

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**PREPARATION AND INVESTIGATION OF ELECTRICAL,
THERMAL AND MECHANICAL PROPERTIES OF
CARBONACEOUS NANO-FILLERS CONTAINING
ACRYLONITRILE BUTADIENE STYRENE (ABS) COMPOSITES**

ALİND A ÖYKÜ AKAR
**A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF CHEMICAL ENGINEERING**

GEBZE
2022

T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

KARBON ESASLI NANO KATKI
TAKVİYELİ AKRİLONİTRİL BÜTADİEN
STİREN (ABS) KOMPOZİTLERİN
HAZIRLANMASI VE ELEKTRİKSEL,
TERMAL VE MEKANİK ÖZELLİKLERİN
İNCELENMESİ

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SUMMARY

Polymer composites have been studied intensively for industrial applications such as electrical conductance, ohmic heating, electromagnetic (EMI) shielding, and electrostatic discharge (ESD) in recent years, especially in engineering plastics with carbon fiber (CF) inclusions. Acrylonitrile-butadiene-styrene terpolymer (ABS) with CF additives is one of these potential materials to become an industrial solution to achieve the demanded attributes for these properties. However, increasing the CF loadings in order to improve the conductivity of polymer composites has a detrimental effect on the mechanical and tribological performance of the material such as the reduction of strength and flexibility.

Using CF and CNT together as ABS additives facilitates an increase in the electrical conductivity of bulk material. The inclusion of graphene along with CF improves the mechanical and tribological performance of the composite while providing increased heat and electrical conductance. The cost of the resultant composite is naturally higher than ABS-CF at a 20% loading ratio, but better properties might be attained with minute additions of GR and CNT which does not affect the cost dramatically. Also, the possibility of decreasing the CF content while retaining acceptable characteristics using other additives might lower the production costs.

In this study, the proposed use scenario for resultant materials is mainly the electrical and thermal conductance applications in the automotive industry. In this application area, mechanical strength is also of utmost importance, and the inclusion of fillers may result in undesired properties. For this reason, keeping optimal mechanical strength while improving other properties is another objective of this work.

Keywords: Acrylonitrile-butadiene-styrene terpolymer (ABS), Carbon fiber, Carbon nanotubes (CNTs), Graphene, Fullerene.

ÖZET

Polimer kompozitlerin elektriksel iletkenlik, ısı iletkenlik, elektromanyetik koruma ve statik yük koruması gibi özellikleri ve bunların endüstriyel uygulamaları üzerine yoğun çalışmalar yapılmakta olup, özellikle karbon elyaf takviyeli mühendislik plastikler konusundaki araştırmalar yoğunlaşmıştır. Akrilonitril-bütadien-stiren terpolimerin karbon katkılı kompozitleri; potansiyel olarak bu özellikleri karşılayan bir endüstriyel çözüm sunabilir. Ancak, kompozitin yapısındaki karbon elyaf oranı arttıkça saf ABS polimere göre mekanik ve tribolojik özelliklerde (sağlamlık, esneklik vb.) düşüşler gözlemlenmektedir.

Karbon elyaf ve karbon nanotüpler birlikte ABS katkısı olarak kullandığında; malzemenin elektriksel iletkenliği artış göstermektedir. Grafen ilavesi ise mekanik özellikleri ve sürtünmeden kaynaklanan elektriksel yükün bertarafını geliştirirken, öte yandan malzemenin elektriksel ve ısı iletkenliğini de arttırmaktadır. Malzemenin maliyeti; ekstra karbon katkıları yüzünden salt ABS/karbon elyaf katkılı kompozite (% 20) göre daha yüksek olsa da, çok az miktarda grafen ve karbon nanotüp eklenmesi bile malzemenin özelliklerini önemli ölçüde değiştirebilmektedir.

Bu çalışmada; polimer kompozitin kullanım alanı olarak otomotiv sektöründe elektriksel ve termal iletkenlik sağlaması belirlenmiştir. Bu uygulama alanında, iletkenliğin yanı sıra mekanik özellikler de büyük önem arz etmekte, bu özellikler sağlanamazsa istenmeyen sonuçlara yol açabilmektedir. Bu yüzden polimerin mekanik özelliklerin korunumu da çalışmanın bir diğer hedefidir.

Anahtar Kelimeler: Akrilonitril-Bütadien-Stiren Terpolimer (ABS), Karbon Elyaf, Karbon Nanotüp (CNTs), Grafen, Fulleren.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations</u> <u>and Acronyms</u>	<u>Explanations</u>
E	: Young's Modulus
ε (%)	: Elongation at break
ϕ_c	: Percolation Threshold
σ	: Tensile stress
Ω	: Ohm (resistance)
Hz	: Hertz (frequency)
F _N	: Force (Newton)
km	: Kilometer
T _g	: Glass transition temperature
J	: Energy (Joule)
I	: Current (Ampere)
V	: Voltage
Bar	: Pressure
A	: Area (m ²)
°C	: Temperature (Degrees Celcius)
rpm	: Revolutions per minute
tan δ	: Loss factor
ABS	: Acrylonitrile butadiene styrene
AFM	: Atomic force microscopy
C60	: Buckminster fullerene
CNT	: Carbon nanotubes
CF	: Carbon fiber
DMA	: Dynamical mechanical analysis
GR	: Graphene
MFI	: Melt-flow index
Shore A, D	: Hardness Scale
TGA	: Thermal gravimetric analysis
W	: Wear volume

WR	:	Wear rate
0D	:	Spherical geometry
1D	:	Needle-like geometry
2D	:	Sheet-like geometry

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1. INTRODUCTION

Polymers are finding their way into numerous industrial applications primarily because of their lower weight and usually superior application properties. One of the oldest and most widespread application areas among others is the automotive industry. This industry provides jobs to millions of people and makes a considerable contribution to the economy of the countries. In fact, it is usually taken as an indicator of a country's economic growth. Therefore, changes in material usage can have a major impact on polymer demand and the financial performance of polymer producers.

There are many parts in a vehicle and one-third of these are currently manufactured using polymers. Acrylonitrile-butadiene-styrene terpolymer (ABS) is one of them and it is being used in a wide variety of automotive parts such as lighting, instrument panels, bumpers, seats, door handles, interior trim, dashboard, etc [1]-[4].

1.1. Fundamentals of Polymer Composites

Polymer matrix composites are the most sophisticated form of composite material due to their high adaptability for simple manufacture. To achieve the goal of becoming a matrix for polymer composites, either thermosets or thermoplastics are utilized. Furthermore, it is well recognized that thermoplastics have several advantages over thermosets, including the ability to be treated and molded with great ease using traditional processing processes and technologies. Numerous factors influence the characteristics of polymer composites. Among these are interfacial adhesion, filler form and orientation, and polymer matrix characteristics. Furthermore, the interface of reinforcement and polymer has a significant impact on the mechanical strength of the composite material. Because the interfacial adhesion is strong, the reinforcing material may accommodate strength and stiffness while transferring load from the matrix [5], [6].

Many aspects of polymer composition may be altered, including interfacial interactions between polymer and filler, as well as mechanical qualities. Rheological behavior, resilience to environmental conditions, and manufacturing constraints are among the polymer composite qualities that may be affected. Although high adhesion results in the development of the best polymer composite qualities, several undesirable issues such as decreased toughness, increased mold shrinkage, and so on may arise.

Many coupling agents, which change the surfaces of additives, have been found for polymers in order to enable effective bonding. Moreover, quantifying the importance of interfaces in composites, which emerge as a result of the mechanism and strength of contact developing between two phases, has shown to be challenging [7], [8].

1.2. Hybrid Polymer Composites

Hybrid composites are materials produced by combining two or more distinct types of additives in a common matrix. They often have the ability to provide a wide variety of qualities that cannot be obtained with a single form of reinforcement. The key aspects controlling the characteristics of the hybrid composite are filler form and size, content, orientation, arrangement of both fillers, and filler to a matrix. The hybrid composite behavior is a weighted sum of each component with a more favorable balance of benefits and drawbacks. In addition, with a hybrid composite that contains two or more types of filler, the advantages of one of the fillers might compensate for what is lacking in the other. As a consequence, appropriate material design can achieve a balance of performance and cost [9], [10].

1.3. Acrylonitrile-Butadiene-Styrene Terpolymer (ABS)

Acrylonitrile-butadiene-styrene terpolymer (ABS) is a widely used engineering thermoplastic polymer. ABS is a rubber toughened thermoplastic, which is characterized by its notch insensitivity and lower costs. ABS polymer consists of a two-phase system of styrene-acrylonitrile (SAN) co-polymer which acts as a continuous phase and polybutadiene acts as the dispersed phase, giving the material excellent mechanical properties while doubling as an impact modifier. The components of ABS impart some desired properties to the bulk polymer; for example, acrylonitrile (A) imparts chemical resistance and weathering stability while butadiene (B) gives typical characteristics of rubber toughness, and styrene (S) provides glossiness and ease of processing to the polymer while lowering the costs [11]-[16].

The ratio of the ABS components can be modified to match the criterion for various applications such as architecture & construction, personal care products, toys, computer and business equipment, medical devices, and automotive interior components. Fiber reinforcement might also be incorporated into ABS to improve

mechanical properties such as tensile strength, flexural modulus, and hardness. Another reason for the widespread usage of ABS is its price point which lies between the regular low-priced commodity thermoplastics and the high-cost niche performance engineering plastics [11], [12], [16].

One drawback of using ABS is its inherent flammability; therefore, improvement of the thermal stability of ABS is very important, while keeping in mind that the heat distortion temperature of general grades of ABS is lower than 100°C. Also, the overall mechanical properties of ABS are nominal when compared with other engineering plastics. These deficiencies have limited its application in many fields [11]-[14], [17].

1.4. Carbon Fiber for Use in Conducting Composites

The use of polymers for computer housings and other many other electronic devices has been growing steadily due to their advantages over metals, such as lightweights, the flexibility of design, low production costs, their ease of use in production by forming with extrusion or injection molding [18].

For electronic applications, one of the most effective and widespread techniques is to improve the conductivity of plastics and attain an acceptable level of EMI shielding by the inclusion of conductive fillers into the polymer. Among various types of conductive fillers; carbon fibers have proven themselves to be one of the best candidates for EMI shielding. However, since the electrical resistivity of carbon fibers is substantially lower than a metal of the same proportions, a copious amount of carbon fiber is needed as inclusions to achieve the same shielding. Although shielding capability might be improved by the addition of more carbon fibers into the polymer, the difficulty of processing composites with a high fiber content arises when using conventional manufacturing methods such as extrusion or injection molding. Adding more carbon fibers into a composite also brings along the problem of higher production costs due to the high price of carbon fiber additives [18].

Polymer composites incorporating carbon fiber inclusions have widespread applications in military, industrial and commercial fields; for the purpose of shielding electromagnetic waves, and thus, allowing proper operation of the equipment [19-21]. In addition to electrical properties, also being light-weight structural materials, carbon

fiber reinforced plastics (CFRP) might also be utilized in aerospace vehicles, automobiles, etc [22].

For CF-reinforced polymer composites, the polymer acts as the matrix while CF constitutes the discontinuous phase. The polymer used as matrices for PCs is broadly classified as thermosetting and thermoplastic resins. Thermoplastic polymers have received significant attention as matrix materials because of many advantages including the absence of a curing stage and having less hazardous chemical compositions while exhibiting improved recycling characteristics and mass production capability when compared to thermosetting resins. Thermoplastic resins are often fabricated utilizing standard industrial practices such as injection, rotation, compression molding, extrusion, and vacuum forming [22], [23].

1.5. Carbon Allotropes as Nano Additives for Use in Conducting Composites

Conductive polymer nanocomposites (CPNs) are heterogeneous polymer composites where conductive nano-filler particles are dispersed into the non-conductive polymer matrix. Polymer nanocomposites are in high demand for various industrial fields due to their desired properties such as light weight, low cost, and design flexibility [24], [25].

The thermal and electrical conductivity of polymers could be improved by conductive additives like graphite, carbon black, fullerenes, carbon nanotubes (CNTs), graphene, and ceramic or metal particles. For example, graphene has been of intense interest because of the impartation of better mechanical, thermal, and electrical properties to PCs. Graphene (GR) is an allotrope of carbon that has a single layer, is sp^2 hybridized, and is arranged in a two-dimensional hexagonal lattice [26], [27].

Among the many types of conductive nanofillers, CNT is a promising candidate due to its high aspect ratio & electrical conductivity. Polymers reinforced with carbon nanotubes (CNTs) also received great attention in research circles due to the superior mechanical properties imparted to PCs by CNTs [26]-[29].

The unique electrical properties of CNTs are due to their 1D structure which mitigates the scattering of electrons. The high aspect ratio of CNTs allows electrical percolation at very low nanofiller loadings, while the high intrinsic conductivity allows the production of CPNCs with good electrical properties [26].

Carbon nanotubes (CNTs) based polymer composites have various engineering applications (EMI shielding, anti-static coatings, high-strength low-density corrosion-resistant components, lightweight energy storage, etc.), due to their excellent mechanical, electrical, chemical, magnetic, etc. properties. Electronics and automotive are the major industries that utilize CNT-infused polymer composites. CPNCs of this type can also be used in batteries, fuel cells, transducers, sensors, and flexible transparent electrodes while their use as electronic casing prevents electrostatic discharge (ESD) and electromagnetic interference (EMI) occurrences [26]-[28].

CNT inclusion into polymer matrices creates materials that exhibit superior mechanical, thermal, electrical, and barrier properties that are suitable for replacing many of the existing materials used for engineering applications. In electronic applications, particularly in the semiconductor field, CNTs are utilized to dissipate unwanted static charge buildup. In the automotive industry, CNTs are used as a conductive agent as an aid in electrostatic painting [30]. The electrical resistivity of conductive polymer composites (CPCs) determines their possible applications. For example, the CPC materials for EMI shielding typically require better electrical conductivity while the electrostatic dissipation applications in plastic fuel tanks might tolerate higher electrical resistivity values in the bulk material [27].

Since most commodity polymers are in practice, insulating, the electrical performance of a CPC depends on the continuous conductive networks formed by the conductive fillers. When the conductive filler content in a PC reaches a critical value, the CPC material will experience an insulator/conductor transition; then the electrical conductivity dramatically increases by several orders of magnitude due to the conducting channels formed within the material. This critical volume fraction of the composite is defined as the percolation threshold (ϕ_c). As the conductive filler content increases, additional conductive pathways may be established in the polymer matrix, which gradually increases conductivity until a saturation plateau is reached [27].

The properties of obtained PCs will highly depend on the type of filler used, its dimensions and aspect ratio as well as the filler incorporation technique. Three methods are commonly utilized for the incorporation of CNTs into PCs: a) Film casting of suspensions of CNTs in dissolved polymers; b) In-situ polymerization of monomer in presence of CNTs; and c) Melt-mixing of CNTs with polymers [29], [30].

Among the conventional CPC fabrication methods (i.e., solution processing, melt mixing, and in situ polymerization), melt mixing practices such as twin-screw

extrusion, internal mixing, and injection molding are the most popular techniques for the commercial fabrication of CPC materials because these techniques are compatible with current industrial methods. Nevertheless, CPCs fabricated via conventional melt-mixing techniques usually have a higher ϕ_c than other techniques. CPCs with high ϕ_c suffer from various drawbacks: (i) high melt viscosities, (ii) reduced economic affordability, and (iii) inferior mechanical properties (lower ductility and toughness) [29].

The higher price of CNTs concerning other fillers is one of the major handicaps for the prevalent use of CNT-based materials in industrial applications. Thus, for CPNCs based on CNTs, the amount of CNTs used to form a nanocomposite with desired electrical properties should be as low as possible in order to reduce cost [28]-[30].

The critical concentration of the conductive nano-filler should be dispersed within the insulating polymer matrix to transfer the nanocomposite from the insulating state to a semi-conductive or conductive state [26], [31].

Of these fillers, fullerene is a member of the carbon nanostructures family which has a zero-dimensional structure. Research efforts based on fullerene chemistry with the combination of macromolecular chemistry led to the development of easily processable fullerene-containing polymeric materials [32], [33]. However, organic modifications are necessary since pristine fullerene tends to form aggregates very easily and it is particularly difficult to handle. The formation of self-aggregation causes poor miscibility of fullerene which limits its applications [34], [35]. Polymer composites containing fullerenes have a great potential for versatile applications which include optical interrupters, polymer photoconductors, electrodes in lithium batteries, and electro-optical structures in nano-electronics and nonlinear optics [36], [37]. Fullerene might be used as an additive in several thermoplastic polymers including polyethylene [38], [39], polypropylene [40], [41], polyamide [32], poly (ethylene-co-acrylic acid) [43], and polyurethane elastomer [44], [45], in which melt extrusion method is the preferred method.

1.6. Literature Survey

ABS terpolymers containing CF additive are one of the potential materials to become an industrial solution to achieve much-demanded limits, such as electrical

conductance, ohmic heating, electromagnetic (EMI) shielding, and electrostatic discharge performances [16]-[21]. The number of research topics based on investigations of properties of ABS and its composites has been extended remarkably in the recent decade due to high interest in its application fields utilizing 3D printing technology [22]-[27].

Research studies regarding the use of CNT as a nano-additive for ABS-based composites were conducted for the main purpose of imparting some electrical conductivity to polymer structure in addition to mechanical and thermal resistance. In this regard, ABS terpolymer was compounded with CF and its related performances were investigated in the literature [32]-[40].

