the formation of different conductive network structures.

These results can be used to design CB and CNT-based conductive polymer composites with different strain sensing capabilities to meet different requirements [28].

1.3.1.3 Poly(vinyl alcohol) (PVA) based piezoresistive strain sensors

Gonçalves et al., designed water-based piezoresistive polymer composites by using poly(vinyl alcohol) (PVA) as a matrix and multilayer carbon nanotubes (MWCNTs) as fillers [29]. CNTs are widely used in the development of piezoresistive conductive polymer composites due to their high aspect ratio, good electrical and mechanical properties. PVA is a water soluble synthetic polymer with good mechanical properties. In this study, it was chosen because it offers good mechanical properties for the development of deformation sensors. To prepare the composite, MWCNT and PVA were dried and composites were prepared from the solution by casting. MWCNT ratio was determined as 0.5, 0.75, 1, 2, 5, 6 and 15 MWCNT by weight. The MWCNTs were dispersed in an ultrasonic bath then PVA was added. The solution was then stirred at 90°C in the magnetic stirrer until the polymer was completely dissolved.

The MWCNT/PVA films were coated on clean glass substrates with a film thickness of 80 to 120 µm and dried. Piezoresistive sensors were developed using screen printing and spraying techniques by considering the viscosity.

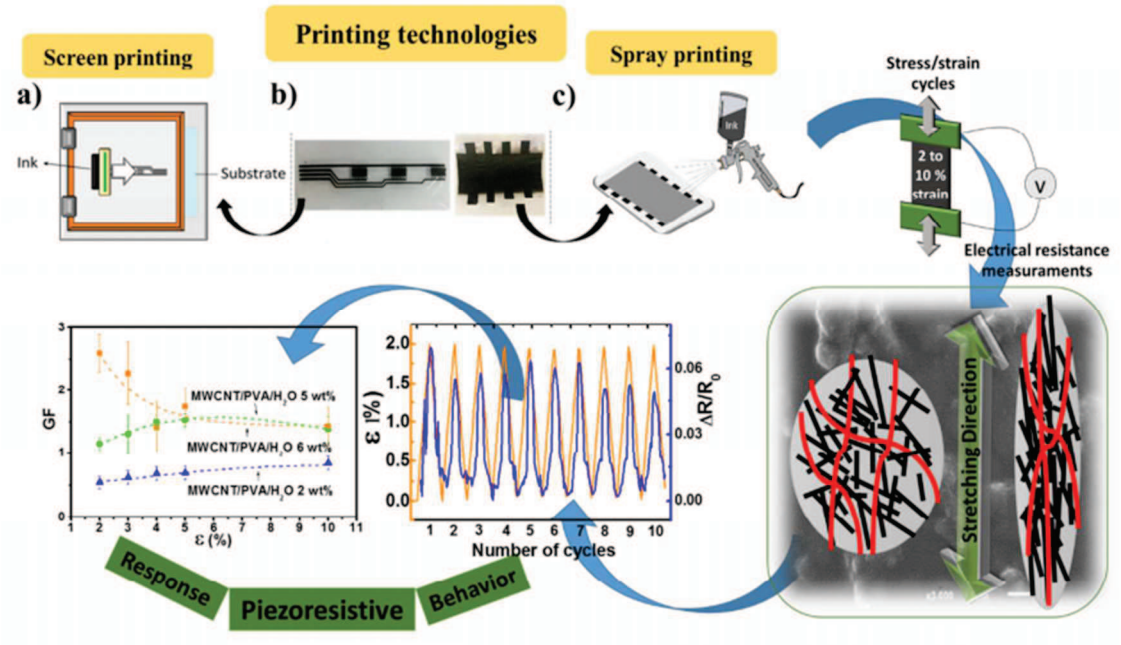

Figure 1.4: Steps for obtaining water-based printable piezoresistive sensors for large strain applications. [29]

As shown in Fig. 1.4, the viscosity adjusted solution was printed as a strain sensor by spraying and screen printing techniques and the piezoresistive properties of the sensor were examined.

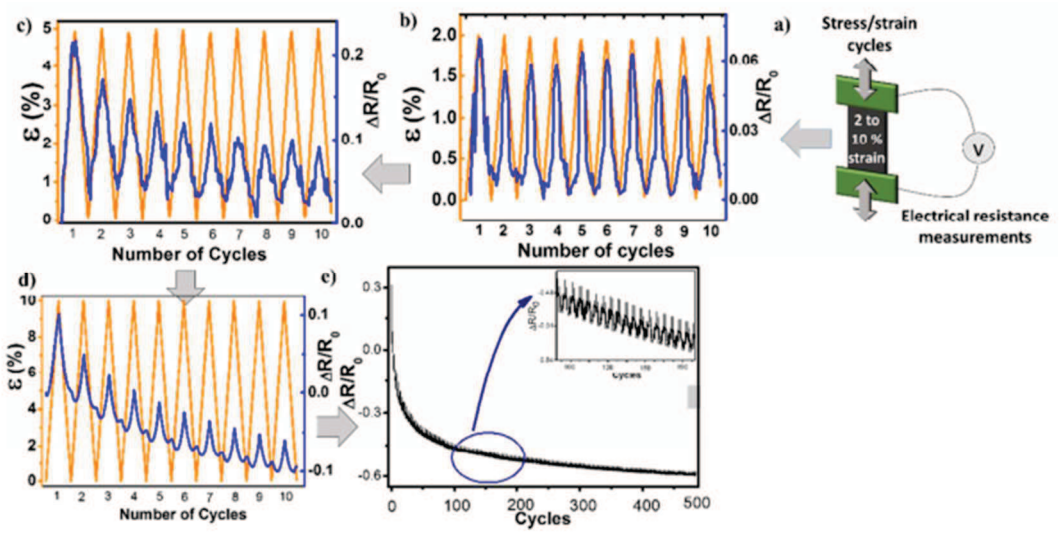

Figure 1.5: a) Testing system b, c, d) 10 cycle piezoresistive test results for 2, 5 and 10% strain for the 6% wt MWCNT / PVA composite e) piezoresistive response for 500 cycles [29]

Fig. 1.5 shows the electrical resistance variation of MWCNT/PVA composites with different ratios of MWCNT over 10 cycles at different strain levels. When the mechanical deformation (Fig. 3b-d) is increased, the electrical resistance increased and when the strain decreased the electrical resistance decreased. Fig. 3e) shows the piezoresistive behavior of the sensor in 500 cycles to evaluate the electrical and mechanical response of the sensor during the repeated cycle loading. As a result, due to their easy processing, piezoresistive response to large deformations and their printability (through screen and spray techniques), these sensors are particularly suitable for large-scale piezoresistive applications [29].

1.3.1.4 Polyethylene (PE) based piezoresistive strain sensors

Shaodi Zheng et al., used high density polyethylene (HDPE) and carbon black to obtain highly extensible films by cast film extrusion and examined the piezoresistive behavior of the films [30]. Due to the nested structure of the crystalline and amorphous phases, semi-crystalline polymers exhibit distinct nonlinear viscoelastic behavior [33], that makes them suitable for highly stretchable electronic devices. In order to prepare HDPE/CB composites, the high density polyethylene pellets and carbon black were mixed by using a twin screw extruder. Then HDPE/CB (7 vol%) film was fabricated by extrusion casting film method using a single screw extruder. Subsequently, cast films were heat treated at 110°C for 2 hours before characterization. In order to learn more about the microstructure development of conductive films and to evaluate the reproducibility of the strain sensor, medium cyclic elongations were applied to conductive films (HDPE / CB-5 and HDPE / CB20) and the piezoresistive properties of the films were examined. Changes in the electrical resistance (R/R_o) depending on the strain change are shown in Fig. 1.5 and 1.6.

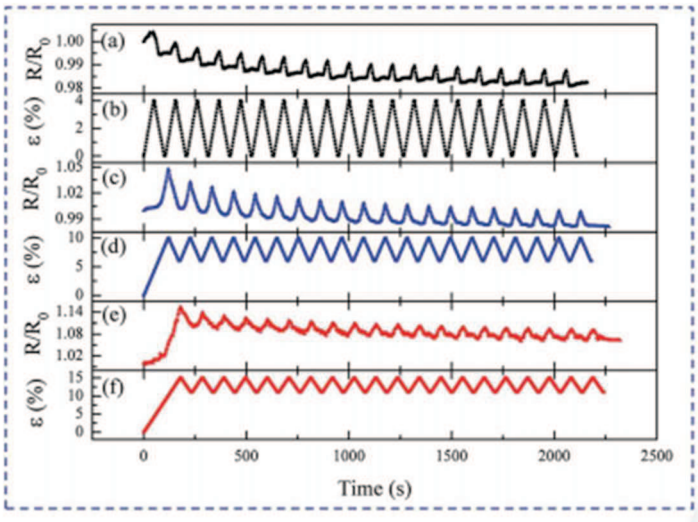

Figure 1.6: a) The piezoresistive behavior of HDPE/CB-5 cast film under tensile loading(a, c, e); cyclic deformation of films(b, d, f) [30]

As shown in Fig. 1.6, the R/R_o increases when strain is applied, the strain decreases as it is withdrawn. This can be explained in this way; when the strain is applied, the polymer chains shifted and the conductive particles move and separate from each others this result in increasing in relative resistance. The resistance decreases when strain is removed.