Li et al. stated that the percolation threshold of CNT-reinforced polymeric nanocomposites is related to several factors including disentanglement, aspect ratio, and uniform distribution of CNT. They reported that the percolation threshold was achieved in the loading range of 0.1-1.0 wt.% which depends on the processing techniques they applied [11].

Marsden et al. and Ambrosetti et al. implied that lower threshold values can be achieved by nano-additives with conductive plate-like structures [2],[3]. However, CNT exhibited a relatively lower percolation threshold compared to GR since GR showed a tendency to form aggregate and wrinkles resulted in a decrease in effective aspect ratio by hindering the network formation [14], [15].

Fullerene was compounded with several thermoplastics to develop multifunctional composite materials [46].

Olga et. al studied the mechanism of fullerene-polystyrene interaction, the structural characteristics of films, and their antimicrobial activity was researched. They found that the polystyrene/fullerene composite films manifested bacteriostatic and fungistatic effects [47].

Hassanien et. all prepared polymer composite films of chitosan doped with different weight ratios of fullerene (1%, 2%, 3%, and 4%) using the solution casting method. Thermogravimetric analysis of chitosan with different concentrations with varying weight ratios of fullerene films was analyzed. Dielectric measurements and UV-visible spectroscopy was used to investigate the dielectric properties and optical characteristics (refractive index, absorption coefficient, optical band gap, and specific polarizability) of the chitosan/fullerene composite films, respectively [48].

By using functional polymers to react with fullerenes, or synthesizing polymers in the presence of fullerenes, various kinds of polymeric fullerenes can be prepared: side-chain polymers, main-chain polymers, dendritic fullerenes, star-shaped polymers, fullerene end-capped polymers, etc. Furthermore, by controlling the functional groups in polymer chains and reaction conditions, many well-defined fullerene polymers have been prepared [49].

Tayfun et. al investigated the influence of nitric acid oxidation and silanization of fullerene on mechanical, melt flow, and electrical properties of TPU-based composites. Thermoplastic polyurethane (TPU) composites were prepared at fullerene loadings varying from 0.5 to 2 wt. %, by the melt-mixing method [50], [51].

Zhang et. al prepared electrically conductive poly (phenylene sulfide) (PPS)/C60 composites and characterized the interface effects of C60 and PPS on PPS/C60 properties. According to their findings, the excellent conductive and mechanical properties of PPS/C60 were attributed to the heterogeneous nucleation of C60 during the crystallization of PPS, the formation of a large number of covalent bonds by main C60-thiol adducts, and minor C60-ArCl alkylation between C60 outer surface and PPS matrix [52].

1.7. Aim of the Study

In the scope of the thesis study, carbonaceous nanomaterials having three different geometries, namely carbon nanotube, fullerene, and graphene, were compounded with carbon fiber-filled ABS copolymer. In addition to ABS-CF composite; the effects of the nano-additive geometries on the mechanical, morphological, melt-flow, electrical, and heat conductance properties were studied. For the preparation of composites, melt blending, and injection molding techniques were selected as being the most common and applicable techniques in the industry. Incorporation of carbonaceous nanoparticles into CF-reinforced composites for the establishment of synergistic interactions between carbon-based additives and CF into the ABS phase through mechanical, thermal, and electrical behaviors. Increasing the electrical conductivity while attaining higher mechanical characteristics is the prime objective of this thesis study.

In addition to the reinforcing effect of CF, the inclusion of carbon nano-additives might improve the mechanical and electrical properties of ABS/CF composites due to

their synergistic effect. One of the main targets of the study is an achievement of the percolation threshold in electrical conductivity with the help of conductive path formation in the composite system which will be examined with an AFM study on conductive mode. The resulting composite materials may gain abrasive resistance with the addition of graphene sheets. It is expected that all the composites would exhibit improvement in mechanical and thermal performance thanks to the imparted extraordinary properties of related nano-additives. Moreover, the resulting materials would be multifunctional since enhancements in mechanical, processing, and electrical behaviors would be achieved with the carbon nano-fillers inclusion.

2. MATERIALS AND METHODS

2.1. Materials

The materials that will be used in this study and their respective companies are shown in Table 2.1 below. The representative image of ABS and carbon-based additives used in this thesis study is shown in Figure 2.1

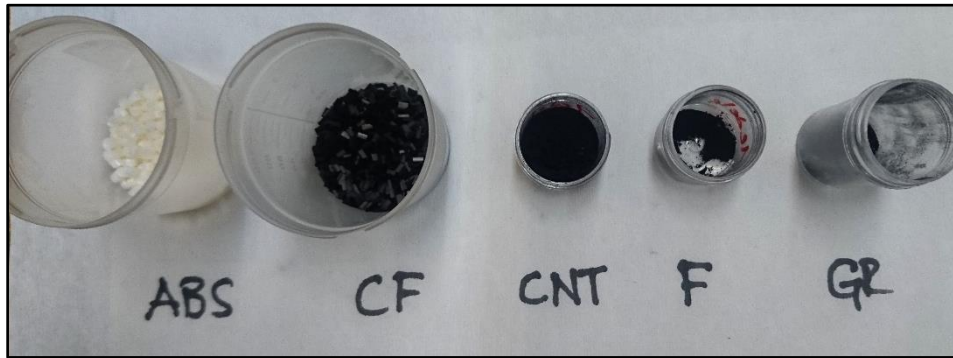


Figure 2.1: Photograph of polymer and additives.

Table 2.1: Materials supplied to be used in the study and producer companies.

Name of Material	Reason of Usage
ABS: Lustran ABS M203FC, Lanxess, Germany	Polymer Matrix
CF: AC 0101, Dowaksa, Turkey	Additive
CNT: NC7000, Nanocyl, USA	Nano-Additive
C ₆₀ : Acros Organics, USA	Nano-Additive
GR: Nanografi, Turkey	Nano-Additive

2.1.1. ABS

Lustran[®] ABS M203FC grade ABS was supplied from Lanxess (Cologne, Germany). It has a density and hardness of 1.05 g/cm³ (at 23 °C) and 110 N/mm² (ISO 2039-1, Ball indentation hardness), respectively. It has a melt volume flow rate of 31 (cm³/ 10 min, under test conditions 220 °C and 10 kg). Electrical (23 °C, 50 % r. h.) and thermal properties of ABS are also listed in Table 2.2 below.

Table 2.2: Typical electrical and thermal properties of ABS.

Properties	Test Conditions	Standards	ABS M203FC	Unit
Coefficient of linear thermal expansion, parallel	23 to 55	ISO 11359-1, -2	0.9	°C
Relative permittivity (ϵ_r)	100	IEC 60250	3	Hz
Relative permittivity	1	IEC 60250	2.9	MHz
Volume resistivity	-	IEC 60093	1E+13	$\Omega \cdot m$
Surface resistivity	-	IEC 60093	1E+15	Ω
Electric strength	1 mm	IEC 60243-1	35	kV/mm

2.1.2. Carbon Fiber

Aksaca AC 0101 grade carbon fiber used in this study was supplied from Dowaksa (Yalova, Turkey). It was purchased commercially in PU-sized and 3 cm chopped CF form. The basic characteristics of this carbon fiber grade are tabulated in Table 2.3 below.

Table 2.3: Properties of carbon fiber.

Properties	Units	Standards	Aksaca AC 0101
Application	-	-	Thermoplastics - ABS, LCP, PA, PC.
Density	kJ/m ²	ISO 10119	1,76
Typical bulk density	(g/l)	-	600
Length	mm	-	3
Monofilament diameter	μm	ISO 1973	7
Sizing emulsion	-	-	Polyurethane based
Sizing content	%	-	1,5 - 3,0
Tensile strength	MPa	ISO 10618	4200
Tensile modulus	GPa	ISO 10618	240
Elongation	%	ISO 10618	1,8

2.1.3. Graphene

NG05 grade carbon fiber used in this study was supplied from Nanografi (Ankara, Turkey). It was purchased in commercially PU-sized and 3 cm chopped CF form. The representative image and basic characteristics of this carbon fiber sample are shown in Figure 2.2 and Table 2.4, respectively.



Figure 2.2: Photograph of graphene nanoplatelets.

Table 2.4: Properties of graphene.

Properties	Unit	Standards	NG05
Thickness	nm	-	5
Diameter	μm	-	7
Specific surface area	m^2/g	BET surface area analysis	150
Conductivity	s/m	-	1100-1600

2.1.4. CNT

NANOCYL[®] NC7000[™] series, thin multiwall carbon nanotubes, produced via the Catalytic Chemical Vapor Deposition (CCVD) process, were supplied from Nanocyl SA (Sambreville, Belgium). The representative image and basic characteristics of this carbon fiber sample are shown in Figure 2.3 and Table 2.5, respectively.

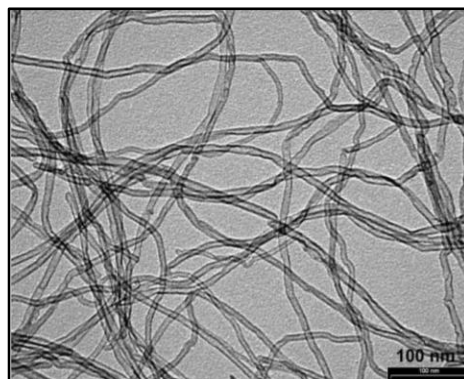


Figure 2.3: TEM image (with scale: 100 nm) of multiwall carbon nanotubes.

Table 2.5: Properties of CNT.

Properties	Unit	Standards	NC7000™
Application	-	-	Automotive, EMI-shielding, sensors, coatings.
Average diameter	10^{-9} m	Transmission Electron Microscopy (TEM)	9.5
Average length	μm	Transmission Electron Microscopy (TEM)	1.5
Carbon purity	%	Thermogravimetric analysis (TGA)	90
Transition metal oxide	%	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	< 1%
Surface area	m^2/g	BET surface area analysis	250-300
Volume resistivity	Ohm-cm	Resistivity on powder	10^{-4}

2.1.5. Fullerene

Fullerene (C_{60}), with a mesh size of 180–200 μm , was supplied from Acros Organics (Fisher Scientific, USA), to be used in this study.



Figure 2.4: Photograph of fullerene.

2.2. Surface Treatments of Carbon-based Fillers

For surface treatments, nitric acid (HNO_3 , 65%) was supplied by Merck company. Chemical oxidations of CNT, fullerene, and graphene nano-fillers were carried out using similar oxidation routes in the literature [46-48]. The reason for the treatment was to oxidize the carbon surface to form new moieties on their surface wall in addition to the elimination of unwanted carbon compounds in the soot.

During surface treatments, 1.6 g of carbon fillers were refluxed at 120°C with 70 ml concentrated HNO_3 solution (65%) for 48 hours with an experimental set-up prepared as shown in Figure 2.5. The mixture was diluted with distilled water and filtrated using a $0.45\ \mu\text{m}$ membrane filter, then the resultant product was washed with distilled water and dried under vacuum for 2 hours.



Figure 2.5: Surface treatments of carbon nanofillers.

2.3. Preparation of Composites

In this study, the production of composites was carried out using a lab-scale twin-screw co-rotating micro-extruder (MC 15 HT micro-compounder®, Xplore Instruments) and injection-molding process.

2.3.1. Processing of the ABS Composites

There have been numerous approaches employed to produce polymer composites such as solution mixing, in-situ polymerization, and melt blending. Extrusion, i.e., melt blending, is considered the most applied process and is regarded as the most convenient approach for producing PC materials in large capacities.

2.3.1.1. Extrusion

Melt mixing of ABS with CF and carbonaceous nanoparticles was carried out using a lab-scale counter-rotating micro-compounder (MC 15 HT, Xplore Instruments, Netherlands) with compositions as given in Table 2.6.

Table 2.6: Compositions for experimentation cases.

Sample	Composition
ABS (blank)	-
ABS+20% CF	-
ABS+20% CF	0.1% CNT
	0.5% CNT
	1.0% CNT
ABS+20% CF	0.1% C60
	0.5% C60
	1.0% C60
ABS+20% CF	0.1% GR
	0.5% GR
	1.0% GR

After the pre-mixing of polymer granules and additives, the mixture was fed continuously into the extruder hopper. During processing, lab-scale twin-screw

extruder process parameters were adjusted as in Table 2.7 and a representative photograph of the device is given in Figure 2.6 below.

Table 2.7: Micro-scale extruder process parameters.

Parameters	Specification	Unit
Processing temperature	230	°C
Mixing time	5	min
Screw speed	100	rpm



Figure 2.6: Photograph of lab-scale micro compounder machine.

2.3.1.2. Injection Molding

After compound preparation, the materials were ground and shaped for characterization tests. Test samples of the composites with the dimensions of 7.6 x 2.0x80 mm³ were prepared by Daga Instruments micro-injection molding instrument

as represented in Figure 2.7. The gauge length of dog bone-shaped samples was 50 mm.

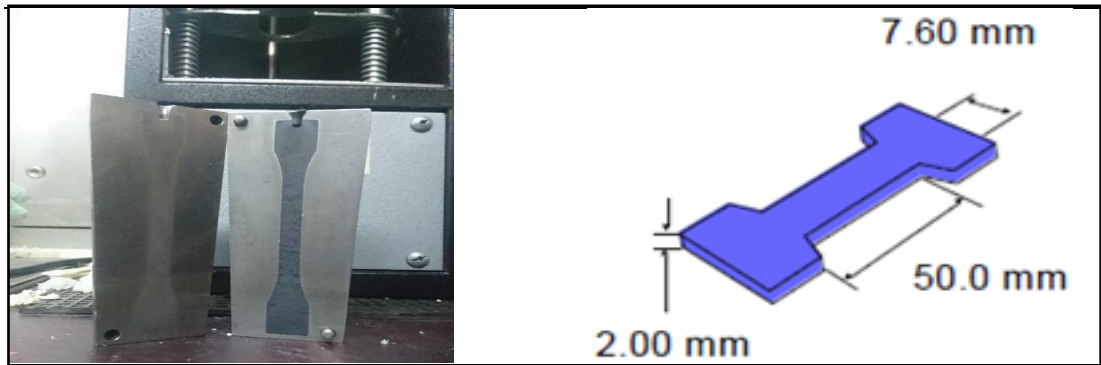


Figure 2.7: Representation of the test specimen.

Injection molding parameters and the representative photograph of the micro-injection molding device are given in Table 2.8 and Figure 2.8, representatively.

Table 2. 8: Injection molding parameters.

Parameters	Values	Unit
Barrel temperature	235	°C
Mold temperature	80	°C
Injection pressure	8	Bar
Holding time	5	min



Figure 2.8: Photograph of the micro-injection molding machine.

2.3.1.3. Compression Molding

The film samples of ABS and relevant composites were fabricated by a lab-scale hot-press device (Rucker PHI, England) for AFM characterizations. Processing temperature of 230°C and compression pressure of 8 bars were supplied during compression molding. Film samples were prepared with a thickness of 100 microns for each composite.

2.4. Characterization Steps of Composites

After melt mixing of ABS with CF and carbonaceous nanoparticles, the compounds produced were ground and shaped for product tests by a micro-injection molding instrument, according to the specimen standards for each characterization test.

2.4.1. Mechanical Characterizations

Mechanical analyses were done by using Lloyd tensile testing machine and a Coesfeld impact tester with a 4J pendulum.

2.4.1.1. Tensile Tests

Tensile test measurements of ABS and its composites were carried out in accordance with the ASTM D-638 standard using Lloyd LR 30 K universal tensile testing machine. 5 kN load cell and 5 mm/min crosshead speed was used during the test.



Figure 2.9: Tensile testing device.

2.4.1.2. Impact Test

Unnotched Izod impact energy values of ABS and composites were measured using a Coesfeld-Material impact tester with the pendulum of 4J according to ASTM D256 standard.



Figure 2.10: Impact testing equipment.

2.4.1.3. Hardness Measurements (Shore D)

The TQC Shore Hardness device, which complies with DIN 53505, ISO 868, and ASTM D 2240 was used for hardness measurements of ABS and its composites.

2.5. Wear Resistance (Reciprocating Ball-on-Flat Sliding Wear)

The wear test was applied following ASTM G133 standard using a UTS tribometer T10 test device with 10 N load, 10 mm stroke, and a total sliding distance of 20 m back and forth. Wear volume and specific wear rate were calculated with the formulas given below.

$$W = A \times \text{Stroke (mm}^3) \quad (2.1)$$

$$W_R = \frac{W}{F_N \times l} \quad (\text{mm}^3/\text{Nm}) \quad (2.2)$$

Where: “W” is the wear volume (mm³), “A” is the wear surface area (mm²), “W_R” is the specific wear rate, “F_N” is the applied load (N) and “l” is the total slide distance (m).

2.6. Melt Flow Index Test (MFI)

MFI values of ABS and its composites were determined using a Coesfeld Meltfixer LT. Test measurements have been performed under a specified load of 2.16 kg at a process temperature of 230 °C.



Figure 2.11: Melt flow indexer.

2.7. Dynamic Mechanical Analysis

Perkin Elmer DMA 8000 test device was utilized to determine thermo-mechanical behaviors of composites using dual cantilever bending mode at the temperature range between -100°C and 100°C with a heating rate of 5°C/min at a constant frequency of 1 Hz. Dynamic Mechanical Analysis (DMA) was carried out at İstanbul University and Dow Aksa.

2.8. Thermal Characterization

Thermal characterizations were done by using Netzsch Jupiter STA 449 F3 simultaneous. Test parameters were applied during TGA analysis including a temperature range from 30 °C to 650 °C, a constant heating rate of 10 °C/min, and a constant nitrogen flow of 50 ml/min.

2.9. Morphological Investigations

Morphological characterization with the help of SEM analysis will be conducted. JSM-6400 Electron Microscope (Figure 2.12) was utilized for morphological analysis. Surfaces of fractured samples obtained from the impact test were coated with a thin layer of gold to obtain a conductive surface. SEM micrographs were taken at x 200 and x2000 magnifications.

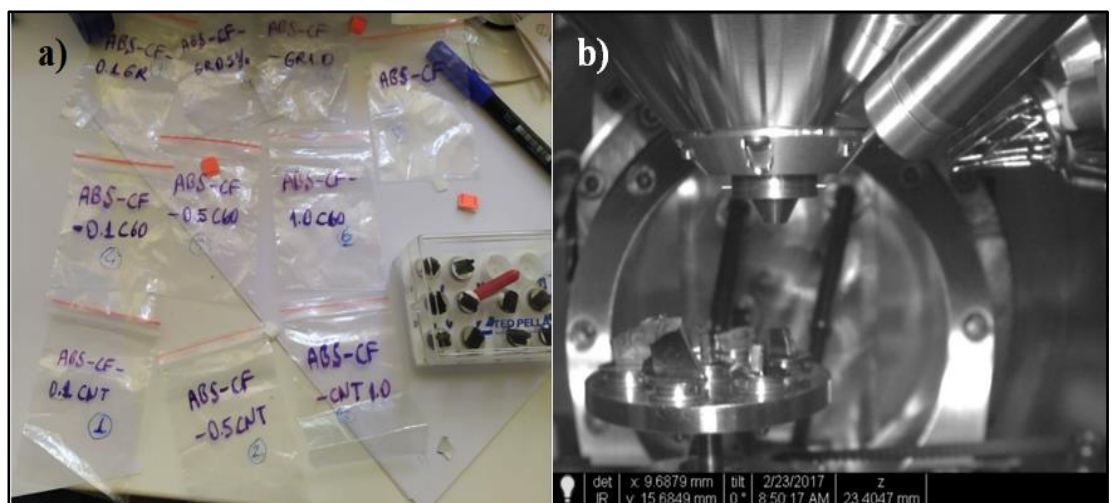


Figure 2.12: The representative photographs of a) Composite samples, and b) SEM apparatus.

2.10. AFM Studies

Conductive Atomic Force Microscopy (AFM) was used for investigations on electrical properties. Topographical, electrical, and indentation measurements were obtained by Nanosurf CoreAFM, Switzerland (Figure 2.13) using a beam-shaped cantilever in the static mode which has a spring constant of 0.2 N/m and tip radius of 7 nm. Samples were indented at rates of 1 $\mu\text{m/s}$.

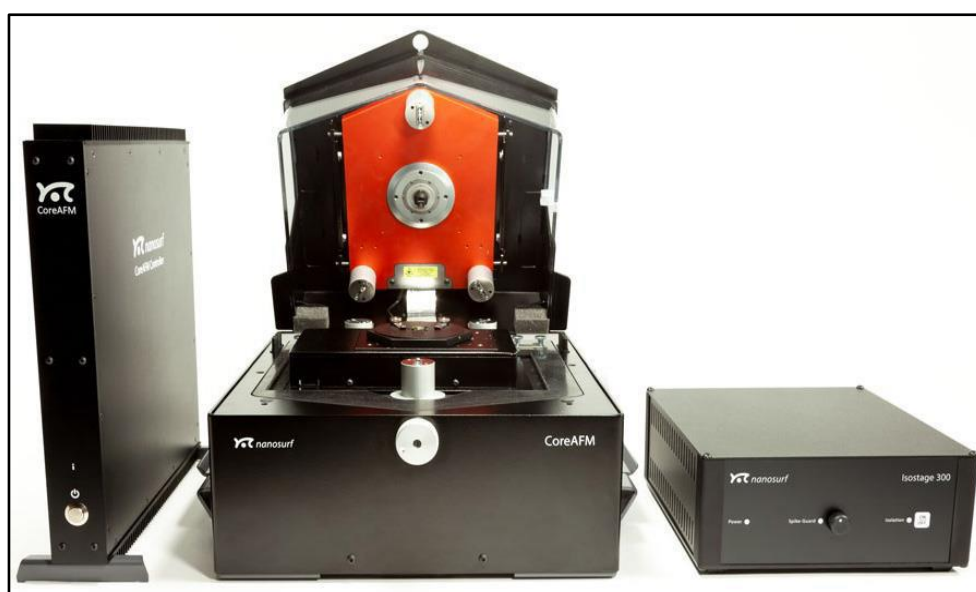


Figure 2.13: Photograph of AFM device.

AFM tip provided in static force modulation mod for samples was illustrated in Figure 2.12. Young's modulus values of samples were analyzed by nano indentation measurement with the help of the displacement of the AFM tip as shown in Figure 2.14.

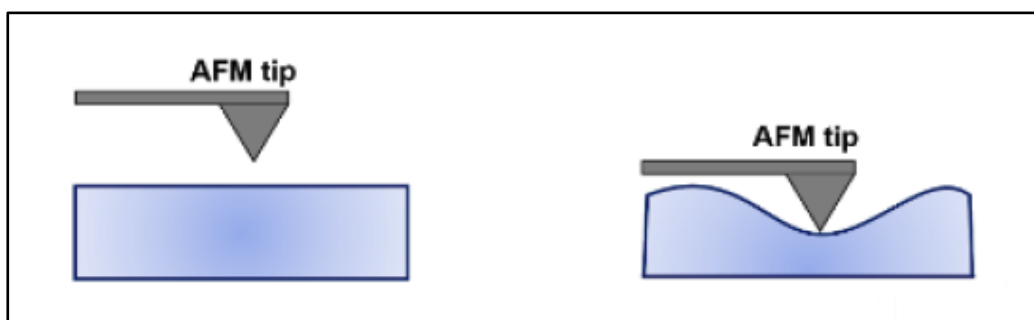


Figure 2.14: Representation of nano-indentation analysis with AFM tip.

3. RESULTS and DISCUSSION

After melt mixing of ABS with CF and carbonaceous nanoparticles, the compounds produced were ground and shaped for product tests by a micro-injection molding instrument, according to the specimen standards for each characterization test.

3.1. Mechanical Characterizations

3.1.1. Tensile Tests

Tensile strength, percent elongation at break, and tensile modulus parameters were recorded and tabulated as an average of at least three samples. The summary of the tensile strength tests is given in Table 3.1 and characteristic stress vs. strain curves are represented in Figure 3.1.

Table 3.1: Summary of the tensile properties of ABS and composites.

Samples	σ (MPa)	ε (%)	E (GPa)
ABS	39.7 $\pm$ 0.6	10.3 $\pm$ 0.3	1.21 $\pm$ 0.1
ABS/CF	46.6 $\pm$ 0.8	6.9 $\pm$ 0.9	1.55 $\pm$ 0.2
ABS/CF+C60 0.1	52.4 $\pm$ 0.4	7.2 $\pm$ 0.6	1.78 $\pm$ 0.2
ABS/CF+C60 0.5	56.6 $\pm$ 0.7	7.6 $\pm$ 0.7	1.83 $\pm$ 0.1
ABS/CF+CNT 0.1	48.6 $\pm$ 0.3	6.4 $\pm$ 0.5	1.56 $\pm$ 0.3
ABS/CF+CNT 0.5	61.3 $\pm$ 0.6	6.5 $\pm$ 0.3	2.11 $\pm$ 0.1
ABS/CF+CNT 1.0	68.7 $\pm$ 0.8	7.5 $\pm$ 0.7	1.97 $\pm$ 0.3
ABS/CF+GR 0.1	48.8 $\pm$ 0.4	6.9 $\pm$ 0.6	1.62 $\pm$ 0.2
ABS/CF+GR 0.5	58.6 $\pm$ 0.6	8.1 $\pm$ 0.4	1.91 $\pm$ 0.1
ABS/CF+GR 1.0	59.2 $\pm$ 0.4	9.5 $\pm$ 0.8	1.98 $\pm$ 0.2

According to Table 3.4, carbon fiber addition significantly increases the tensile of ABS polymer. Additionally, nano-filler inclusions lead to higher strength values, especially for increasing amounts of CNT and GR. An increasing tensile trend could be observed with loading amounts of these nanoparticles, as remarked by circles in Table 3.4. As a comparison of 0.1 wt. % amounts of nano-additives, fullerene exhibited

the highest tensile strength value. 0.5 wt. % fullerene loaded sample gave a higher tensile strength and further fullerene addition yielded a remarkable reduction in tensile value. This might be caused by the agglomeration of fullerene particles for 1.0 wt. % composition. A general trend was achieved for all the nano dimensional additive inclusions in which percent elongation improved with their filling ratios. The lowest increase in elongation value was observed for CNT additions due to their high aspect ratio. The highest strain value was attained by the composite containing the highest amount of graphene. In the case of tensile modulus results, the modulus value of unfilled ABS was enhanced by CF addition. Moreover, ABS/CF/carbonaceous ternary composites showed remarkable improvement in tensile modulus compared to ABS/CF binary composites.

As an overall result, nano-dimensional carbon additives donated multi-functional characteristics, while increasing both tensile strength and strain values, for the ABS/CF composite system. The surface area in polymer/filler interface rises as the number of nanoparticles that interact the surrounding polymer matrix increases, resulting in interface-determined nanocomposite performance. This phenomenon offers a simplified explanation for the superior characteristics of nanocomposites over standard micro- or macro-composite systems [53, 54]. At low filler loadings, the composites have good mechanical characteristics since the increased contact surface between the hybrid fillers and the polymer matrix causes an improvement in the mechanical resistance of the ternary composites which is related to the linkage with the polymer chains. The creation of a co-supporting network of mixed carbon nanofillers may result in synergistic effects that enhance the characteristics of hybrid composites even further [55, 56].

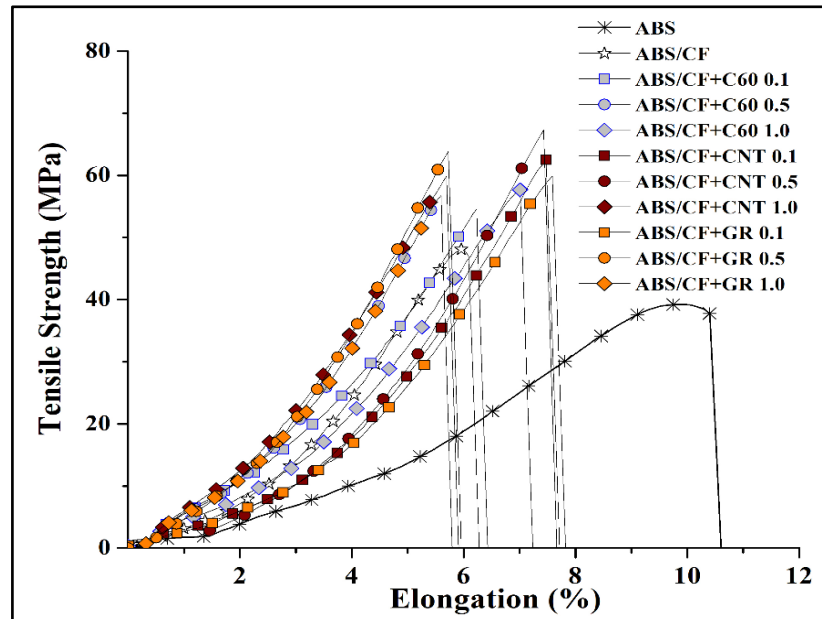


Figure 3.1: Stress versus strain curves of ABS and composites.

Necking behavior was observed for unfilled ABS in the stress-strain curve shown in Figure 3.4 whereas ABS/CF showed a lower necking amount as can be seen in Figure 3.5. The absence of necking tendency of composites involving nano-additives was found in which test samples broke immediately as their maximum tensile strength values were reached during the tensile test.

3.1.2. Impact Test

Unnotched Izod impact energy values of ABS and composites are displayed as an average value of three samples in Figure 3.2.

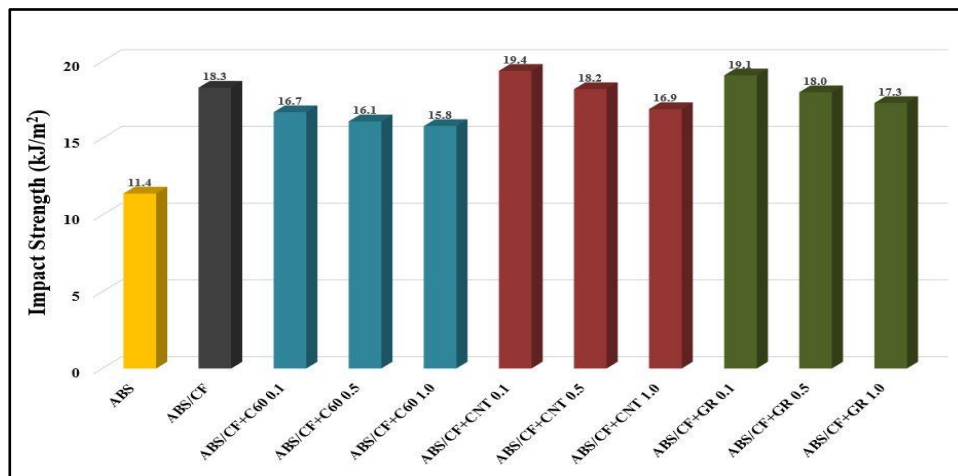


Figure 3.2: Impact test results of ABS and composites.

CF addition significantly increases the impact strength of ABS. According to impact test data, impact strength value decreased with an increasing amount of nano filler additions. The impact strength value of composites for 0.1 wt. % CNT and GR additions gave the highest values and 0.5 wt. % additions of these nano fillers are nearly identical to ABS/CF, as indicated with circles in Figure 3.2. Fiber-like structure of CNT and sheet-like structure of GR might be responsible for the enhancement of impact behavior since these structures enriched the resistance to impact deformation with the help of high load-bearing capacity. C60-containing composites displayed lower impact values compared to CF-reinforced ABS composites.

3.1.3. Shore Hardness Measurements

The summary of D-type Shore hardness results is given in Table 3.2 below.

Table 3.2: Summary of the Shore hardness test results of ABS and composites.

Samples	Shore D
ABS	77
ABS/CF	77
ABS/CF+C60 0.1	77
ABS/CF+C60 0.5	77
ABS/CF+C60 1.0	78
ABS/CF+CNT 0.1	77
ABS/CF+CNT 0.5	77
ABS/CF+CNT 1.0	78
ABS/CF+GR 0.1	77
ABS/CF+GR 0.5	78
ABS/CF+GR 1.0	78

According to Table 3.2, carbon fiber addition caused no change in the Shore hardness value of ABS while carbonaceous additives significantly increase the hardness of the material. Especially, graphene additions lead to higher hardness values at lower concentrations. However, there is no remarkable change in Shore hardness with the addition of carbon fillers, but this may be due to low concentrations of nano-additives used.

3.2. Tribological Properties

Tribological test data involving wear volume and specific wear rate parameters and surface areas graph of wear surfaces of composites were represented in Table 3.3 and Figure 3.3, respectively.

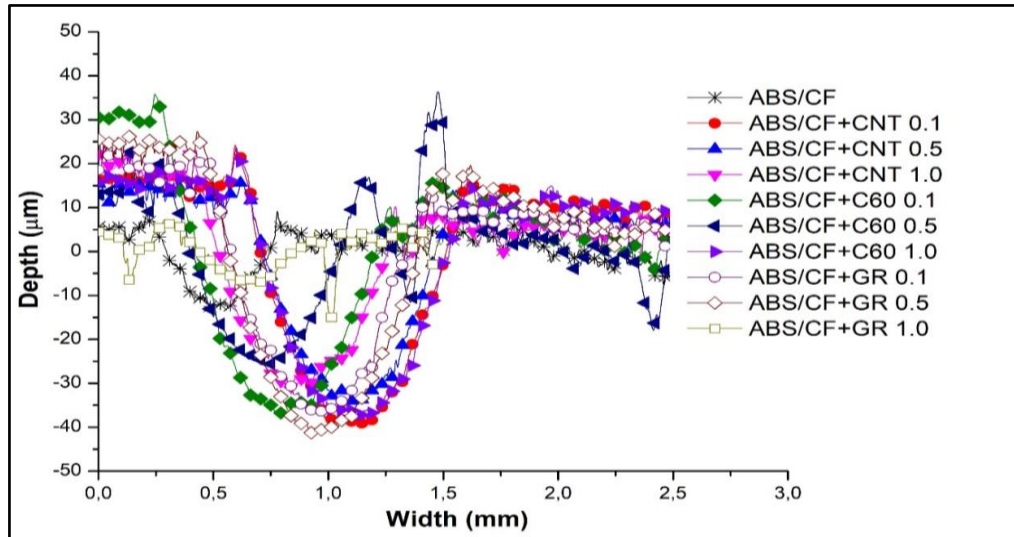


Figure 3.3: Surface area curves of ABS and its composites.

Table 3.3: Summary of the tribological properties of ABS and composites.