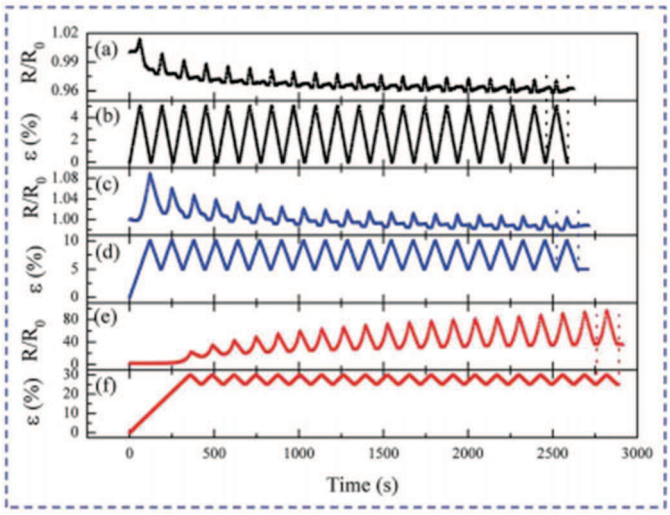

Figure 1.7: a) The piezoresistive behavior of HDPE / CB-20 cast film under tensile loading(a, c, e); cyclic deformation of films(b, d, f) [30]

It is seen that the R/R_o changes directly with the change of strain. R/R_o exhibits stability by time of strain deformation, even after twenty cycles of loading. This means that this material can be used for real-time detection materials.(Fig.1.7) [30].

1.3.1.5 Polyethylene Oxide (PEO) based piezoresistive strain sensors

Park et al. worked on the strain-dependent electrical resistance characteristics of multi-walled carbon nanotube (MWCNT)/polymer composite films that include polyethylene oxide (PEO) as the polymer matrix and multi-walled carbon nanotube (MWCNT) as filler. CNTs were used because of their excellent strength and strength properties which are desirable as a reinforcing material. In this study, PEO is used as a matrix, but the results are practicable for polymer composites that contain MWCNT. Two different composites containing 0.56 vol% and 1.44 vol% MWCNT were produced and they tested to investigate the relationship between the electrical resistance and strain. Briefly, multiple specimens with different volume fractions of MWCNT were fabricated and an experimental system was developed to measure electrical resistance and strain at the same time. The MWCNT / PEO composite films that contain 0.56 vol% and 1.44 vol% of MWCNT were tested in order to investigate the relationship between electrical resistance and strain.(Fig.1.8)

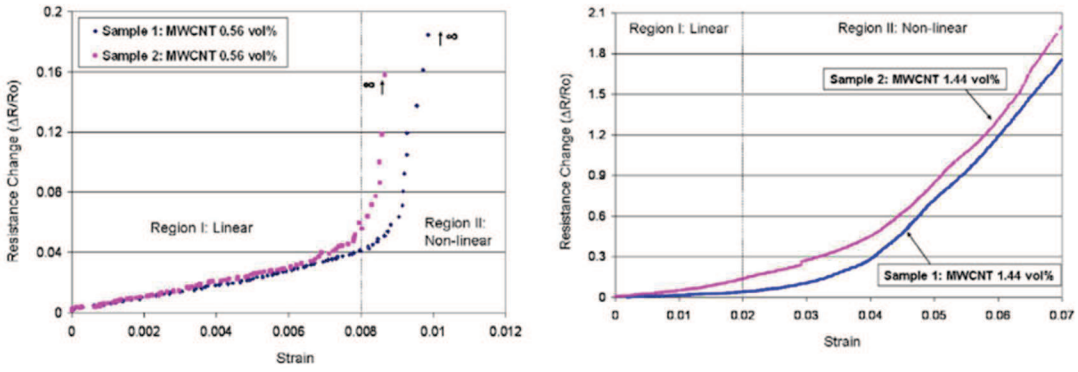

Figure 1.8: Electrical resistance change versus strain in 0.56 vol% and 1.44vol% MWCNT containing composites. [31]

Comparing films containing 1.44 vol% and 0.56 vol% MWCNT, it is seen that the electrical resistance of the film containing 1.44% MWCNT increases linearly in a larger strain range. Due to their superior performance and repeatable characteristics in electrical resistance variation, the MWCNT / PEO films, can be used in strain and embedded sensors [31].

1.3.2 Thermoset based piezoresistive strain sensors

Thermoset polymers are used in electrically conductive composites due to their thermal and mechanical properties, good adhesion to the filler, good chemical resistance and dimensional stability. In polymer based piezoresistive strain sensors, thermoset polymers such as epoxy [34] and thermosetting vinyl ester [35] are used as polymer matrix. Conductive fillers such as multi-walled carbon nanotubes (MWCNTs) [34] and graphene nanoplatelets (GNPs) [35] are used to give conductivity to the structure.

1.3.2.1 Epoxy based piezoresistive strain sensors

Sanli et al., produced composites using epoxy and multi-walled carbon nanotubes (MWCNTs) and analyzed the electrical properties of composites. Due to its good adhesion, dimensional stability, good thermal and chemical and mechanical strength, epoxy resin is chosen as polymer matrix material. Carbon nanotubes(CNTs) are preferred to use in smart materials and strain sensors [36] because they have outstanding mechanical and thermal properties with electrical conductivity and [34] advanced electrical properties [37]. In order to obtain the composites, MWCNTs of 0.3, 0.4, 0.5 and 0.75 percent by weight were mixed with the epoxy resin and the mixture was allowed to stir for 30 minutes (30 W, 25°C) in the horn sonicator. The mixture was then magnetically stirred and hardener was added and stirred for further 10 minutes. Amount of hardener was reported to affect the flexibility of the films. The samples were kept in a vacuum chamber. The piezoresistive properties of films were examined. For different CNT concentrations, strain-related relative resistance changes are shown in Fig. 1.9.

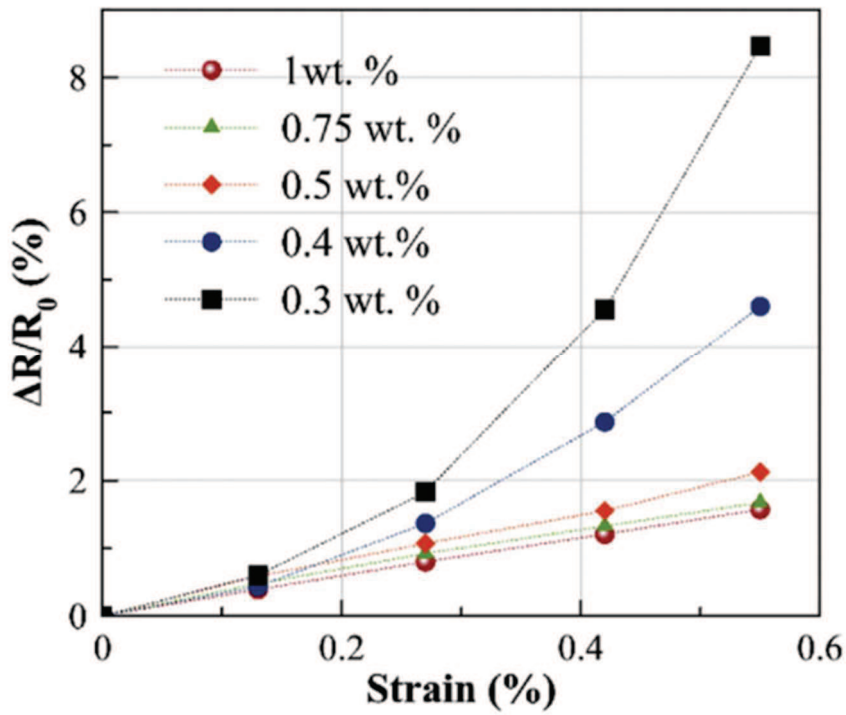

Figure1.9: Relative resistance change of MWCNTs/epoxy nanocomposites(containing different filler ratio) under tensile strain. [34]

As shown in Fig. 1.9, the sensitivity decreases with increasing MWCNTs content. The highest sensitivity value was obtained for a concentration of 0.3 wt% MWCNT. This is because MWCNTs show high sensitivity around the percolation threshold.

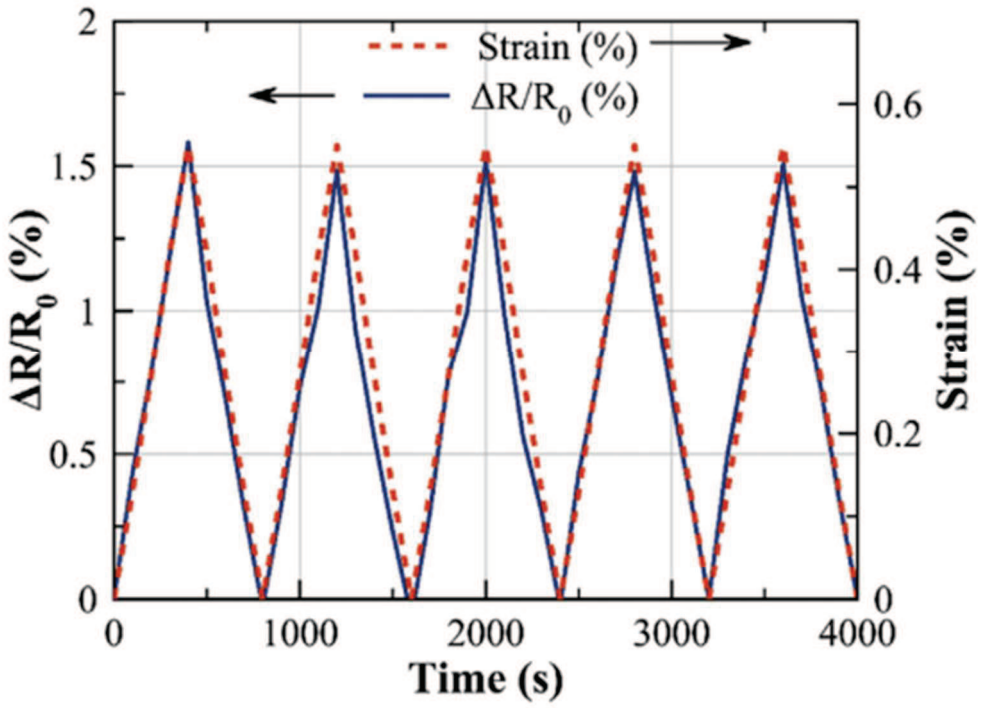

Figure 1.10: Strain-related relative resistance change of MWCNT / epoxy nanocomposite for 1wt% MWCNT content (for 5 cycles). [34]

To ensure the reliability and reproducibility of the sensor measurements, the sensor at a concentration of 1% MWCNT by weight was tested for 5 cycles at a rate of 0.1mm / min. (Fig.1.10) When looking at the standard deviation of the cyclical strain values of 1wt% MWCNTs, this composite showed high repeatability and found to be suitable for use in strain sensor applications [34].