Samples	Wear volume W (mm ³)	Specific wear rate W_R
ABS	0.067±0.02	0.083±0.01
ABS/CF	0.072±0.08	0.09±0.09
ABS/CF+C60 0.1	0.272±0.03	0.340±0.04
ABS/CF+C60 0.5	0.229±0.05	0.286±0.07
ABS/CF+C60 1.0	0.280±0.02	0.350±0.03
ABS/CF+CNT 0.1	0.256±0.01	0.320±0.02
ABS/CF+CNT 0.5	0.224±0.03	0.280±0.04
ABS/CF+CNT 1.0	0.202±0.06	0.253±0.07
ABS/CF+GR 0.1	0.232±0.07	0.290±0.08
ABS/CF+GR 0.5	0.156±0.02	0.195±0.03
ABS/CF+GR 1.0	0.048±0.05	0.060±0.06

The abrasion resistance term refers to resistance to wear deformation. As the abrasion loss parameter decreases, the abrasion durability of a material increases. Similarly, improvement in specific wear rate is the declaration of reduction in wear resistance performance [57, 58].

According to Table 3.3, wear volume and specific wear rate value of ABS/CF showed an increasing trend after the addition of nano-dimensional fillers with an exception of a 1.0% GR loaded composite sample. ABS/CF+GR 1.0 yielded lower wear volume compared to ABS/CF. The reduction in wear volume values was observed with the increase of the nanoparticle concentration, which indicated that filler content has a positive effect on the abrasion resistance performance of composites as the lowest wear volume and specific wear rate parameters were reached at lower loadings of additives. Additionally, the geometry of nanoparticles plays a key role in the abrasion resistance of material [57-59].

Composite samples containing C60 particles displayed the worst performance, whereas GR-filled candidates exhibited the best abrasion resistance performance among the composites. These findings may be related to the advantage of the plate-like structure of GR sheets over other dimensions. Owing to the large surface area of the 2D dimension, GR sheets provide effective resistance to wear deformation.

3.3. Melt Flow Index Test (MFI)

MFI indicates the tendency of thermoplastic melt to flow in one direction. It is defined as the mass of material flowing through a capillary of a certain diameter and length [60, 61]. MFI is inversely related to the melt viscosity of the material. MFI parameters give experimental information on the processability of polymeric materials. The rheological properties of ABS and its composites directly influence their melt flow behavior. ABS's shear thinning, and non-Newtonian tendencies allow for viscosity adjustment throughout its processing stage [62-65].

MFI test results of ABS and its composites are represented in Figure 3.4.

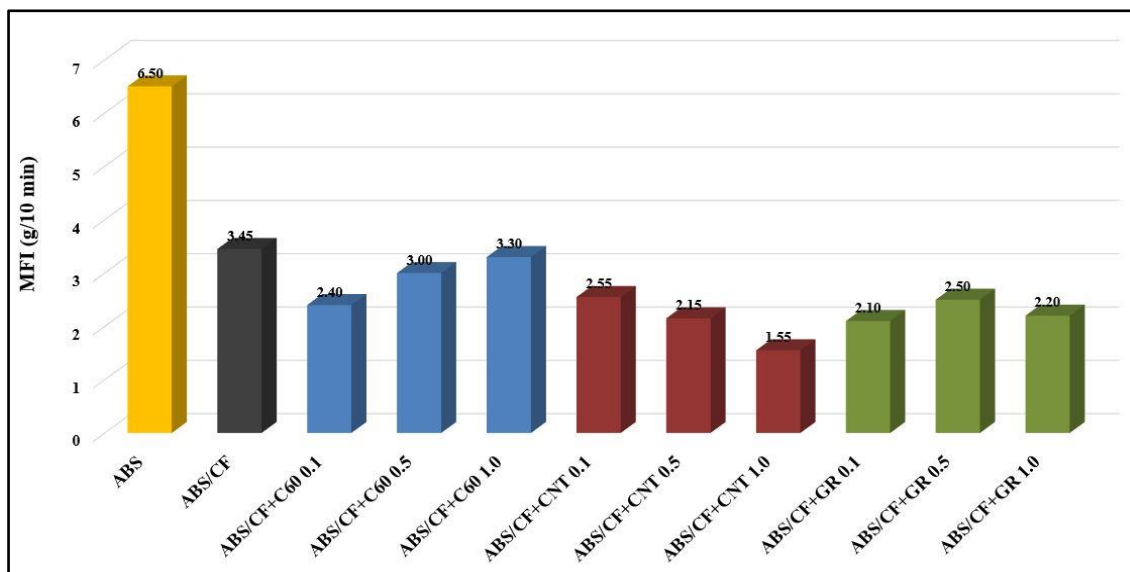


Figure 3.4: MFI test results of ABS and composites.

With CF additions, the MFI value of ABS was significantly reduced due to the high aspect ratio of CF. Similarly, CNT inclusion exhibited the same behavior as CF stemming from the high aspect ratio of its tubular structure. Fullerene-containing samples displayed increasing MFI value with filling ratios. 1.0wt. % fullerene loading gave a nearly identical MFI value with that of ABS/CF, which may be caused by the presence of agglomerated parts of fullerene particles.

3.4. Dynamic Mechanical Analysis

Dynamic mechanical properties of ABS/CF+CF0 composites were examined in terms of storage modulus, loss modulus, and $\tan \delta$ curves with respect to the temperature which is given in Figure 3.5.

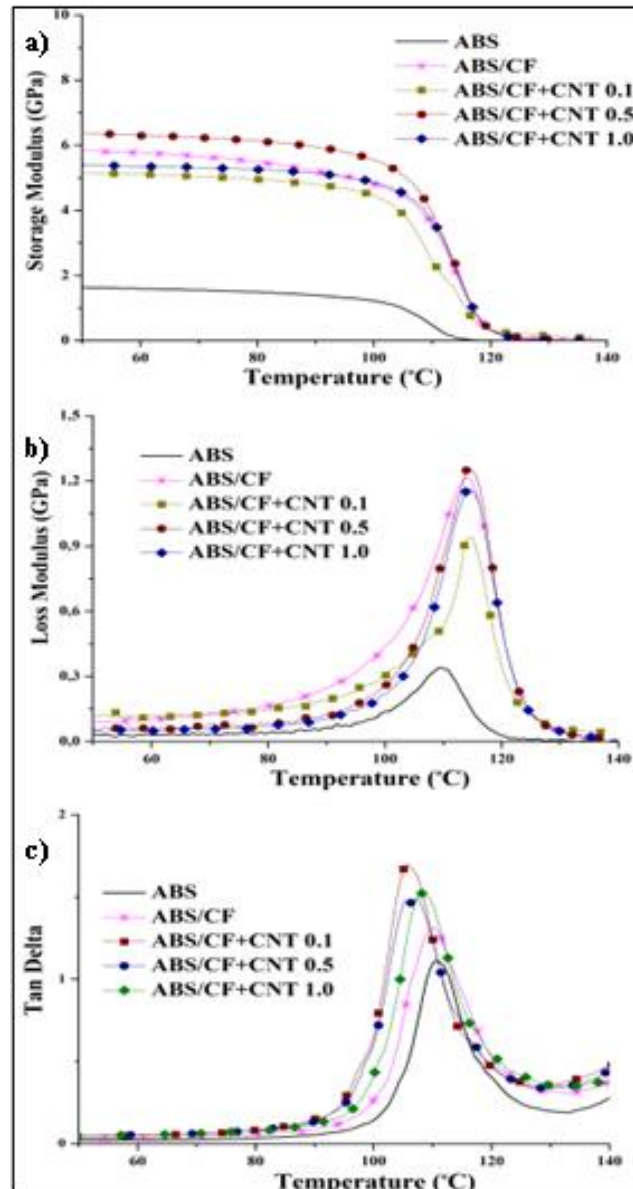


Figure 3.5: a) Storage Modulus, b) Loss Modulus, and c) Tan Delta curves of ABS and ABS/CF+CNT composites.

The sharp lowering in the storage modulus curve is related to glass transition temperature (T_g) during the relaxation stage of the polymer chains throughout the thermal transition.

The storage modulus of ABS was found to be extended up as filled with both CNT and CF. Composites involving CNT displayed higher storage modulus compared to CF-reinforced ABS. The greatest modulus value was achieved for the ABS/CF+0.5% CNT sample. Similar findings for loss modulus of composites were observed. DMA curves indicated that T_g of ABS was not affected by the inclusion of additives regardless of their types.

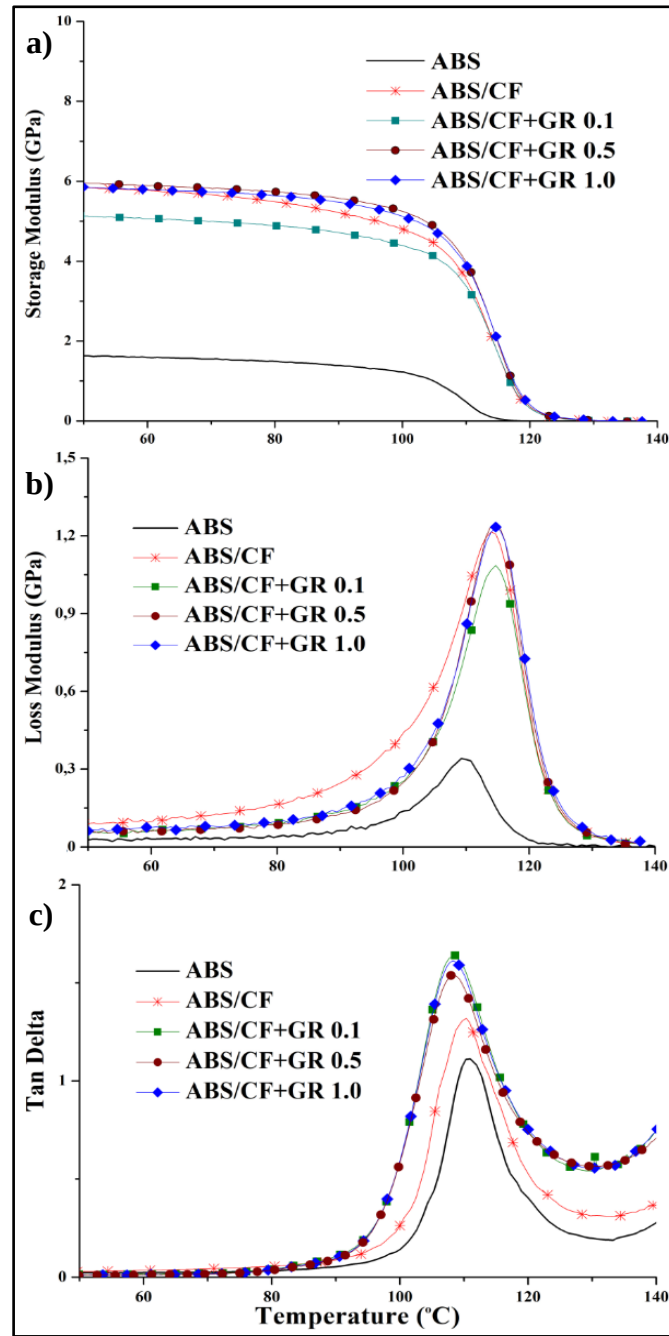


Figure 3.6: a) Storage Modulus, b) Loss Modulus, and c) Tan Delta curves of ABS and ABS/CF+GR composites.

Tan δ curves of ABS and composites in Figure 3.5 implied that the peak value of Tan δ curve of unfilled ABS stayed constant after the reinforcement with CF as opposed to CF-containing composites in which lower peak values were observed since the mobility of ABS polymer chains were restricted by the high amount of CNT additive in addition to CF phase.

Storage modulus, loss modulus, and tan δ curves of ABS/GR samples concerning the temperature are given in Figure 3.6. The sharp decrease in the storage

modulus curve is linked to glass transition temperature (T_g) during the relaxation stage of the polymer chains during the thermal transition.

The storage modulus of ABS was found to be an increasing trend as filled with both GR and CF. Composites filled with GR displayed higher storage modulus compared to CF-reinforced ABS. The greatest modulus value was achieved for the ABS/CF+0.5% GR sample.

Tan δ curves displayed that T_g of ABS shifted to lower values by the addition of GR. It can be also observed that Tan δ peaks of GR-containing composites showed broad compared to that of neat ABS.

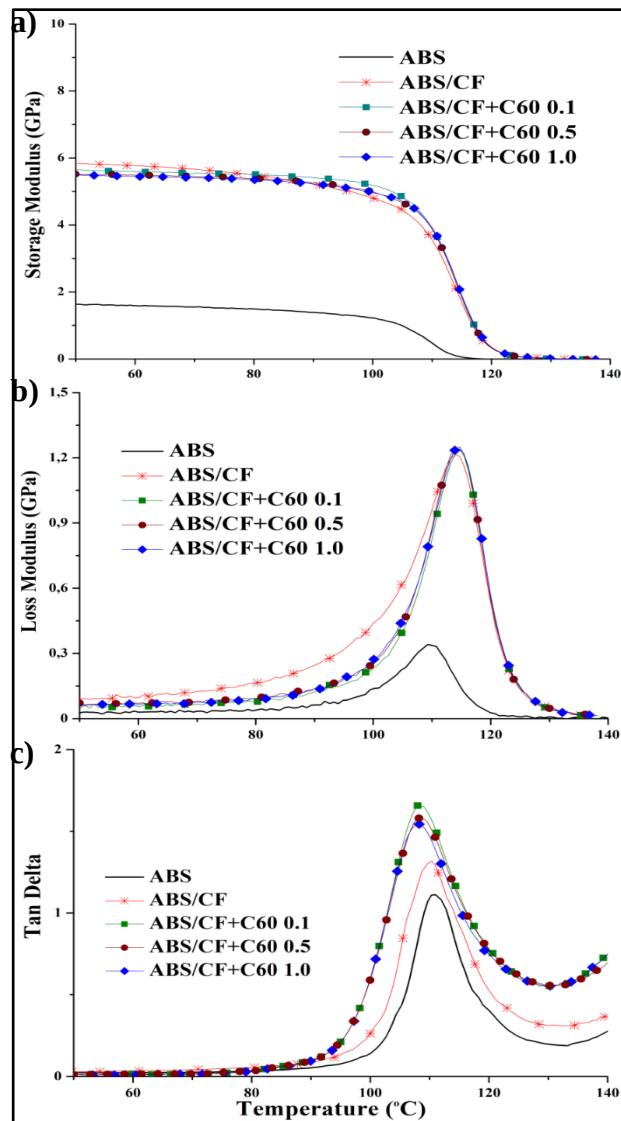


Figure 3.7: a) Storage Modulus, b) Loss Modulus, and c) Tan Delta curves of ABS and ABS/CF+C60 composites.

The storage modulus of unfilled ABS gave improvement after the inclusion of C60. ABS/CF+C60 composites yielded higher storage modulus concerning ABS and ABS/CF samples according to Figure 3.7. The greatest modulus value was obtained for the ABS/CF+C60 0.5 sample.

Tan δ curves displayed that T_g of neat ABS shifted to lower values by the inclusion of C60. Additionally, the Tan δ peak of ABS got broadened with the help of C60 loadings.

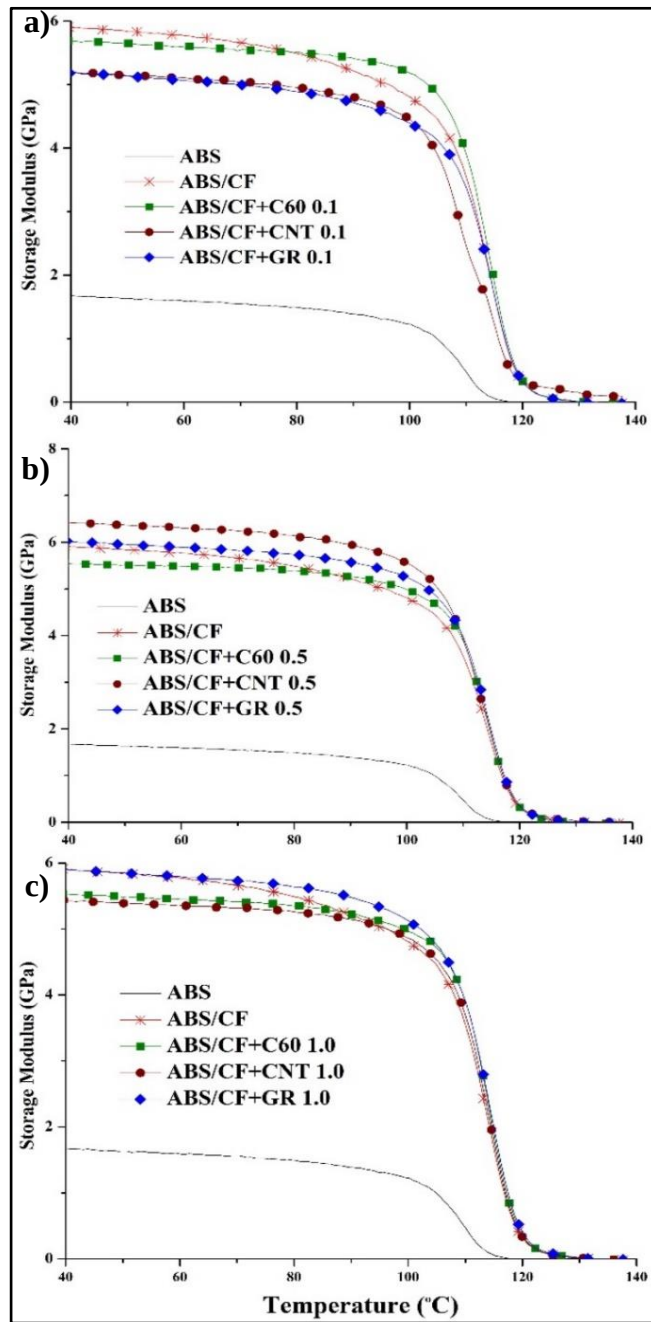


Figure 3.8: Storage Modulus curves with respect to additive contents of a) 0.1%, b) 0.5%, and 1.0%.

The comparisons of additives in terms of their effect on thermo-mechanical properties were made with the help of curves with respect to their identical contents. According to storage modulus curves with respect to additive content in Figure 3.8, C60, CNT and GR exhibited higher storage modulus for the filling ratios of 0.1, 0.5, and 1.0%, respectively.

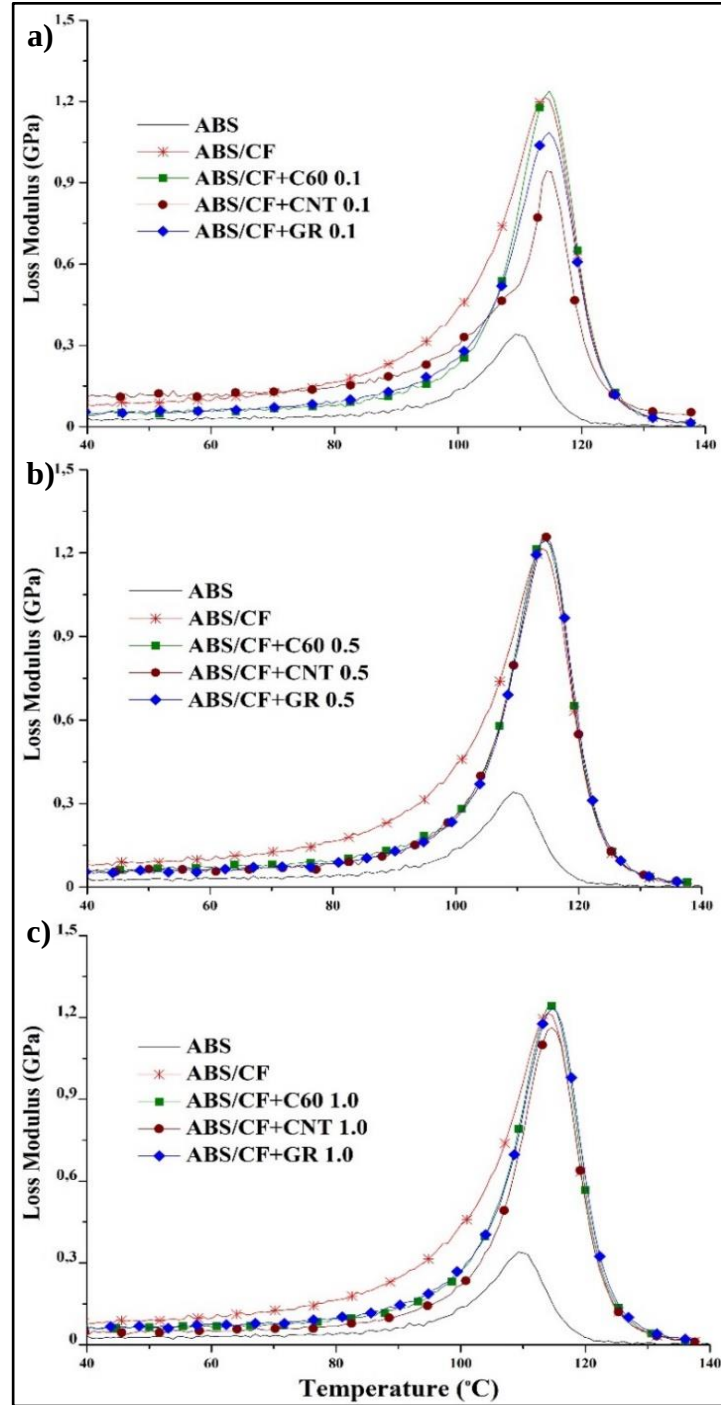


Figure 3.9: Loss Modulus curves with respect to additive contents of a) 0.1%, b) 0.5%, and 1.0%.

Figure 3.9 represents the loss modulus curves with respect to additive content. A similar trend with storage modulus findings was observed in which C60, CNT, and GR exhibited relatively higher loss modulus for the filling ratios of 0.1, 0.5, and 1.0%, respectively.

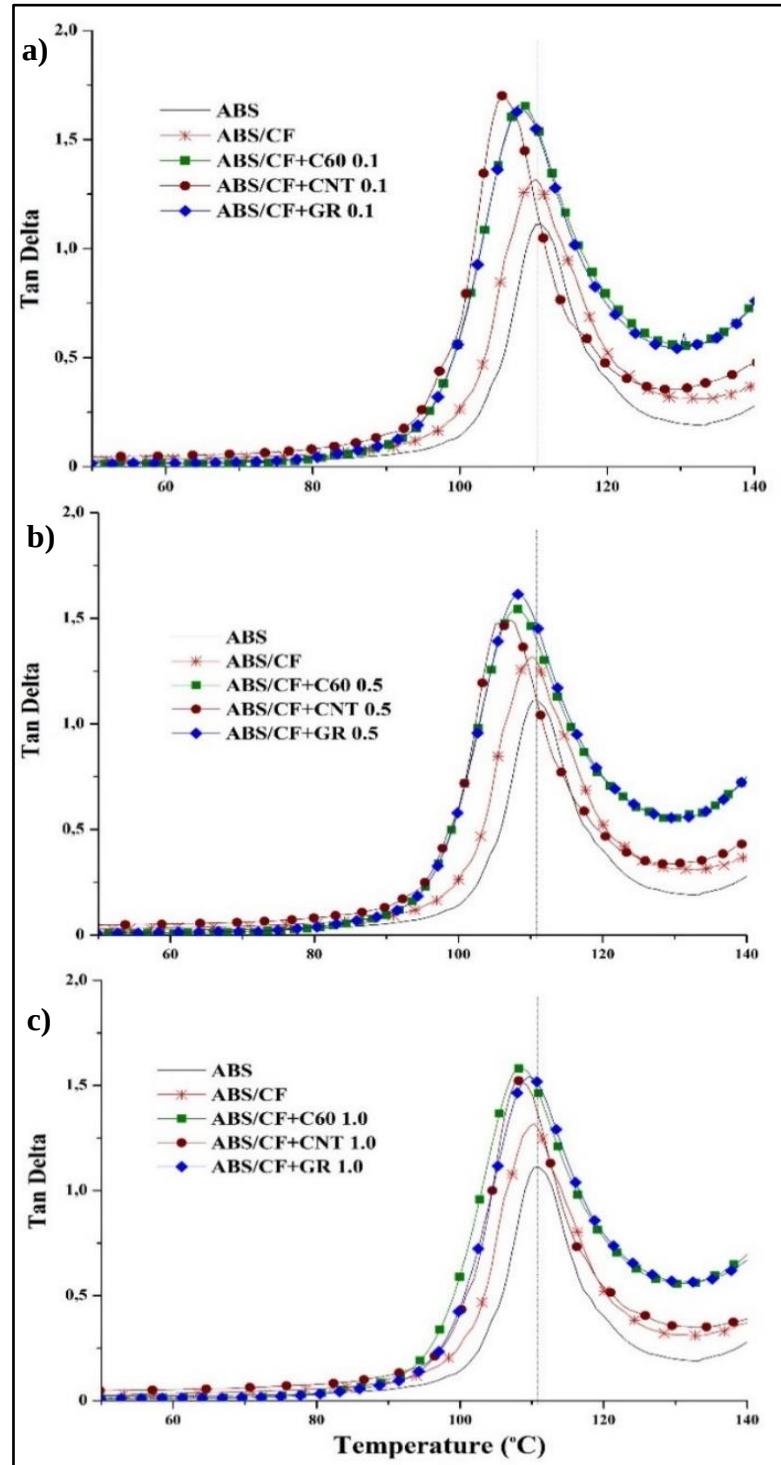


Figure 3.10: Tan Delta curves with respect to additive contents of a) 0.1%, b) 0.5%, and 1.0%.

Figure 3.10 shows the Tan Delta curves with respect to additive content. It can be seen from these curves that CNT-containing samples displayed more indicative lowering in T_g values compared to GR and C60-filled composites.

3.5. Thermal Characterization

TGA thermograms of unfilled ABS and relevant composites are displayed in Fig. 3.11.

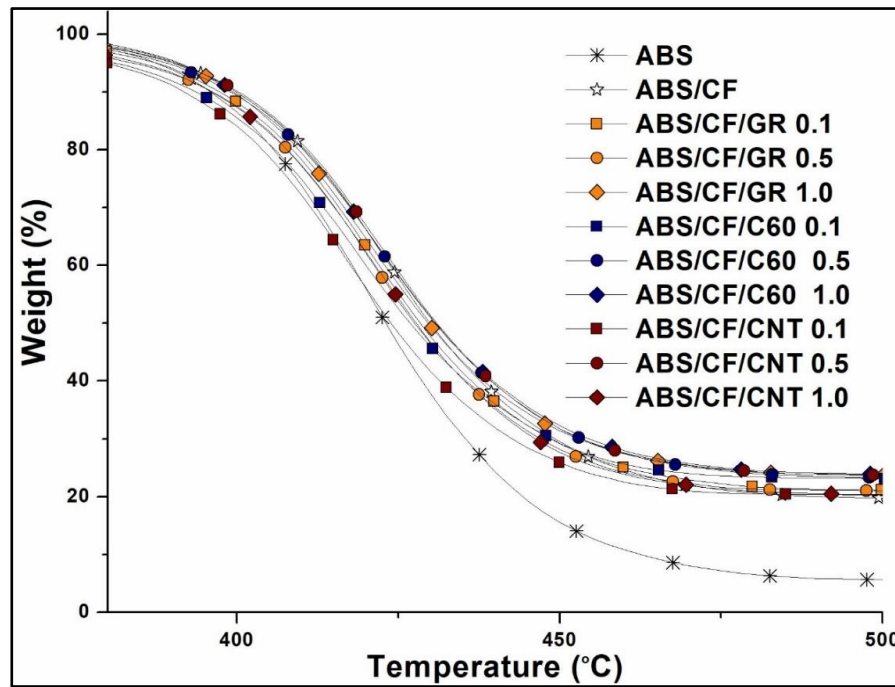


Figure 3.11: TGA curves of ABS and composites.

Thermal decomposition of ABS terpolymer takes place in a single step in the range of nearly 380°C to 450°C in which thermal degradation of aliphatic butadiene and aromatic styrene segments in the ABS chain occurs [66-68]. Composites incorporated with nano-additives exhibited a reduction in the decomposition rate compared to unfilled ABS. Higher amounts of C60 and CNT additions yielded relatively more thermally stable behavior than ABS/CF. Ternary composites containing GR showed nearly identical TGA curves with that of binary ABS/CF composite. On the other hand, inclusions of nano-fillers with the lowest filling ratio (0.1%) caused no remarkable improvement in the thermal stability of ABS/CF. The increase in the char yield with an increase in GR, C60, and CNT contents was clearly observed in TGA curves. Composites filled with C60 gave relatively higher char yield among composites which may be attributed to the formation of thermally stable residue

at the end of the analysis. Similar results were observed in the literature that 0.5% and 1.0% composition of C60 displayed enhancement in thermal stability and char residue of different polymeric matrices [69-71].

3.6. Morphological Characterizations

SEM micrographs of ABS/CF and ABS/CF+CNT composites are represented in Figure 3.12.

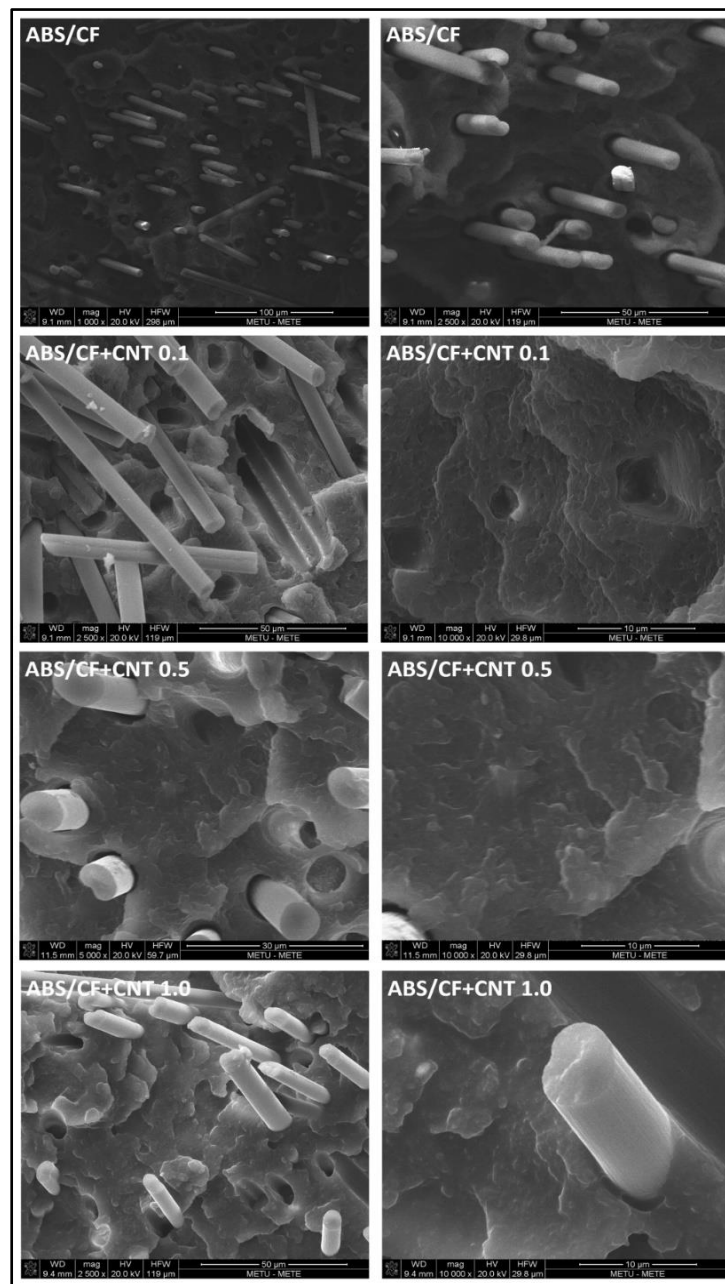


Figure 3.12: SEM images of ABS/CF and ABS/CF+CNT composites.

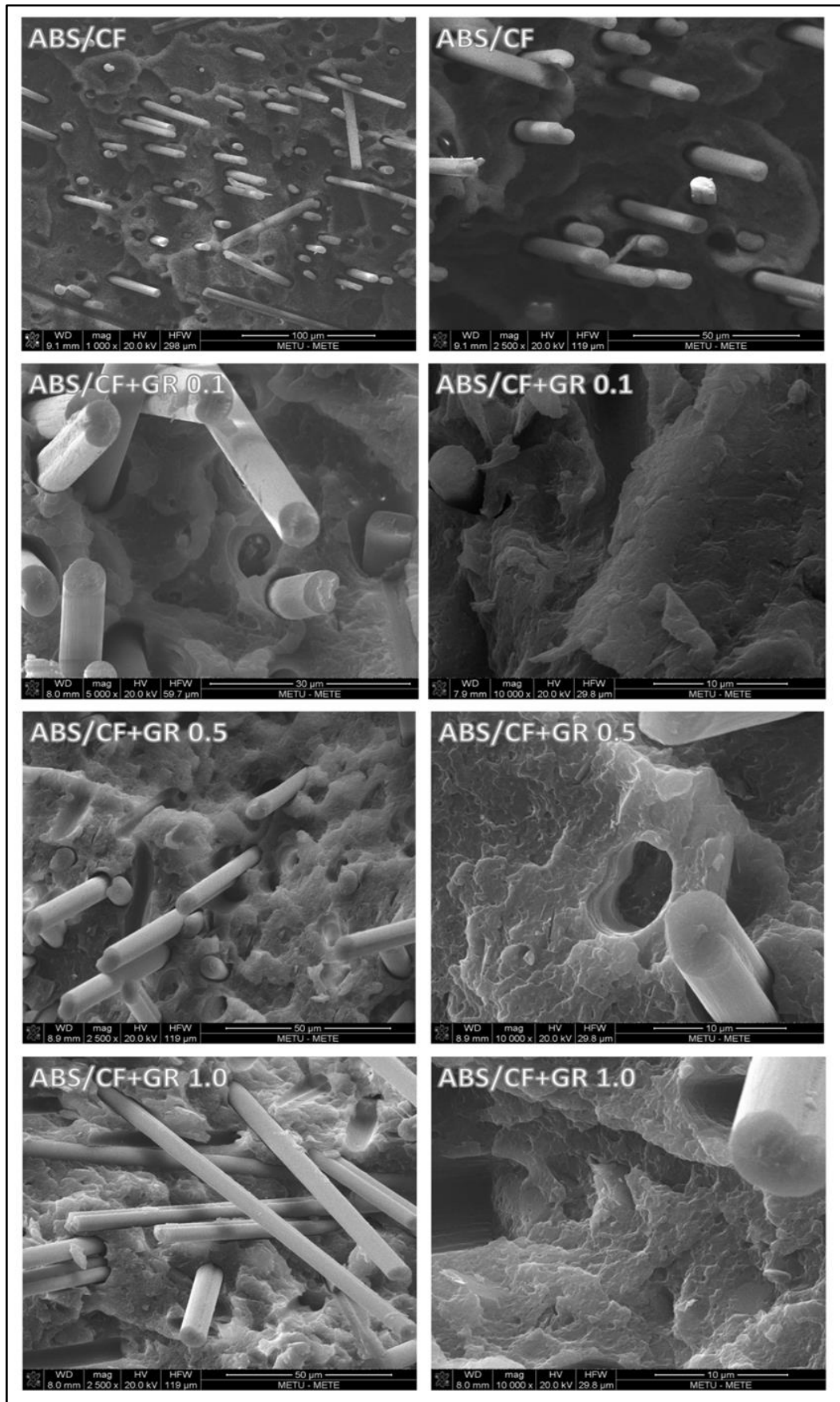


Figure 3.13: SEM images of ABS/CF and ABS/CF+GR composites.