1.3.2.2 Thermosetting (vinyl ester) based piezoresistive strain sensors

Tamburrano et al. produced polyvinyl ester-based composites filled with graphene nanoplatelets (GNPs) by solution processing method. To obtain a flexible, light and low cost composite made of thermoset resin with a high piezoresitivity, polyvinyl ester is used as the binding matrix material and graphene nanoplatelets (GNPs) as the conductive filler. In order to produce a composite, the GNPs (with different ratio 0.1, 0.25, 0.5, 1, 2 and 4 wt%) were mixed with the acetone and dispersed by an ultrasonic probe. The solution was then added to the polyvinyl ester resin that mixed with Co based accelerator and sonicated and curing agent was mixed. The mixture was castred into molds and cured for 24 hours. Tests were performed to characterize the electrical, mechanical and electromechanical properties of thermosetting resin based GNP nanocomposites under both static and dynamic conditions.

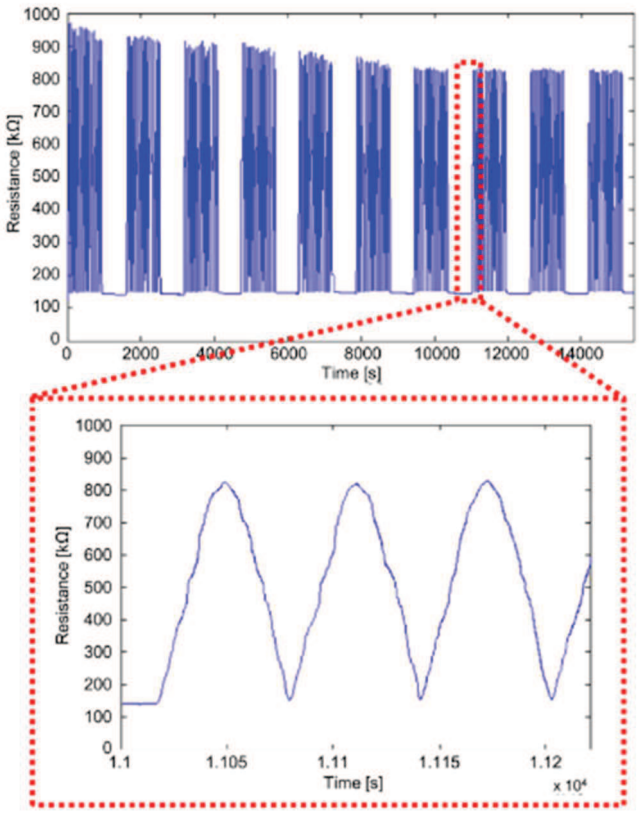

Figure 1.11: Resistance change during strain cycles [35]

Nanocomposites are subjected to cyclic mechanical loading / unloading tests to stabilize the response of resistance. As shown in Fig. 1.11, the resistance change was stabilized after cycles. The resistance change due to a certain strain has been found to be reversible and repeatable after several stabilizing cycles. The results show that thermosetting resin based GNP nanocomposites may be suitable and useful for structural health monitoring application [35].

1.3.3 Elastomer based piezoresistive strain sensors

The elastomers are a type of polymers that can extend over a few times its length when tension is applied to it and can turn to its original shape when the strain is removed. They are characterized by their elastic recovery after deformation. They are used for conductive composites and piezoresistive sensors because of their wide temperature range, their toughness and wear resistance under static and dynamic stress. In piezoresistive strain sensors, elastomers such as silicon [38] and polydimethylsiloxane (PDMS) [39] can be used as binding materials and carbon nanotube (CNT) [38] and carbon nanofibres(CNFs) [39] as conductive fillers.

1.3.3.1 Silicon based piezoresistive strain sensors

Amjadi et al., produced a soft and skin-compatible nanocomposite films by using carbon nanotube and silicone rubber. Ecoflex (platinum-catalyzed silicon) is selected as a binder material because it has high mechanical compatibility with the human skin, has a very good interfacial bond with the CNT, and has high water-resistance [38] with good thermal stability [40], and is suitable for long-term sensor applications. CNTs are used as conductive fillers because they have very good mechanical, thermal and electrical properties. The CNT–Ecoflex nanocomposite was produced in the following steps; The CNT solution was coated on patterned polyimide (PI) films at 100°C and the thin films were annealed. Subsequently, liquid Ecoflex (on average 0.5 mm thick) was poured onto the patterned CNT thin films, cured then film was taken from the substrate. Copper wires were bonded to the two ends of the films. Then another liquid Ecoflex layer covered to obtain a layered (Ecoflex layer / CNT thin film nanocomposite / Ecoflex layer) structure.

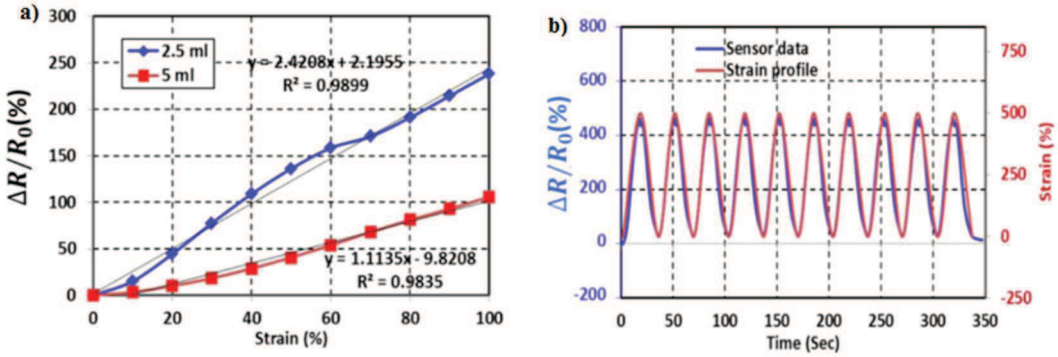

Figure 1.12: Electromechanical characterization of the CNT - Ecoflex nanocomposite based strain sensor: (a) the piezoresistive response of two strain sensors with different network densities. (b) Response of a voltage sensor over 10 cycles in 0-500% tensile strain. [38]

Fig. 1.12(a) shows the relative change in resistance due to applied strain for composites with different CNT concentrations. As shown, the strain sensors react with a very good linear response to the applied strain. As the density of the network decreased, the relative resistance change was found to increase. In the low density network, the sensitivity is much higher because the less parallel transmission path contributes to the electrical conductivity. Fig. 1.11 (b) illustrates the electrical response of the strain sensor for 10 cycles with 0 to 500% tensile strain. The resistance of the sensor was recovered even after 500% tensile strain. This indicates the super-stretchability of the strain sensor. The result shows that, highly stretchable strain sensors can be used for many applications including human motion detectors, flexible robotics, artificial reality applications, and entertainment applications [38].

1.3.3.2 Polydimethylsiloxane(PDMS) based piezoresistive strain sensors

Wu et al., produced a stretchable, conductive porous polydimethylsiloxane (PDMS) / CNT nanocomposite using a porous PDMS and a CNT-coated sugar template. In this study, the PDMS polymer was chosen as matrix and made porous to increase the deformation ability. As a conductive filler, CNT was preferred because of its high aspect ratio, cost efficiency and electrical conductivity. To obtain proper adhesion between PDMS and CNT, CNTs on the surface of the sugar particles are embedded in the pores of PDMS and porous-polydimethylsiloxane(p-PDMS) /CNF nanocomposites were prepared as follows; CNT coated sugar was pressed at a pressure of 2 MPa to form a thin layer of 40x9x2 mm. The PDMS and curing agent 10: 1 were stirred, degassed and CNF-coated sugar template was filled with the mixture.p-PDMS / CNF nanocomposites containing 0.1, 0.3, 0.5, 0.7, 1.4 and 2.8wt% CNT were prepared. In order to compare with porous-PDMS / CNF composite, dip-coating-PDMS/CNF composite was produced by the dipping-coating method. The porous PDMS layers were prepared as described in the previous composite were treated in the oxygen plasma chamber for 3 minutes to increase the adherence of the material to the p-PDMS surface. The p-PDMS layer was then immersed in a dispersion of CNT, isopropanol (IPA) and graphene oxide (GO) and then allowed to dry in the vacuum oven.The prepared dc-PDMS composite contains 3wt% of CNF. Electromechanical properties of nanocomposites were investigated. As shown in Fig. 1.13, tests were performed under semi-static tensile load to determine the strain sensing property of two different types of nanocomposites.

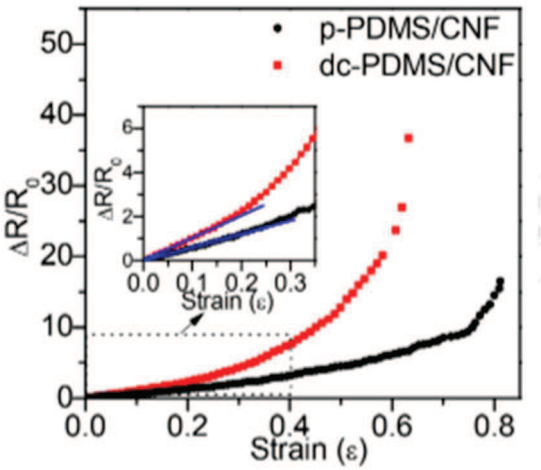

Figure 1.13: Comparison of strain-dependent resistance changes for two different PDMS nanocomposite(0.3wt% CNF) (ΔR/R0 versus strain) [41]

Fig. 1.13 shows that for both nanocomposites there is a change in the resistance, ΔR/R0 depending on the applied strain. The ΔR/R0 values for both nanocomposites show an almost linear response up to 20-30% strain. On the other hand, non-linear responses are observed beyond these values. When two

composites were compared, Dc-PDMS/CNF nanocomposite was found to exhibit a higher sensitivity than p-PDMS / CNF nanocomposites, which may be due to the microstructures of the composites [41].

1.3.4 Thermoplastic elastomer based piezoresistive strain sensors

Conductive composite polymers are achieved by adding some conductive fillers in to the insulating polymers [42]. Because of their rigidity and limited elongation the conventional metal or semiconductor based sensors have restricted application in flexible devices. Since thermoplastic elastomers have high flexibility, large specific surface area, and lightweight they have been effectively used in conductive polymer composites [42]. Thermoplastic elastomers have both the processability of the thermoplastics and the mechanical behavior of the elastomers [43]. Thermoplastic elastomers such as poly(styrene–butadiene–styrene) (SBS) [44] and styrene-ethylene/butylene-styrene (SEBS) [45] can be used as polymer matrix. Carbon based conducting such as few-layer graphene (FLG) [44], and carbon black [45] are the most mostly used fillers to manufacture conductive polymer composites (CPCs) [42].

1.3.4.1 Poly(styrene–butadiene–styrene) (SBS) based piezoresistive strain sensors

Wang et al., produced a sensitive and stretchable piezoresistive strain sensor by wet spinning using poly (styrene-butadiene-styrene) (SBS) and few layer graphene (FLG). As a thermoplastic elastomer, SBS has been used as polymer matrix due to its very good elasticity, good mechanical property [44], durability [46] and high abrasion resistance [47]. Few-layer graphene (FLG) has been used as a conductive filler due to its excellent mechanical and electrical properties. FLG was dispersed in tetrahydrofuran (THF) and sonicated in a water bath. Then, by adding SBS to the FLG / THF suspension, the solution was mixed for 24 hours and then sonicated for a further 1 hour. Fiber spinning was carried out by wet spinning method. Fibers were injected into a ethanol filled coagulation bath. The dynamic durability of wearable strain sensors is important for practical applications. To determine the dynamic strain sensing behavior of SGFs, a cyclic stretching-releasing profile was employed between 0-50% strain (Fig. 1.14).

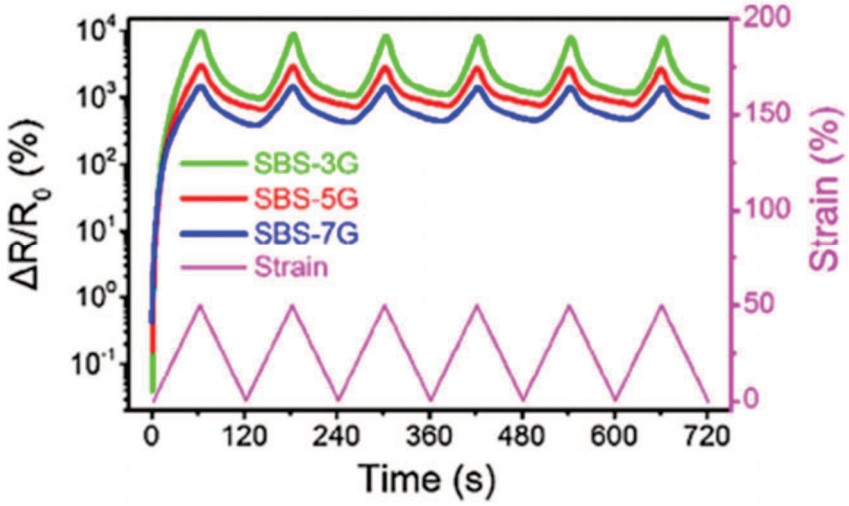

Figure 1.14: Dynamic strain sensing behavior of SGFs containing different amounts of FLG at a strain between 0 and 50% under cyclic stretching-releasing. [44]

It is seen that in all samples, the ΔR/R increases by the increase in the strain, the ΔR/R decreases with the decrease in strain in each cycle. It was found that the content of FLG had a significant effect on strain detection behavior of SGFs. Test results show that SGFs with higher FLG content are more durable and dependable, but have low amplitude. Stretchable, strain sensors are used in wearable electronics, medical monitoring and health applications. The reported methodology can be used for the production of various piezoresistive strain sensors (Fig.1.14) [44].

1.3.4.2 Styrene-ethylene/butylene-styrene (SEBS) based piezoresistive strain sensors

Corinne Mattmann et al., used styrene-ethylene-butylene-styrene(SEBS) block copolymer as matrix and carbon black(CB) as conductive filler to produce strain sensors which can measure the great strain (80%) values in textile. SEBS as a thermoplastic elastomer has been chosen as the binder matrix due to its flexibility and mechanical properties. Carbon black is used due to its electrical conductivity and mechanical properties. In order to fabricate conductive composites, SEBS was thawed and carbon black was added and stirred at 180°C for 10 hours at a rotation speed of 10 rpm to ensure homogeneity. The mixture was heated in the rheometer cylinder at 180 ° C under 0.5 MPa pressure for 2 minutes and compressed. Fibers were fabricated by using a 300μm extrusion die (Due to die swelling, fiber diameter increased to 1515μm).

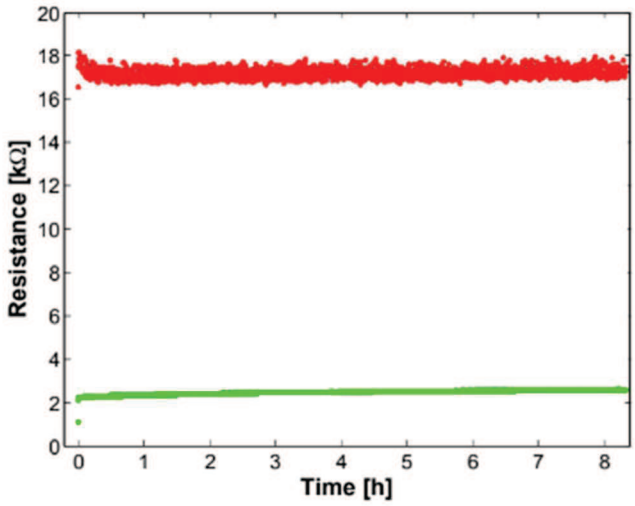

Figure 1.15: Maximum and minimum resistance values within the first 8 hours of the sensor subjected to stretching-releasing cycle for 16 hours. [45]

In order to examine the performance of the sensor in long-term use, the change in its resistance during the long-term cycle has been investigated. When the sensor is used for a long time without resting, the sensor properties are expected to be more stable. Therefore, the sensor was tested for~3800 cycles at ~ 475 cycles/hours for 16 hours.

Fig. 1.15 shows the maximum and minimum resistance values of the sensor in the first 8 hours. The lowest resistance is increased by approximately 0.5kΩ. The probable cause of this is due to slowly increasing textile deformation. Maximum resistance decreases in the first half hour, then reaches the minimum level by approaching the initial level and increases slowly again. Based on these, the sensor properties can be considered to be largely constant over time. The sensor can be used in wearable strain sensors due to its wide stress range and stable sensor properties in continuous use [45].

2.METHODS

The purpose of this study is to produce commercially feasible, industrially applicable, flexible, and sensitive SEBS/rGO composites that are compatible with human body and can be used as strain sensors. In the presented study, styrene-ethylene-butylene-styrene(SEBS)co-polymer was used as the thermoplastic elastomer (TPE) matrix and reduced graphene oxide (rGO) was used as conductive. Coating solution was prepared based on previous work and fabrics were coated by the conductive mixture. After drying morphological and electro-mechanical properties were characterized.

2.1. Materials

SEBS with the Mw 160000 g/mol was supplied from Taipol. The block ratio S/EB is 20/80. Toluen was used as a solvent to make appropriate SEBS solutions. Toluen was supplied from Merck. Reduced graphene oxide was obtained according to following method that was previously reported by our research group [48, 49].

Firstly, 1 g of graphite wasmixed with 0.5 g of sodium nitrate (NaNO3) then 23 ml of sulfuric acid (H2SO4) was added to the mixture. The mixture was cooled to 0 ° C in an ice bath and 3 g of potassium permanganate (KMnO 4) was slowly added to the mixture.(The temperature should be kept below 20 ° C.) The mixture was then removed from the ice bath and stirred for 30 min at 35 ° C in the mixer. Then 46 ml of distilled water was slowly added to the mixture and the temperature was raised to 98 ° C. 140 mL of purified water, heated at 80 ° C, was added to the mixture which was kept at this temperature for 15 minutes.

Then, 3% hydrogen peroxide (H_2O_2) was added and the light yellow-brown colored mixture was filtered and washed with purified water (Hummers and Offeman, 1958).Then, 100 mg of graphene oxide (GO) obtained by the Hummers method was kept in 100 ml of distilled water in an ultrasonic mixer until a yellow-green-brown colored homogenous mixture was obtained. 1 ml of hydrazinmonohydrate was then added to the homogeneous mixture and left to reflux at 100 ° C until a black precipitateformed. With this step, reduced graphene oxide is obtained.