According to SEM images of composites Figure 3.12, fibers were aligned in one direction for the ABS/CF sample. The alignment of CFs disappeared after CNT loadings as seen in SEM images of CNT-containing composites. CNT additions also caused some debonding formations in composite structures. Nanotube domains were observed as the bundle regions for a 1.0% CNT-filled composite sample. The formation of CNT bundles in a highly loaded composite is the visual evidence of the dropping down in previously discussed performances of composites.

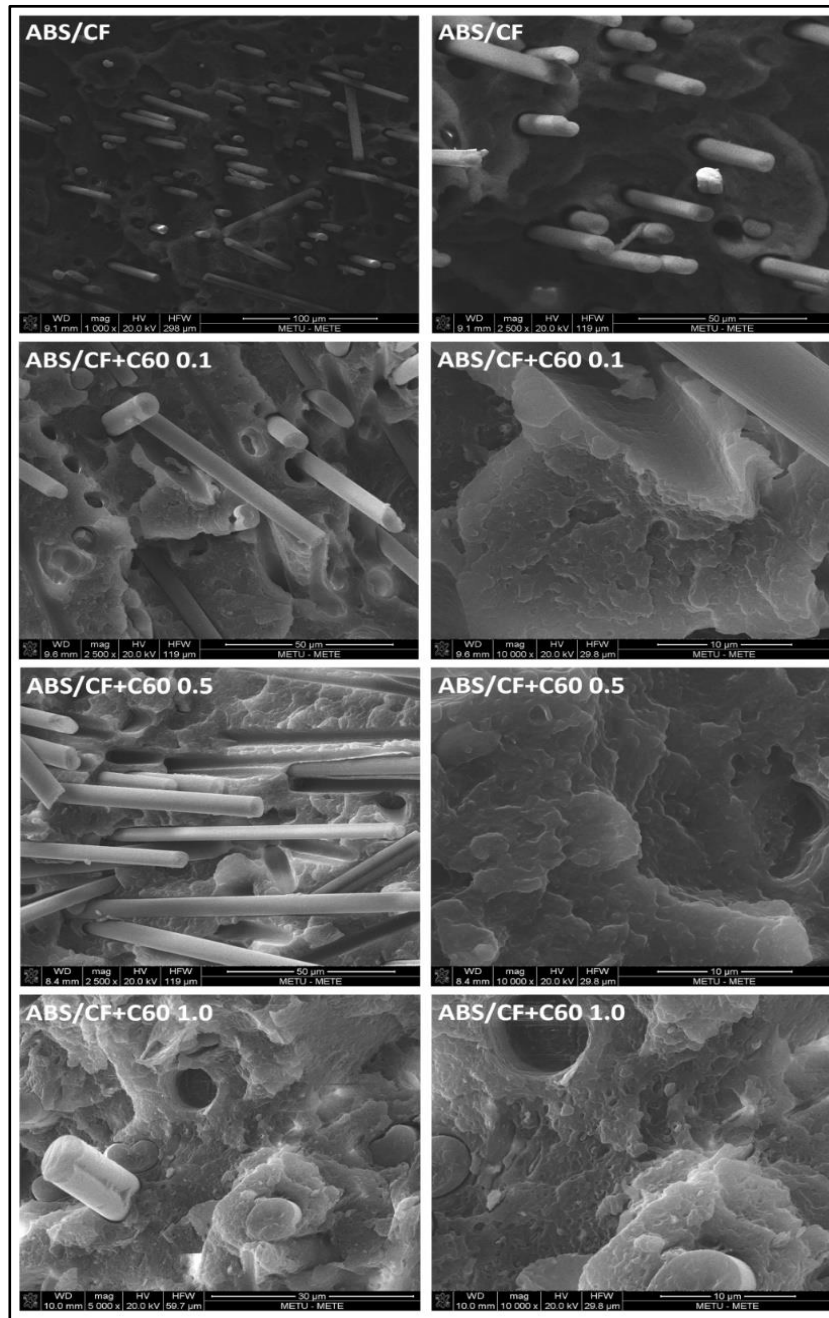


Figure 3.14: SEM images of ABS/CF and ABS/CF+C60 composites.

The representative SEM micrographs of GR-filled composites with two different magnifications are given in Figure 3.13. Like CF inclusion, GR addition caused disorientation in the alignment of individual carbon fibers. The agglomerations were obtained for the composite sample involving 1.0% GR. The formation of GR agglomerates in a highly loaded composite is visual evidence of the reduction in previously discussed behaviors of composites.

The representative SEM micrographs of C60 containing composites with two different magnifications are given in Figure 3.14. C60 particles homogeneously dispersed in ABS matrix according to SEM images of ABS/CF+C60 0.1 and ABS/CF+C60 0.5 composite samples. The agglomerations of C60 were observed for 1.0% C60 loaded composite. The formation of C60 agglomerates in a highly filled composite proves the decrease in previously discussed properties of ABS/CF+C60 composites.

3.7. AFM Studies

3.7.1. Topographical Investigations of Bulk Samples

2D AFM images and cross-section graphs are given in Figure 3.15 below. These results indicate that ABS and its composites exhibited rough surface properties. However, higher roughness values (height profile in cross-section graphs) were obtained for composite samples when compared with unfilled ABS.

2D AFM images and cross-section graphs in Figure 3.16 below indicate that ABS and its composites exhibited rough surface properties. However, higher roughness values (height profile in cross-section graphs) were obtained for composite samples compared to unfilled ABS due to the presence of high amounts of additives with different geometries. Composites involving GR yield relatively higher roughness.

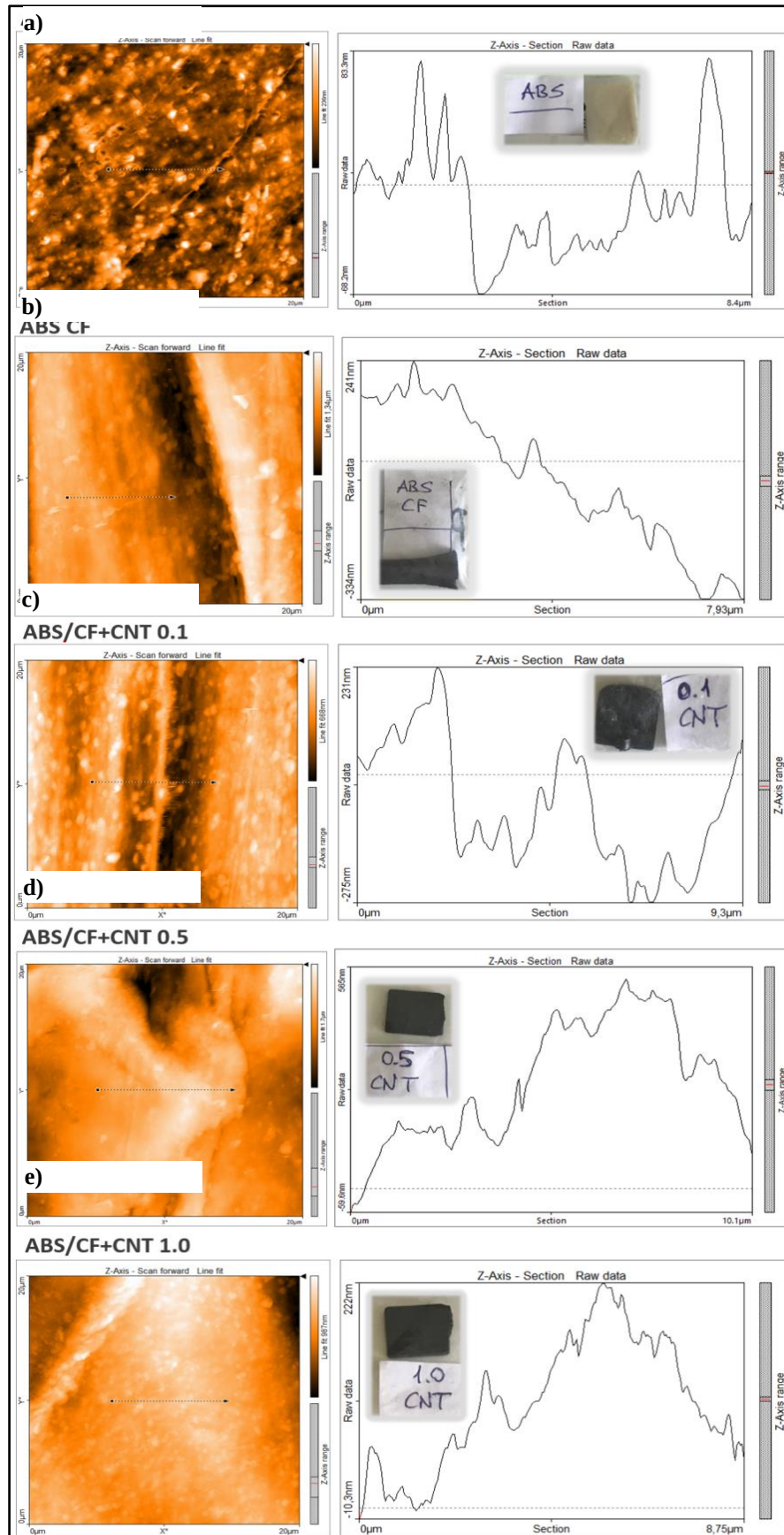


Figure 3.15: Surface topography results of a) ABS, b) ABS/CF, c) ABS/CF+CNT 0.1, d) ABS/CF+CNT 0.5, and e) ABS/CF+CNT 1.0 composites.

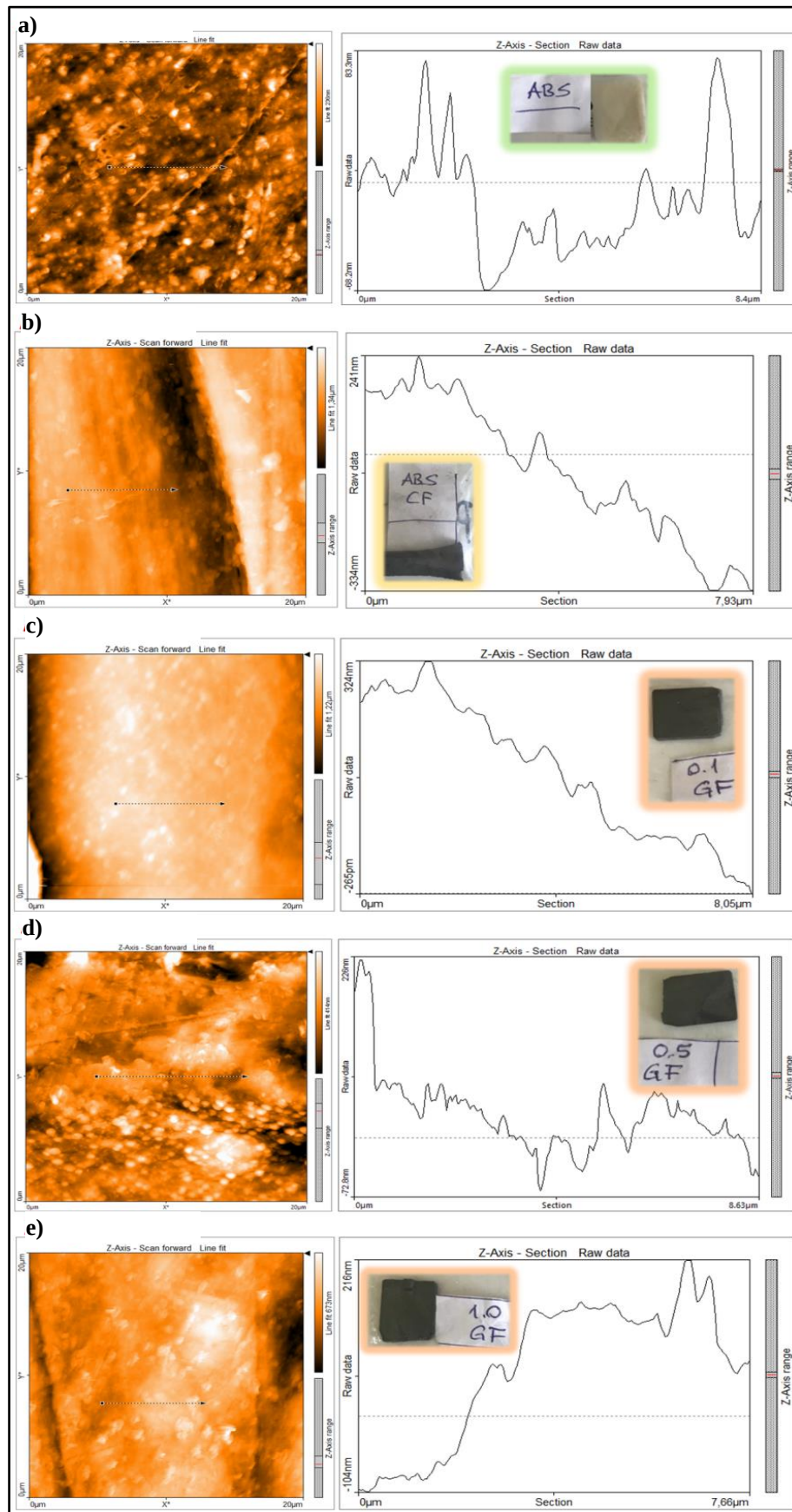


Figure 3.16: Surface topography results of a) ABS, b) ABS/CF, c) ABS/CF+GR 0.1, d) ABS/CF+GR 0.5, and e) ABS/CF+GR 1.0 composites.

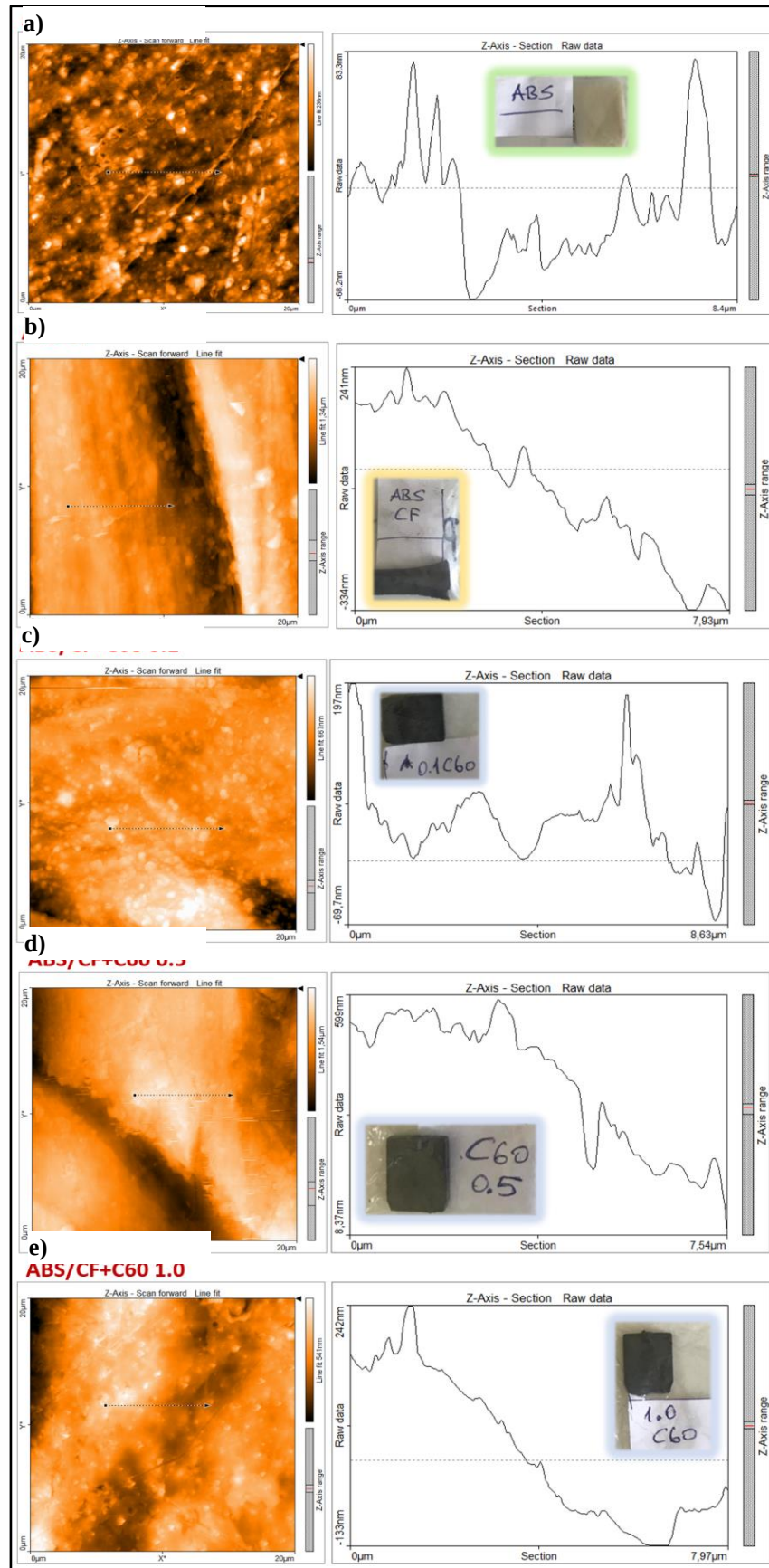


Figure 3.17: Surface topography results of a) ABS, b) ABS/CF, c) ABS/CF+C60 0.1, d) ABS/CF+C60 0.5, and e) ABS/CF+C60 1.0 composites.