The resulting reduced graphene oxide was filtered using a glass filter, washed sequentially with pure water and methanol and dried in a vacuum oven [50, 51].

2.2. Sample Preparations

In the first step SEBS co-polymer was dissolved in toluene. SEBS:toluen weight ratio was 1:2. The mixture of SEBS/toluen was stirred continuously at room temperature and 400 rpm for 48 hours by a magnetic stirrer (Daihan MASH 20 D). In the final step, rGO mixed with SEBS in varying weight percentage by using high shear mixer. (Mazerustar, Kurabo) Composites with level of rGO/SEBS ratios (30/70) was prepared. Folllowing that, printing template and the fabric were prepared in the specified dimensions. The fabric was a knitted fabric with high elastomer content (0.90 mm, 345 gr m^{-2}). As shown in Fig 2.1. coating was carried out by hand with a blade with dimension of (25mm x 75mm). In order to obtain homogeneous coating layer, fabric was well tensioned. The coated fabrics were then allowed to dry. After that, as shown in Fig 2.2 by leaving equal distances, along the centerline of the sample parallel to the longitudinal direction, 4 cupper probes with 10 mm apart, were attached to the samples.

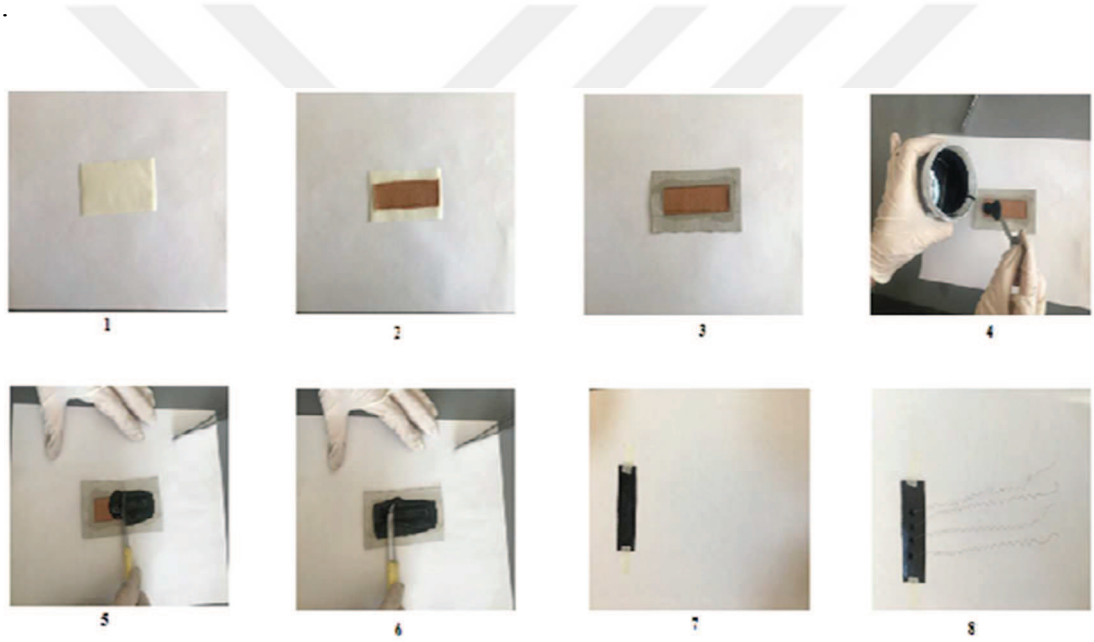

Figure 2.1: Steps involved in preparing of printing paste

2.3. Characterization

Specimen thickness was determined before testing by using a precision thickness meter (Mitutoyo ID-C112E).

Morphological characterization was carried ot by a Field Emission Scanning Electron Microscopy (FESEM) at Middle East Technical University by JEOL JSM-6400.

For the electro-mechanical characterization (strain cycling tests) composite specimens in the form of rectangular (25mm x 75mm) prepared were tested by using Devontrans GPUG/R with a gauge length of 50 mm. To determine the relationship between the mechanical properties of the printed fabric and

their electrical properties, the necessary tests were carried out at 5, 7.5, and 10% strain amplitudes at 20, and 50 mm/min speed. Each sample was tested for 50 cycles. The dynamic resistance measurement on these samples was performed using an set-up consisting of a current source (Keithley 6221) and a nano-voltmeter (Keithley 2182A) under 1 μA input current. The set-up was controlled by a computer for automatic data collection andcontrol. Samples were tested in the tensile tester presented in Fig. 2.2.

Figure 2.2:SEBS / rGO composite, test sample

3.RESULTS AND DISCUSSION

3.1 Piezoresistance

In the case of sensor applications, it is necessary to understand the piezoresistive property of the composite to determine the potential use of the coated textile sensor. In this part piezoresistive response of the textile based sensor is investigated. An ideal piezoresistive sensor should exhibit effective sensing behavior within the appropriate range of strain. In order to analyze this, piezoresistance studies were carried out at 5, 7.5, and 10% strain amplitudes. In this study, the sensors were pre-stretching before testing in order to create a cycling history. The dynamic response of a sensor is important in terms of its ability to react timely under stimulus action. If the sensor does not react at the required frequency, a dynamic error may occur. In all measurements reported in this study, the strain-resistance relationship was examined simultaneously as a function of time. Dynamic response is important not only to obtain continuous data, but also to assess the cyclic stability of the sensor material.

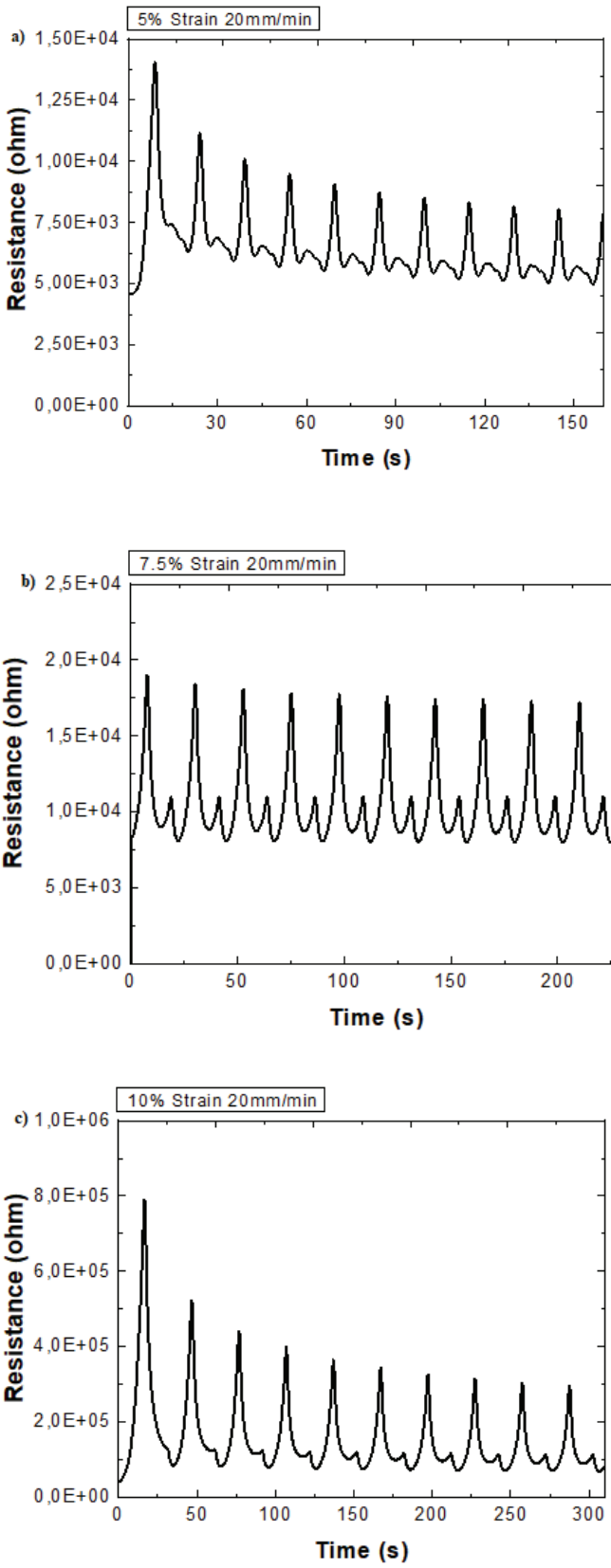

Figure 3.1: Effect of strain (5,7.5,10.%) at constant test speed of 20 mm/min on resistance (10 cycle)

As shown in Fig.17(a,b,c) the resistance varies depending on the applied strain. As the strain increases, the resistance increases. Depending on the tension, the polymer chains move over each other, which increases the distance between the conductive filler, the separation of the conductive fillers causes the resistance to decrease[35]