2D AFM images and cross-section graphs in Fig. 3.17 indicate that ABS and its composites exhibited rough surface properties. However, higher roughness values (height profile in cross-section graphs) were obtained for composite samples compared to unfilled ABS due to the presence of high amounts of C60.

3.7.2. Nano-mechanical Characterization of Bulk Samples

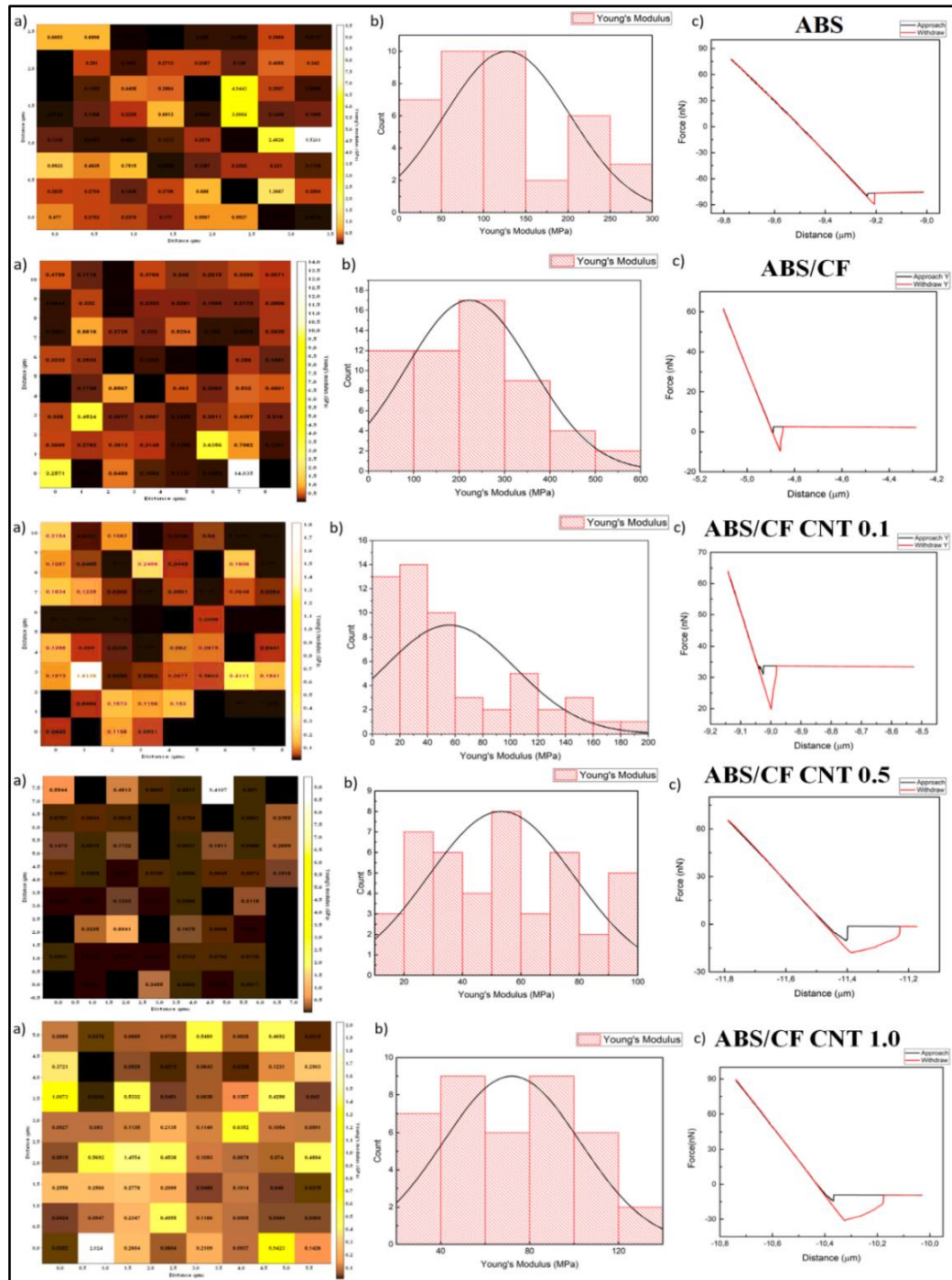


Figure 3.18: a) Young's modulus distribution map, b) Young's Modulus distribution histogram, and c) Force-Distance curve of ABS and ABS/CF+CNT composites.

Young's modulus mapping of ABS and composites and force-distance curves are displayed in Fig. 3.18.

Young's modulus values of samples were analyzed by nano-indentation measurement with the help of the displacement of the AFM tip. The distribution of Young's modulus became more homogeneous for a 0.5% concentration of CNT. Additionally, higher Young's modulus values are achieved for this loading ratio for CNT compared to additive amounts of 0.1% and 1.0%.

According to F-d curves displayed in Fig. 3.18, the maximum pull-off force of composites gave an increasing trend as the filler content increased. The upward change in slope of the force-distance curve of ABS compared to composites points to an increase in stiffness which indicates that CNT inclusions donate stiffness to ABS structure.

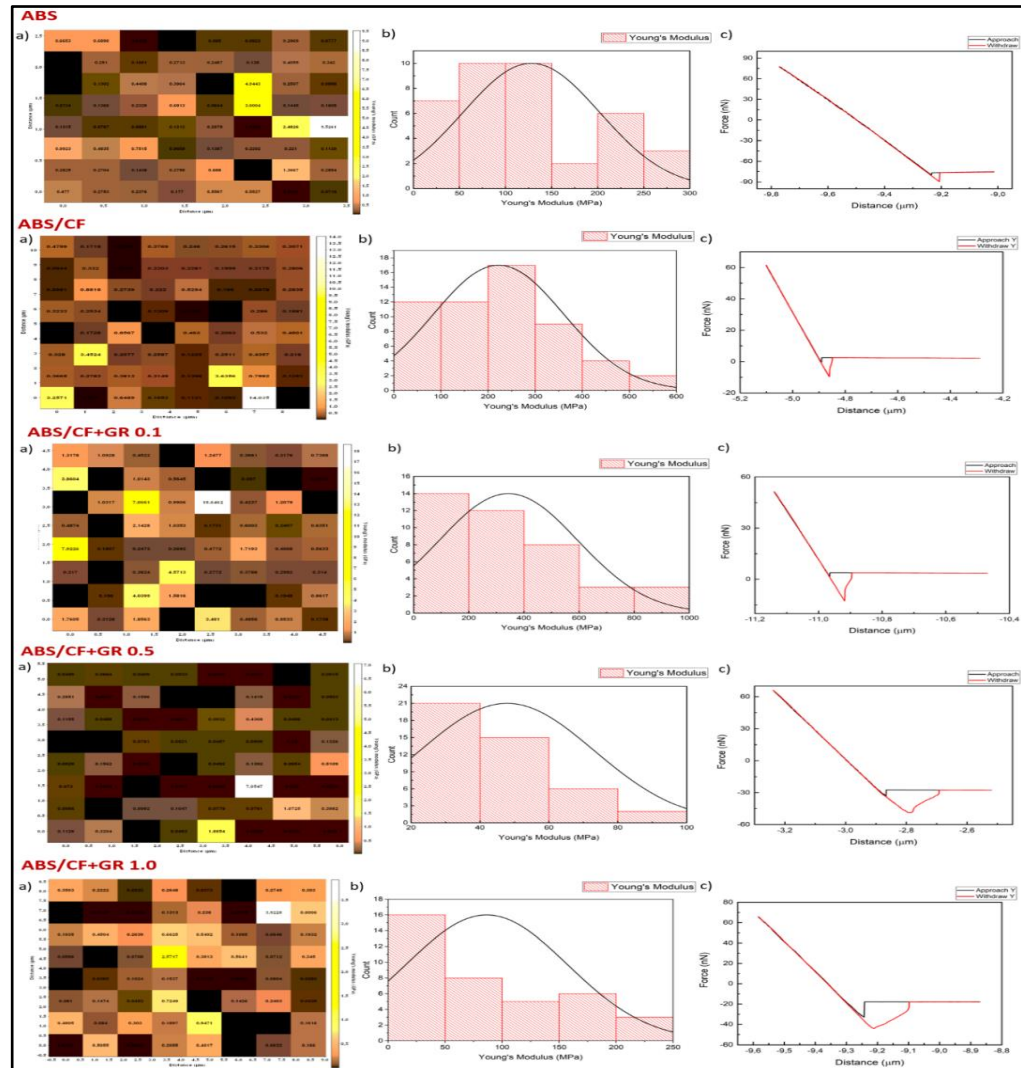


Figure 3.19: a) Young's modulus distribution map, b) Young's Modulus distribution histogram, and c) Force-Distance curve of ABS/CF+GR composites.

Young's modulus mapping of ABS and ABS/CF+GR composites and force-distance curves are displayed in Figure 3.19. The distribution of Young's modulus became more homogeneous for a 0.1% concentration of GR. Additionally, higher Young's modulus values are achieved for this loading ratio for GR compared to the loading level of 1.0%.

The maximum pull-off force of composites gave an increasing trend as GR content increased. the upward change in slope of the force-distance curve of ABS compared to composites refers to an increase in stiffness which indicates GR donates stiffness to ABS structure.

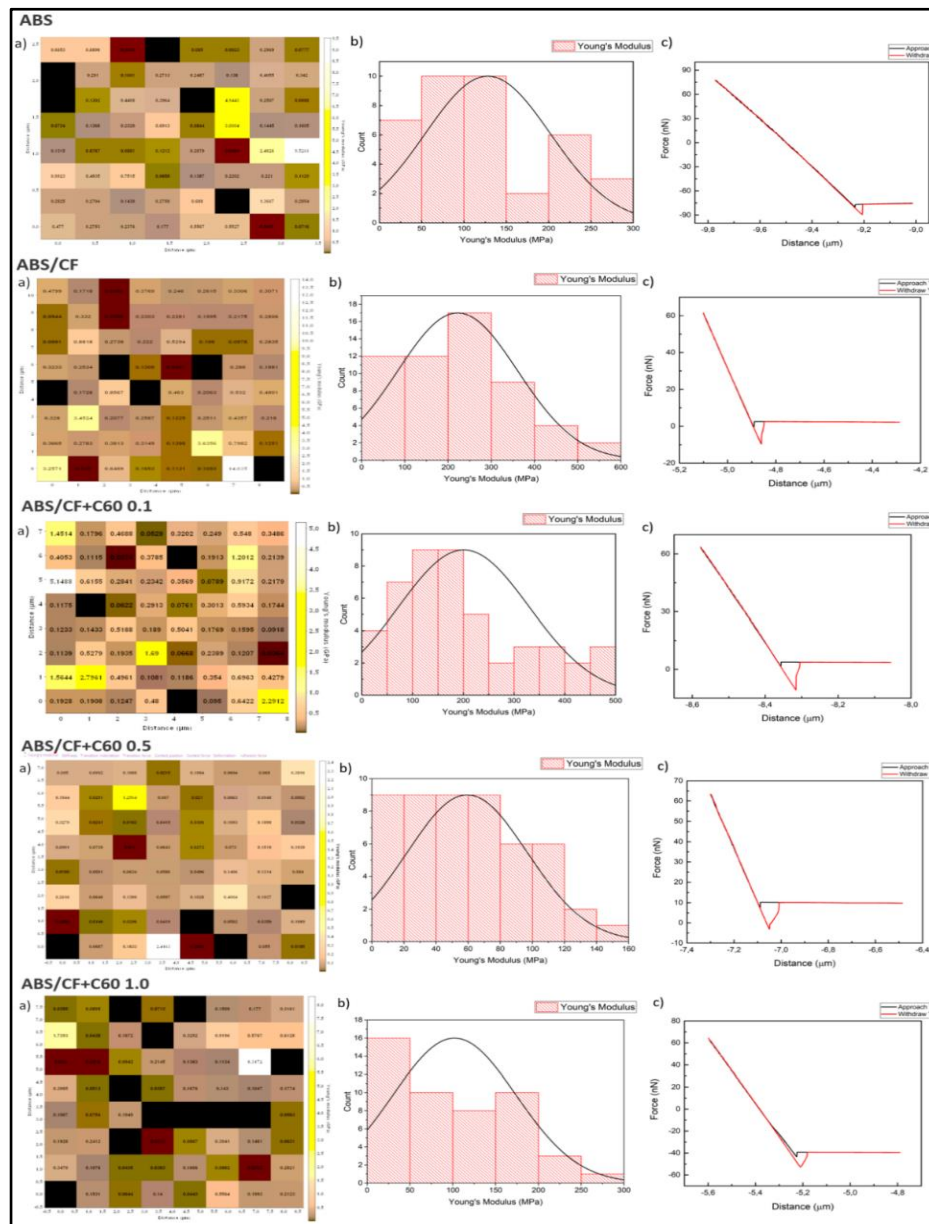


Figure 3.20: a) Young's modulus distribution map, b) Young's Modulus distribution histogram, and c) Force-Distance curve of ABS/CF+C60 composites.

According to Young's modulus mapping and force-distance curves of ABS and ABS/CF+C60 composites in Figure 3.20, the distribution of Young's modulus values was found to be more homogeneous for a 0.1% filling ratio of C60. The highest Young's modulus is obtained for the lowest concentration of GR. F-d curves implied that; the maximum pull-off force of composites showed improvement as the C60 content increased. the upward change in slope of the force-distance curve of ABS compared to composites stem from the increase in stiffness which indicates that C60 additions donate stiffness to ABS structure.

3.7.3. Electrical Conductivity Measurements of Bulk Samples

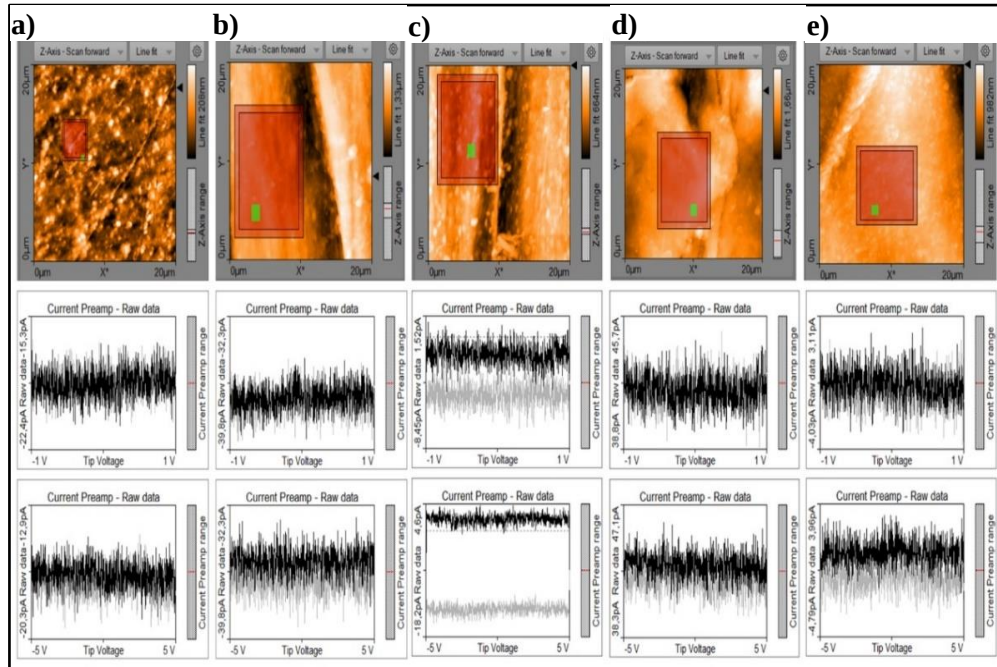


Figure 3.21: Current response of a) ABS, b) ABS/CF, c) ABS/CF+CNT 0.1, d) ABS/CF+CNT 0.5, and e) ABS/CF+CNT 1.0 composites in bulk form.

Figure 3.21 shows the current-voltage characteristics of ABS and composites which were measured from 3 different locations indicated by red squares in AFM images.

According to the I– V curves, the conductivity of unfilled ABS was found to be in a narrow range with a low amount of CNT which indicates that nearly no current flow was obtained. On the other hand, composites filled with 0.1% of CNT exhibited ohmic behavior in the range obtained as more than an order of magnitude wider range of current compared.