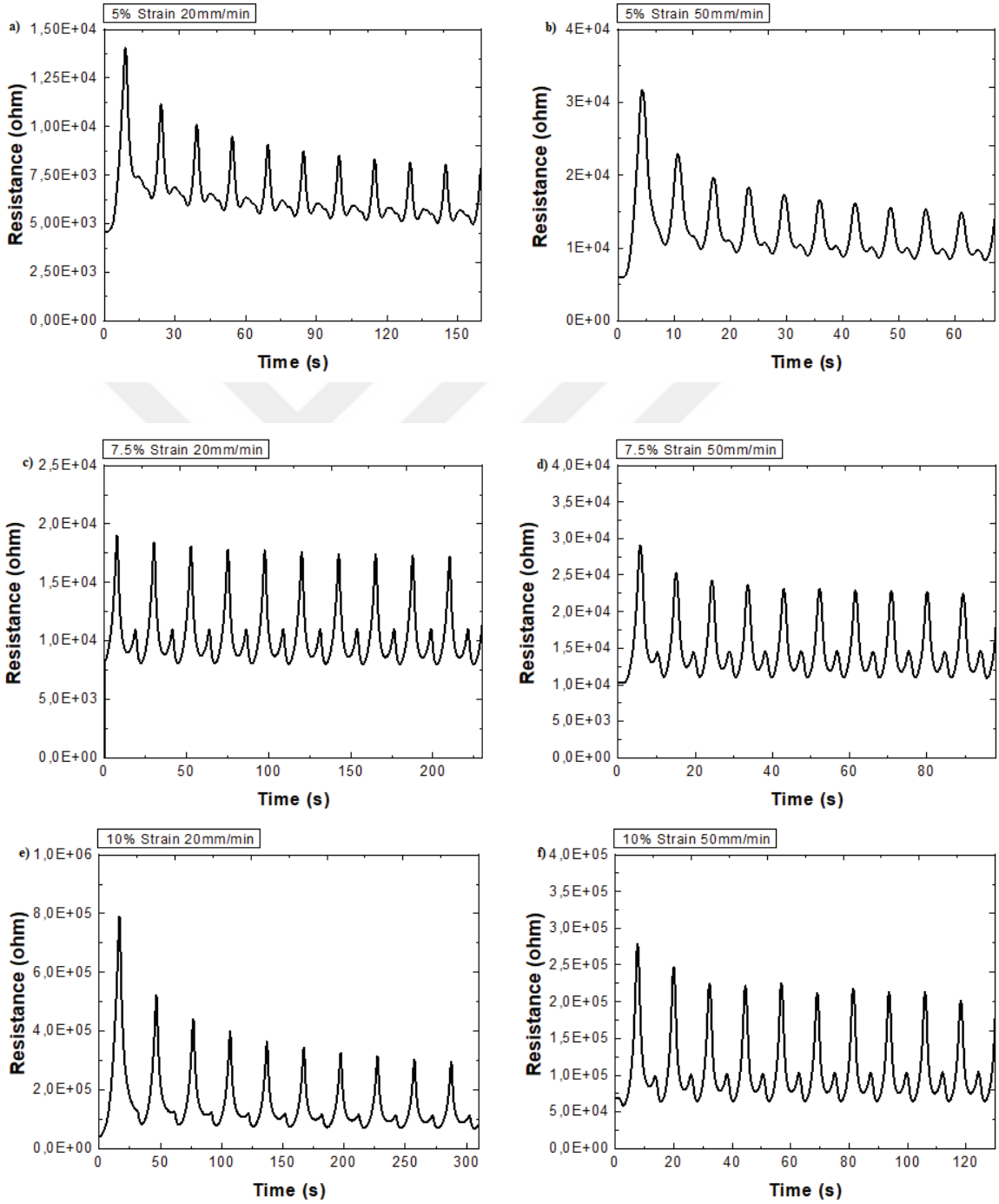

Figure 3.2: Sensor characteristics at different measurement speeds; 5% strain(a,b);7.5% strain(c,d);10% strain(e,f)

At low stress amplitudes (5% and 7% strain), the electrical resistance decreased with increasing strain and then increased during recovery. (Fig.18(a,b,c,d)). This behavior can be attributed to the reversible rGO configuration that is caused by the applied strain. For higher strain amplitudes (10% strain), increased strain caused a reduction in resistance above acertain strain threshold (Fig.18(e,f)); however, a slight increase in resistance was noted with increasing strain. After a few cycles, the electrical response is stabilized, and the subsequent cycles follow almost the same trend except for the beginning and end of the cycles. At higher strain values, the translocation of the particles becomes predominant, resulting in greater separation between particles and greater resistance. Increased resistance during discharge is mainly due to the restoration of the relative position of the rGO particles due to the recovery of the matrix polymer. Nonetheless, in almost all cases, the zero-strain electrical resistance is higher than the end of the first cycle. This occurs due to deformation in the first loading cycle (the highest stress softening occurs in the first cycle) [41].

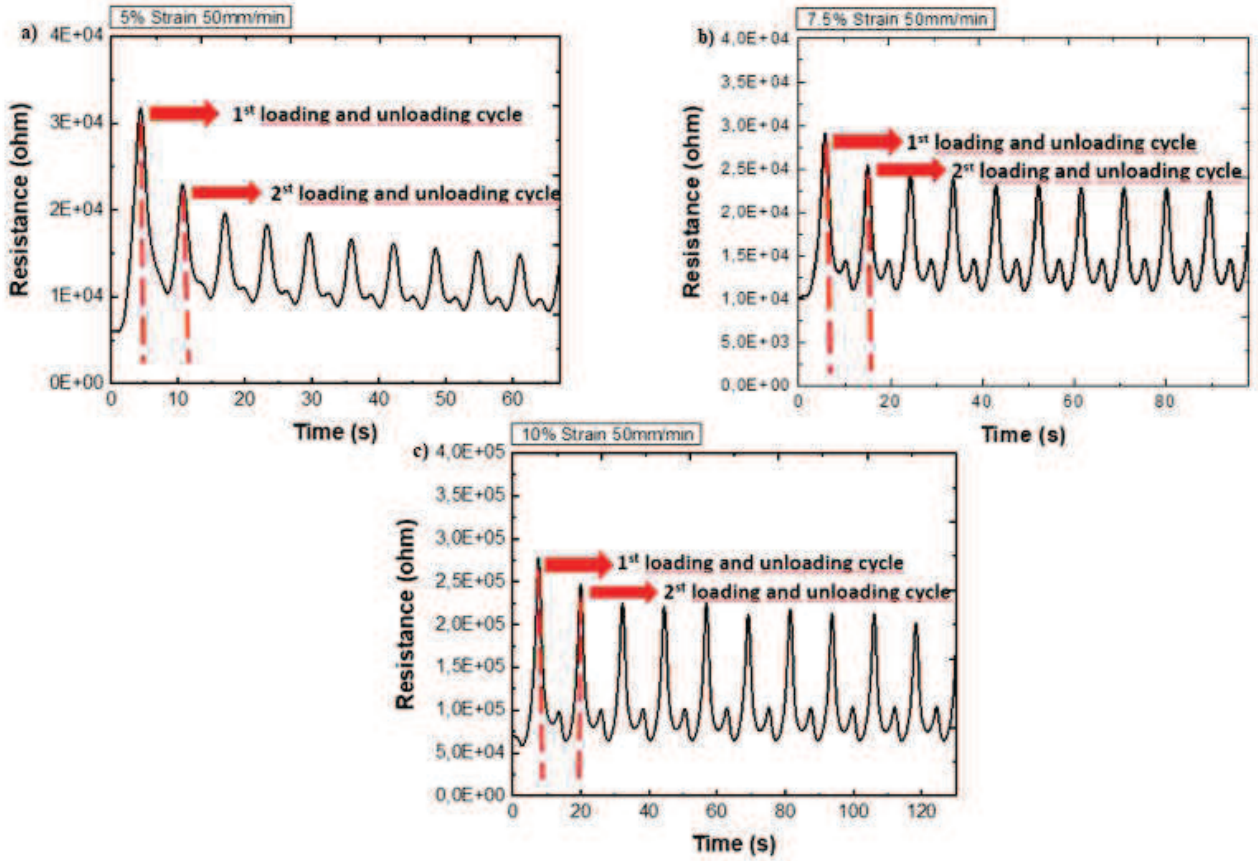

Figure 3.3: Dynamic piezoresistive behavior of sensors as a function of time for 10 cycles at different levels of strain: (a) 5% (b) 7.5% (c) 10%

As shown in Fig. 3.4, at low strain amplitudes (in the range of 5-7.5%), it was found that the electrical resistance decreased with increasing strain and then increased during recovery. The electrical response appears to stabilize after several cycles and follow approximately the same trend.

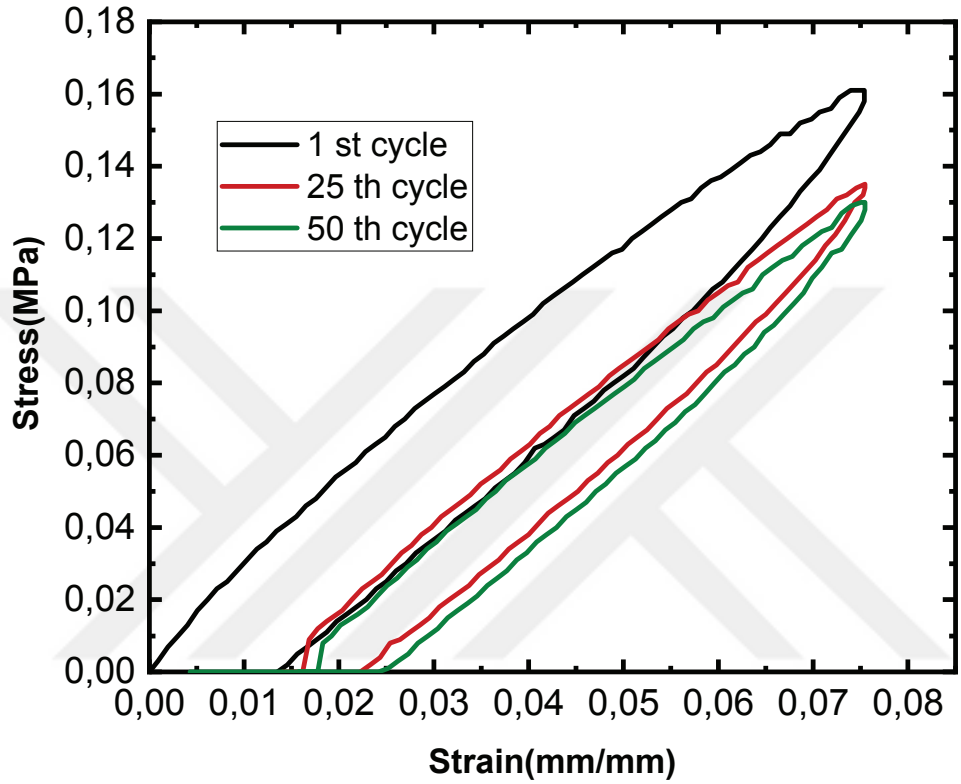

Figure 3.4: Stress-strain behavior of composite (7.5% strain, 50mm/min)

Fig. 3.4 shows the stress–strain responses of the 1st, 25th, and 50 th extension cycles of the SEBS/rGO composites with 30% rGO (wt%) performed at 7.5% strain amplitude and 50mm/min test speed.(7.5% strain) Elastomers show lower maximum stress value compared to the first cycle under constant strain. This is a well-known phenomenon referred to as Mullins Effect [41,46]

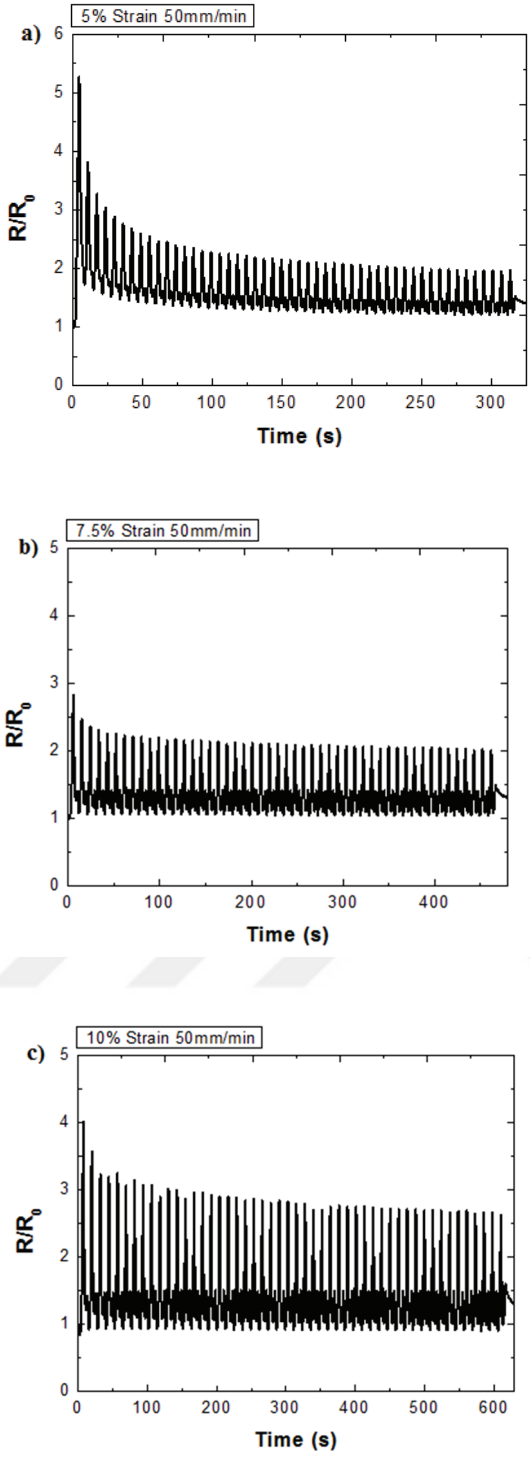

Figure 3.5: Dynamic piezoresistive behavior of printed fabric containing 30% rGO. as a function of time for 50 cycles at different levels of strain: (a) 5% (b) 7.5% (c) 10% (50mm/min)

Since the filler cavity under strain is controlled by polymer matrix deformation, the ability of the polymer to be recovered after the applied strain affects the mechanical and electrical response of the composite through subsequent cycles[44]. When the strain is applied, the intermolecular physical contact breaks down, which is the result of the elastic deformation of the matrix, that increases the interparticle distance and therefore increases the resistance. (Fig.3.5) Although samples showed good

cyclic stability at low level (at 5,7.5%); it showed a higher resistance for 10% strain and stabilized after more cycles. This is assumed to occur due to the stress softening of the composites under cyclic loading.

When a strain is applied on the sensor, depending on the strain, the resistance increases (Fig.18 (a), Fig.3.5 (a)), but at a certain strain value, the conductive fillers close together, the resistance decreases.(Fig.18(b), Fig.3.5 (b)). If greater strain is applied to the sensor, the resistance increases again (Fig.18(c), Fig.3.5 (c)).

4.CONCLUSION

In the this work, SEBS copolymer of thermoplastic elastomer was used as polymer matrix, in order to make the structure electrically conductive, rGO was added into the polymer matrix. Electrically conductive SEBS/rGO composites were coated on the fabric and were tested at speeds of 20mm/min and 50mm/min under 5,7.5 and 10% strain and the electro-mechanical behavior of the sensors was investigated. The test results show that piezoresistive polymer composite has been successfully obtained. This study is important for piezoresistive strain sensor applications.

REFERENCES

[1] **Tao (eds.), X.,** 2015: Handbook of Smart Textiles, 1st ed.; Springer-Verlag Singapur,

[2] **Linz, T.; Vieroth, R.; Dils, C.; Koch, M.; Braun, T.; Becker, K.; Kallmayer, C.; Hong, S.,** 2008:Embroidered Interconnections and Encapsulation for Electronics in Textiles for Wearable Electronics Applications. In Advances in Science and Technology; pp 85–94.

[3] **Gautschi (auth.), D.-I. E. G.,** 2002: Piezoelectric Sensorics: Force Strain Pressure Acceleration and Acoustic Emission Sensors Materials and Amplifiers, 1st ed.; Springer-Verlag Berlin Heidelberg,

[4] **Fraden, J.,** 2003:Electronics Handbook of Modern Sensors Physics Designs and Applications, 3rd ed.; Springer,

[5] **Coyle, S.; Wu, Y.; Lau, K.-T.; Brady, S.; Wallace, G.; Diamond, D**., 2007: Bio- Sensing Textiles Wearable Chemical Biosensors for Health Monitoring. In 4th International Workshop on Wearable and Implantable Body Sensor Networks (BSN 2007); Leonhardt, S., Falck, T., Mähönen, P., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg,; Vol. 13, pp 35–39. https://doi.org/10.1007/978-3-540- 70994-7_6.

[6] **Kang, I.; Schulz, M. J.; Kim, J. H.; Shanov, V.; Shi, D.,** 2006: A Carbon Nanotube Strain Sensor for Structural Health Monitoring. Smart Materials and Structures, 15 (3), 737–748. https://doi.org/10.1088/0964-1726/15/3/009.

[7] **Sungmee Park; Jayaraman, S.,** 2003: Enhancing the Quality of Life through Wearable Technology. IEEE Engineering in Medicine and Biology Magazine, 22 (3), 41–48. https://doi.org/10.1109/MEMB.2003.1213625.

[8] **Munro, B. J.; Campbell, T. E.; Wallace, G. G.; Steele, J. R**., 2008: The Intelligent Knee Sleeve: A Wearable Biofeedback Device. Sensors and Actuators B: Chemical, 131 (2), 541–547. https://doi.org/10.1016/j.snb.2007.12.041.

[9] **Lymberis, A.; Lymberis, A.; Rossi, D. E. D.,** 2004: Wearable EHealth Systems For Personalised Health Management: State Of The Art and Future Challenges, 1st ed.; Studies in Health Technology and Informatics; IOS Press.

[10] **Coyle, M.,** 2002: Ambulatory Cardiopulmonary Data Capture; IEEE; pp 297– 300. https://doi.org/10.1109/MMB.2002.1002333.

[11] **Coyle, S.; King-Tong Lau; Moyna, N.; O'Gorman, D.; Diamond, D.; Di Francesco, F.; Costanzo, D.; Salvo, P.; Trivella, M. G.; De Rossi, D. E**., 2010: BIOTEX—Biosensing Textiles for Personalised Healthcare Management. IEEE Transactions on Information Technology in Biomedicine, 14 (2), 364–370. https://doi.org/10.1109/TITB.2009.2038484.

[12] **Zheng, E.; Chen, B.; Wei, K.; Wang, Q. Lower Limb.,** 2013: Wearable Capacitive Sensing and Its Applications to Recognizing Human Gaits. Sensors, 13 (10), 13334–13355. https://doi.org/10.3390/s131013334.

[13] **Lanata, A.; Scilingo, E. P.; De Rossi, D**., 2010: A Multimodal Transducer for Cardiopulmonary Activity Monitoring in Emergency. IEEE Transactions on Information Technology in Biomedicine, 14 (3), 817–825. https://doi.org/10.1109/TITB.2009.2024414.

[14] **Webster, J. G.**, 1998: Measurement, Instrumentation, and Sensors Handbook, 1st ed.; Electrical Engineering Handbook; CRC Press.

[15] Introduction to Capacitors, Capacitance and Charge. Basic Electronics Tutorials, 2013.

[16] **Baxter; K, L.,** 1997: Capacitive Sensors - Design and Applications; Wiley - IEEE Press.
[17] **Wilson, J. S.,** 2005: Sensor Technology Handbook; Newnes.
[18] **Soloman, S.,** 2009: Sensors Handbook, Second Edition, 2nd ed.
[19] **Harsanyi, G.,** 2000: Sensors in Biomedical Applications Fundamentals Technology and Applications, 1st ed.; CRC Press,.
[20] **Ahuja, D.;** Parande, D. Optical Sensors and Their Applications. 9.
[21] **Hulanicki, A.,** 1991: Glab, S.; Ingman, F. Chemical Sensors: Definitions and Classification. Pure and Applied Chemistry, 63 (9). https://doi.org/10.1351/pac199163091247.
[22] Sensors Set: A Comprehensive Survey; VCH Verlagsgesellschaft mbH, 1995.
[23] **Suhling, J. C.; Jaeger, R. C.,** 2001: Silicon Piezoresistive Stress Sensors and Their Application in Electronic Packaging. IEEE Sensors Journal, 1 (1), 14–30. https://doi.org/10.1109/JSEN.2001.923584.
[24] **Pacelli, M.; Caldani, L.; Paradiso, R.** Textile Piezoresistive Sensors for Biomechanical Variables Monitoring. 4.
[25] **Kanoun, O.; Muller, C**., 2015: Benchirouf, A.; Sanli, A.; Gerlach, C.; Bouhamed, Carbon Nanotube Polymer Composites for High Performance Strain Sensors. In 2015 1st Workshop on Nanotechnology in Instrumentation and Measurement (NANOFIM); IEEE: Lecce,; pp 1–4. https://doi.org/10.1109/NANOFIM.2015.8425352.
[26] **Hou, Y.; Wang, D.; Zhang, X.-M.; Zhao, H.; Zha, J.-W.; Dang, Z.-M.**, 2013: Positive Piezoresistive Behavior of Electrically Conductive Alkyl-Functionalized Graphene/Polydimethylsilicone Nanocomposites. J. Mater. Chem. C, 1 (3), 515–521. https://doi.org/10.1039/C2TC00114D.
[27] **Zhang, Q.-H.; Chen, D.-J.,** 2004: Percolation Threshold and Morphology of Composites of Conducting Carbon Black/Polypropylene/EVA. Journal of Materials Science, 39 (5), 1751–1757. https://doi.org/10.1023/B:JMSC.0000016180.42896.0f.
[28] **Zhao, J.; Dai, K.; Liu, C.; Zheng, G.; Wang, B.; Liu, C.; Chen, J.; Shen, C.,** 2013: A Comparison between Strain Sensing Behaviors of Carbon Black/Polypropylene and Carbon Nanotubes/Polypropylene Electrically Conductive Composites. Composites Part A: Applied Science and Manufacturing, 48, 129–136. https://doi.org/10.1016/j.compositesa.2013.01.004.
[29] **Gonçalves, B. F.; Oliveira, J.; Costa, P.; Correia, V.; Martins, P.; Botelho, G.; Lanceros-Mendez, S.,** 2017: Development of Water-Based Printable Piezoresistive Sensors for Large Strain Applications. Composites Part B: Engineering, 112, 344–352. https://doi.org/10.1016/j.compositesb.2016.12.047.
[30] **Zheng, S.; Deng, J.; Yang, L.; Ren, D.; Yang, W.; Liu, Z.; Yang, M.**, 2015: A Highly-Deformable Piezoresistive Film Composed of a Network of Carbon Blacks and Highly Oriented Lamellae of High-Density Polyethylene. RSC Adv., 5 (39), 31074–31080. https://doi.org/10.1039/C5RA00224A.
[31] **Park, M.; Kim, H.; Youngblood, J. P**., 2008: Strain-Dependent Electrical Resistance of Multi-Walled Carbon Nanotube/Polymer Composite Films. Nanotechnology, 19 (5), 055705. https://doi.org/10.1088/0957-4484/19/05/055705.
[32] **Liu, H.; Li, Q.; Zhang, S.; Yin, R.; Liu, X.; He, Y.; Dai, K.; Shan, C.; Guo, J.; Liu, C.,** 2018: Electrically Conductive Polymer Composites for Smart Flexible Strain Sensors: A Critical Review. Journal of Materials Chemistry C, 6 (45), 12121– 12141. https://doi.org/10.1039/C8TC04079F.

[33] **Zheng, Q.; Zhou, J. F.; Song, Y. H.,** 2004: Time-Dependent Uniaxial Piezoresistive Behavior of High-Density Polyethylene/Short Carbon Fiber Conductive Composites. Journal of Materials Research, 19 (09), 2625–2634. https://doi.org/10.1557/JMR.2004.0355.

[34] **Sanli, A.; Müller, C.,** 2016: Kanoun, O.; Elibol, C.; Wagner, M. F.-X. Piezoresistive Characterization of Multi-Walled Carbon Nanotube-Epoxy Based Flexible Strain Sensitive Films by Impedance Spectroscopy. Composites Science and Technology, 122, 18–26. https://doi.org/10.1016/j.compscitech.2015.11.012.

[35] **Tamburrano, A.; Sarasini, F.; De Bellis, G.; D'Aloia, A. G.; Sarto, M. S.**, 2013: The Piezoresistive Effect in Graphene-Based Polymeric Composites. Nanotechnology, 24 (46), 465702. https://doi.org/10.1088/0957- 4484/24/46/465702.

[36] **Gang Yin; Ning Hu.,** 2011: Karube, Y.; Yaolu Liu; Yuan Li; Fukunaga, H. A Carbon Nanotube/Polymer Strain Sensor with Linear and Anti-Symmetric Piezoresistivity. Journal of Composite Materials, 45 (12), 1315–1323. https://doi.org/10.1177/0021998310393296.

[37] **Monti, M.; Natali, M.; Petrucci, R.; Kenny, J. M.,** 2011: Torre, L. Impact Damage Sensing in Glass Fiber Reinforced Composites Based on Carbon Nanotubes by Electrical Resistance Measurements. Journal of Applied Polymer Science, 122 (4), 2829–2836. https://doi.org/10.1002/app.34412.

[38] **Amjadi, M.; Yoon, Y. J.; Park, I.,** 2015: Ultra-Stretchable and Skin-Mountable Strain Sensors Using Carbon Nanotubes–Ecoflex Nanocomposites. Nanotechnology, 26 (37), 375501. https://doi.org/10.1088/0957-4484/26/37/375501.

[39] **Wu, S.; Zhang, J.; Ladani, R. B.; Ravindran, A. R.; Mouritz, A. P.; Kinloch, A. J.; Wang, C. H.,** 2017: Novel Electrically Conductive Porous PDMS/Carbon Nanofiber Composites for Deformable Strain Sensors and Conductors. ACS Applied Materials & Interfaces, 9 (16), 14207–14215. https://doi.org/10.1021/acsami.7b00847.

[40] **Kim, E. S.; Kim, E. J.; Shim, J. H.; Yoon, J.-S.,** 2008: Thermal Stability and Ablation Properties of Silicone Rubber Composites. Journal of Applied Polymer Science, 110 (2), 1263–1270. https://doi.org/10.1002/app.28633.

[41] **Toprakci, H. A. K.; Kalanadhabhatla, S. K.; Spontak, R. J.; Ghosh, T. K.,** 2013: Polymer Nanocomposites Containing Carbon Nanofibers as Soft Printable Sensors Exhibiting Strain-Reversible Piezoresistivity. Advanced Functional Materials, 23 (44), 5536–5542. https://doi.org/10.1002/adfm.201300034.

[42] **Liu, H.; Dong, M.; Huang, W.; Gao, J.; Dai, K.; Guo, J.; Zheng, G.; Liu, C.; Shen, C.; Guo, Z.**, 2017: Lightweight Conductive Graphene/Thermoplastic Polyurethane Foams with Ultrahigh Compressibility for Piezoresistive Sensing. Journal of Materials Chemistry C, 5 (1), 73–83. https://doi.org/10.1039/C6TC03713E.

[43] **Bautista-Quijano, J. R.; Avilés, F.; Cauich-Rodriguez, J. V.,** 2013: Sensing of Large Strain Using Multiwall Carbon Nanotube/Segmented Polyurethane Composites. Journal of Applied Polymer Science, 130 (1), 375–382. https://doi.org/10.1002/app.39177.

[44] **Wang, X.; Meng, S.; Tebyetekerwa, M.; Li, Y.; Pionteck, J.; Sun, B.; Qin, Z.; Zhu, M.**, 2017: Highly Sensitive and Stretchable Piezoresistive Strain Sensor Based on Conductive Poly(Styrene-Butadiene-Styrene)/Few Layer Graphene Composite Fiber. Composites Part A: Applied Science and Manufacturing2018, 105, 291–299. https://doi.org/10.1016/j.compositesa.2017.11.027.

[45] **Mattmann, C.; Clemens, F.; Tröster, G.**, 2008: Sensor for Measuring Strain in Textile. Sensors, 8 (6), 3719–3732. https://doi.org/10.3390/s8063719.

[46] **Costa, P.; Silva, J.; Ansón-Casaos, A.; Martinez, M. T.; Abad, M. J.; Viana, J.; Lanceros-Mendez, S.,** 2014: Effect of Carbon Nanotube Type and Functionalization on the Electrical, Thermal, Mechanical and Electromechanical Properties of Carbon Nanotube/Styrene–Butadiene–Styrene Composites for Large Strain Sensor Applications. Composites Part B: Engineering2014, 61, 136–146. https://doi.org/10.1016/j.compositesb.2014.01.048.

[47] **Costa, P.; Silvia, C.; Viana, J. C.,** 2013: Lanceros Mendez, S. Extruded Thermoplastic Elastomers Styrene–Butadiene–Styrene/Carbon Nanotubes Composites for Strain Sensor Applications. Composites Part B: Engineering2014, 57, 242–249. https://doi.org/10.1016/j.compositesb.

[48] **Kuruağaç.,** 2017:Investigation of Electrical Properties of Thermoplastic Elastomer Based Composites

[49] **Aydemir.,** 2018:Investigation of Mechanical Properties of Thermoplastic Elastomer Based Composites

[50] **Stankovich et Al.,** 2006a; Stankovich et Al., 2006b; Stankovich et Al., 2006c.

[51] **Stankovich** et Al., 2007.

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PUBLICATIONS/PRESENTATIONS ON THE THESIS

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