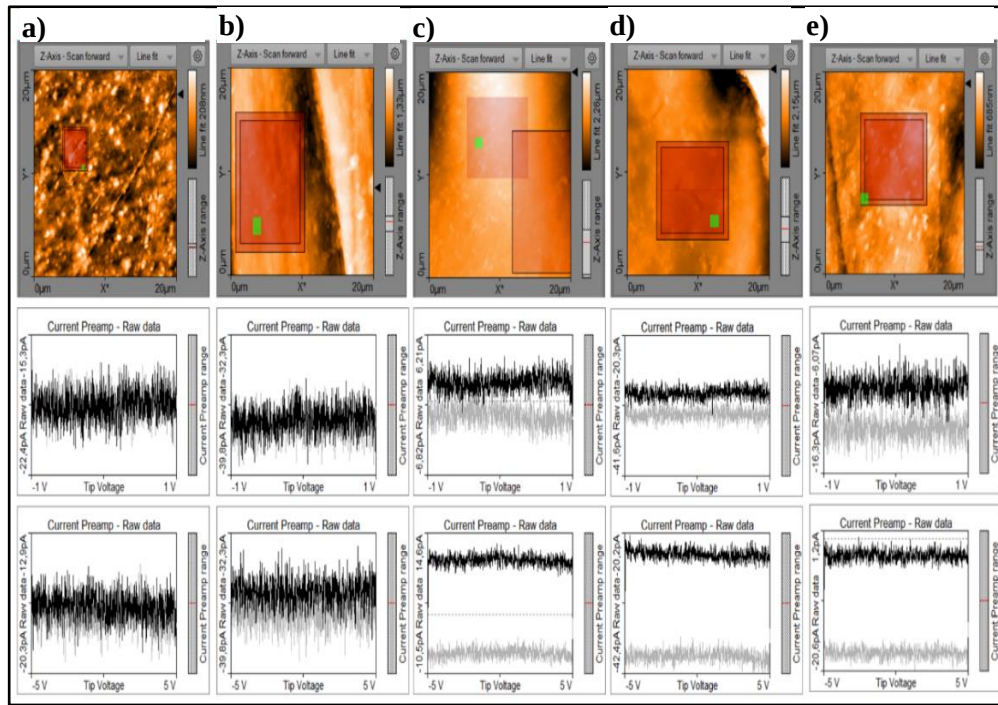


Figure 3.22: Current response of a) ABS, b) ABS/CF, c) ABS/CF+GR 0.1, d) ABS/CF+GR 0.5, and e) ABS/CF+GR 1.0 composites in bulk form.

Figure 3.22 represent the current-voltage characteristics of ABS and ABS/CF+GR composites which were measured from 3 different locations indicated by red squares in AFM images. According to I–V curves, the conductivity of unfilled ABS was found to be in a narrow range with a very low amount which indicates that nearly no current flow was obtained. On the other hand, composite samples exhibited ohmic behavior in the range obtained as more than an order of magnitude wider range of current compared to ABS. GR-filled composites gave a higher amount of current among composites which may be related to the improvement in the number of electron pathways thanks to homogeneously dispersed GR layers in the composite structure. Enhancement of conductivity with an increase in filling ratios of fillers supports the percolation threshold theory attributed to the establishment of a synergistic effect between electrically conductive CF with a high content (20%) and carbonaceous additives with varied adding amounts.

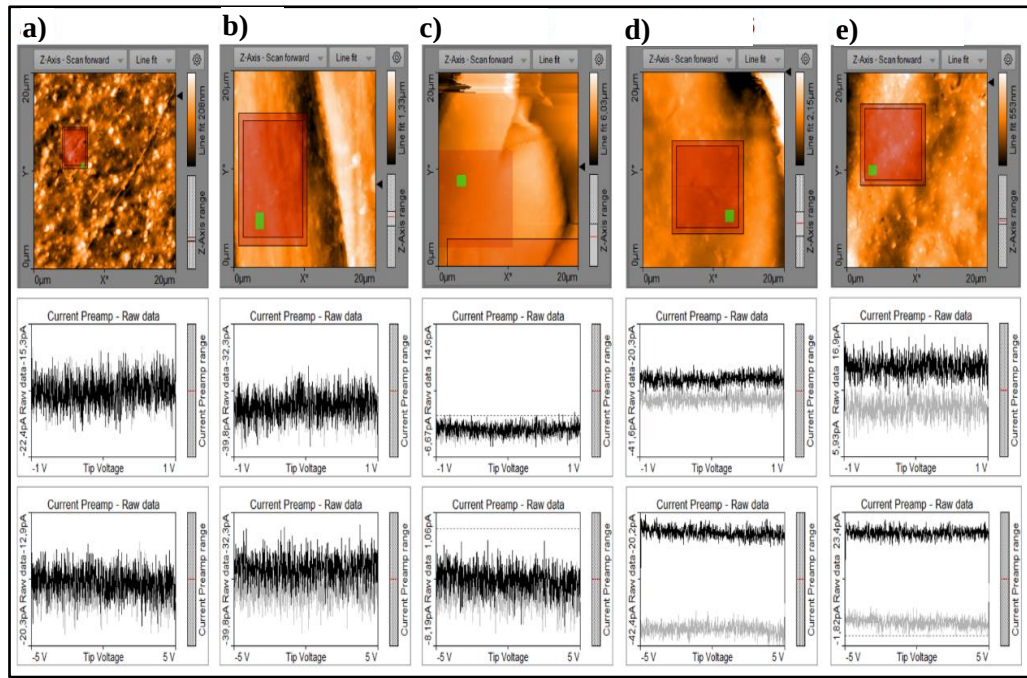


Figure 3.23: Current response of a) ABS, b) ABS/CF, c) ABS/CF+C60 0.1, d) ABS/CF+C60 0.5, and e) ABS/CF+C60 1.0 composites in bulk form.

The current-voltage characteristics of ABS and ABS/CF+C60 composites are given in Figure 3.23 which indicates a conductive path was achieved throughout the physical connection between C60 and CF surfaces. According to the I–V curves, the conductivity of unfilled ABS was found to be in a narrow range with a low amount which indicates that nearly no current flow was obtained. Composites involving C60 exhibited a higher amount of current composites which may be due to enhancement in the number of electron pathways with the help of homogeneously dispersed C60 particles into the polymer phase. Increasing electrical conductivity with an increase in C60 content supports the percolation threshold theory stemming from the establishment of a synergistic effect between electrically conductive CF with a high content (20%) and C60 with low loading levels.

3.7.4. Topographical Nano-mechanical Investigations of Film Samples

The topography of ABS polymer film and its composite films were investigated by AFM and the height profile of the surfaces have been observed. Additionally, maximum and average Young's Modulus (E) parameters were listed in Table 3.4.

Table 3.4: Summary of the nano-mechanical parameters from AFM data.

Samples	Maximum Young's Modulus (MPa)	Average Young's
ABS film	3.18	2.65
ABS/CF	2.44	1.91
ABS/CF+CNT 0.1	0.85	0.80
ABS/CF+C60 0.1	1.53	1.32
ABS/CF+GR 0.1	1.80	1.63
ABS/CF+CNT 0.5	1.04	0.95
ABS/CF+C60 0.5	1.91	1.58
ABS/CF+GR 0.5	0.78	0.69
ABS/CF+CNT 1.0	1.09	1.02
ABS/CF+C60 1.0	2.36	1.95
ABS/CF+GR 1.0	2.86	2.73

The topography of ABS polymer film was investigated by AFM and the height profile of the surface was shown in Figure 3.24.

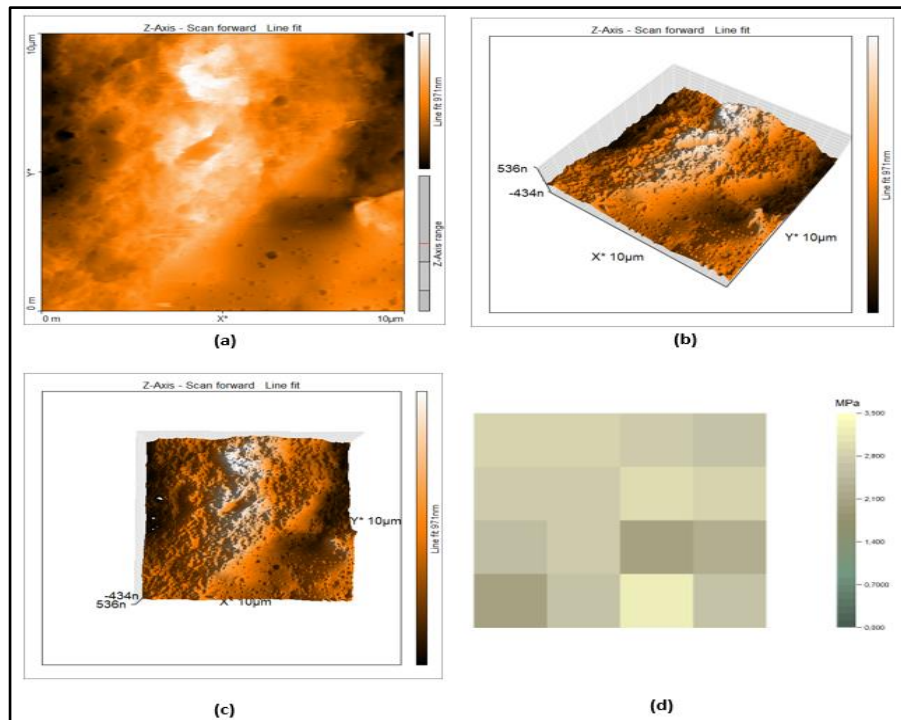


Figure 3.24: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS film.

Due to shrinkage during the solidification process of ABS, there are porous structures on the polymer surface. As Figure 3.24a was examined by AFM analysis, it was understood that porous structures can be seen.

According to Figure 3.24a, the maximum height value of the ABS concerning start point height is 536nm and the minimum height value of the ABS with respect to start point height is nearly 434nm.

Figure 3.24d shows the strength of the surface, which is shown as a color map, the maximum Young's Modulus (E) value is extracted as 3.1764 MPa, minimum E is found to be 2.0479 MPa. The average value of Young's Modulus is 2.6497 MPa.

The topography of ABS/CF film was investigated by AFM and the height profile of the surface was shown in Figure 3.25.

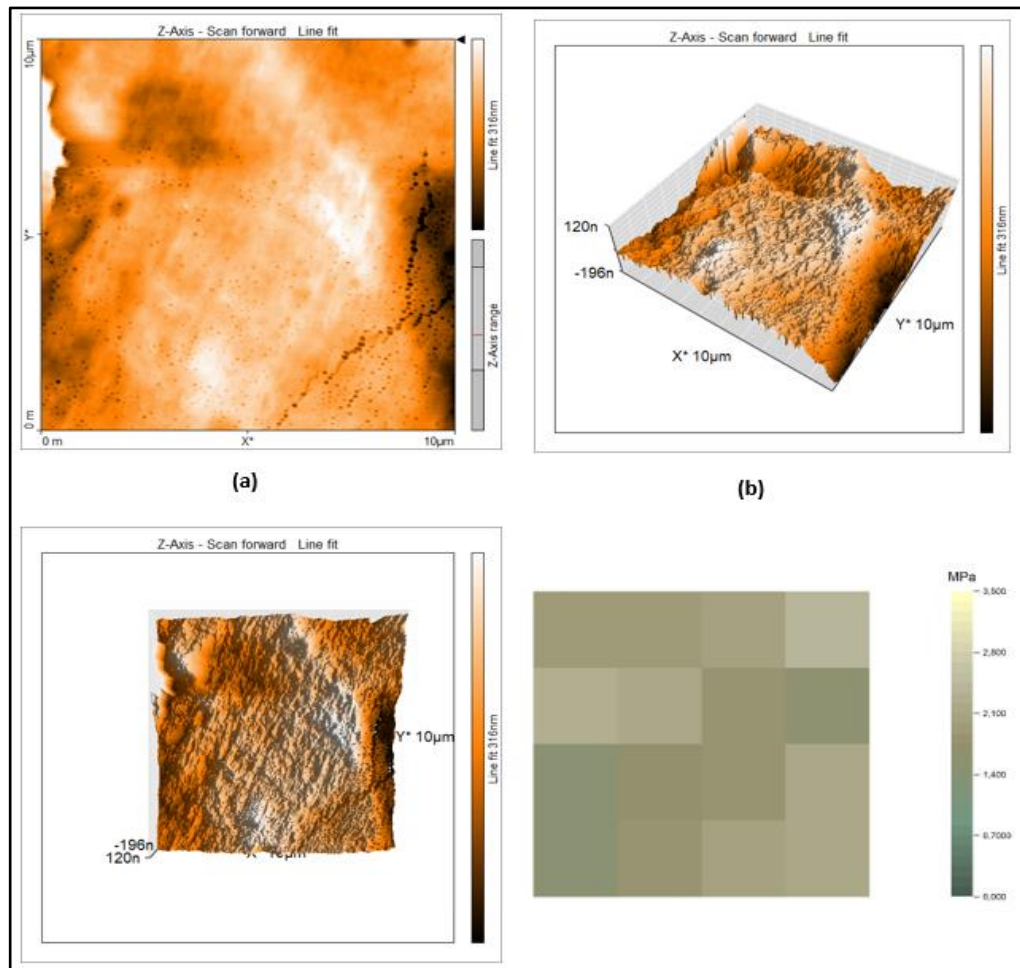


Figure 3.25: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF composite film.

Topography of ABS/CF polymer has been investigated by AFM and the height profile of the surface were shown in Figure 3. 25a. The maximum height value of the

ABS with respect to start point height is 120nm and the minimum height value of the ABS concerning start point height is 196nm.

As Figure 3. 25a examined, it can be deduced that the porous structures increase, and the CF plays a pore-increasing role for the ABS polymer.

The strength of the surface is shown as the color map in Figure 3. 25d. From modulus mapping, the maximum Young's Modulus (E) value is extracted as 2.4435 MPa, minimum E is found to be 1.4058 MPa. The average value of Young's Modulus is 1.9144 MPa.

The topography of ABS/CF+CNT 0.1 film was investigated by AFM and the height profile of the surface was shown in Figure 3.26.

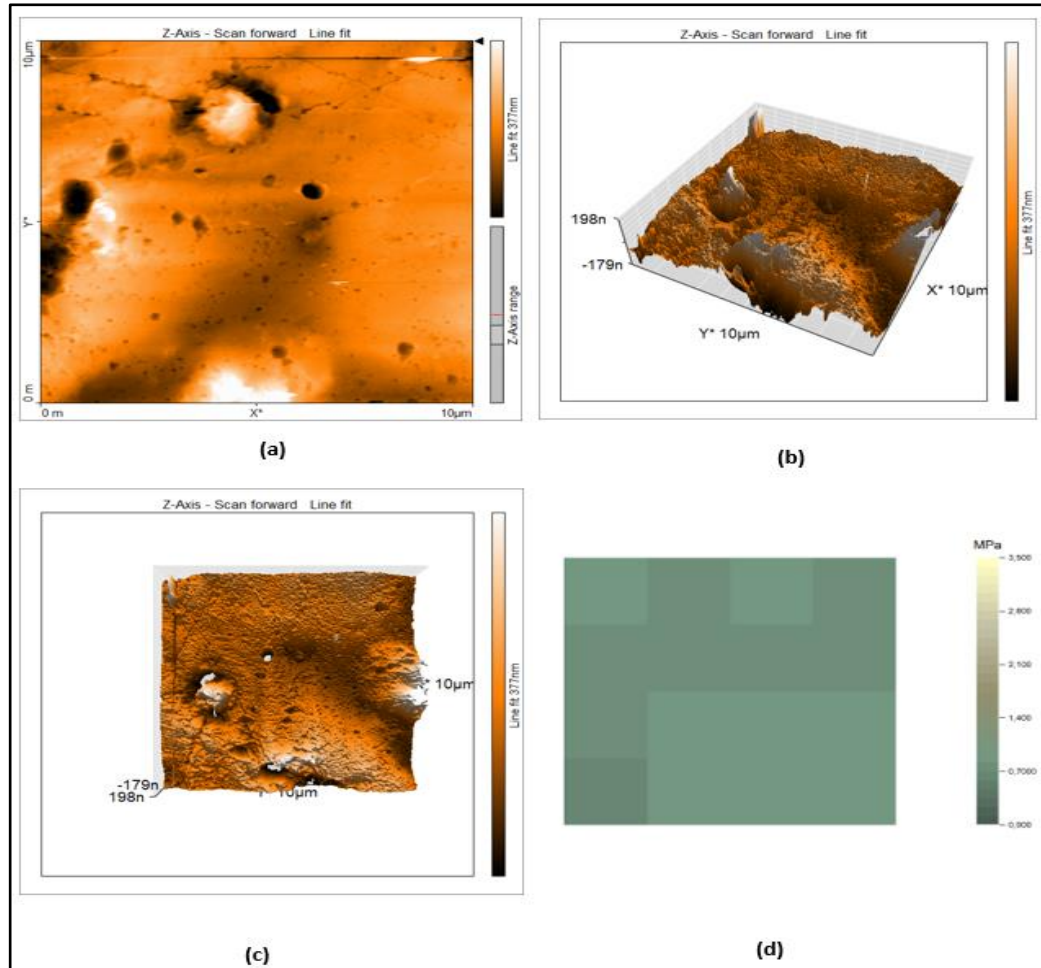


Figure 3.26: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+CNT 0.1 composite film.

Topography of ABS/CF+CNT 0.1 film has been investigated by AFM and the height profile of the surface were shown in Figure 3. 26a, the maximum height value

of the ABS for start point height is 198nm and the minimum height value of the ABS to start point height is -179nm as shown in Figure 3. 26b.

Figure 3. 26d shows the strength of the surface which is shown as a color map. From Figure 3. 26d, the maximum Young's Modulus (E) value is extracted as 0.8466 MPa, and the minimum E is found to be 0.6575 MPa. The average value of Young's Modulus is 0.8043 MPa.

The topography of ABS/CF+C60 0.1 film was investigated by AFM and the height profile of the surface was shown in Figure 3.27.

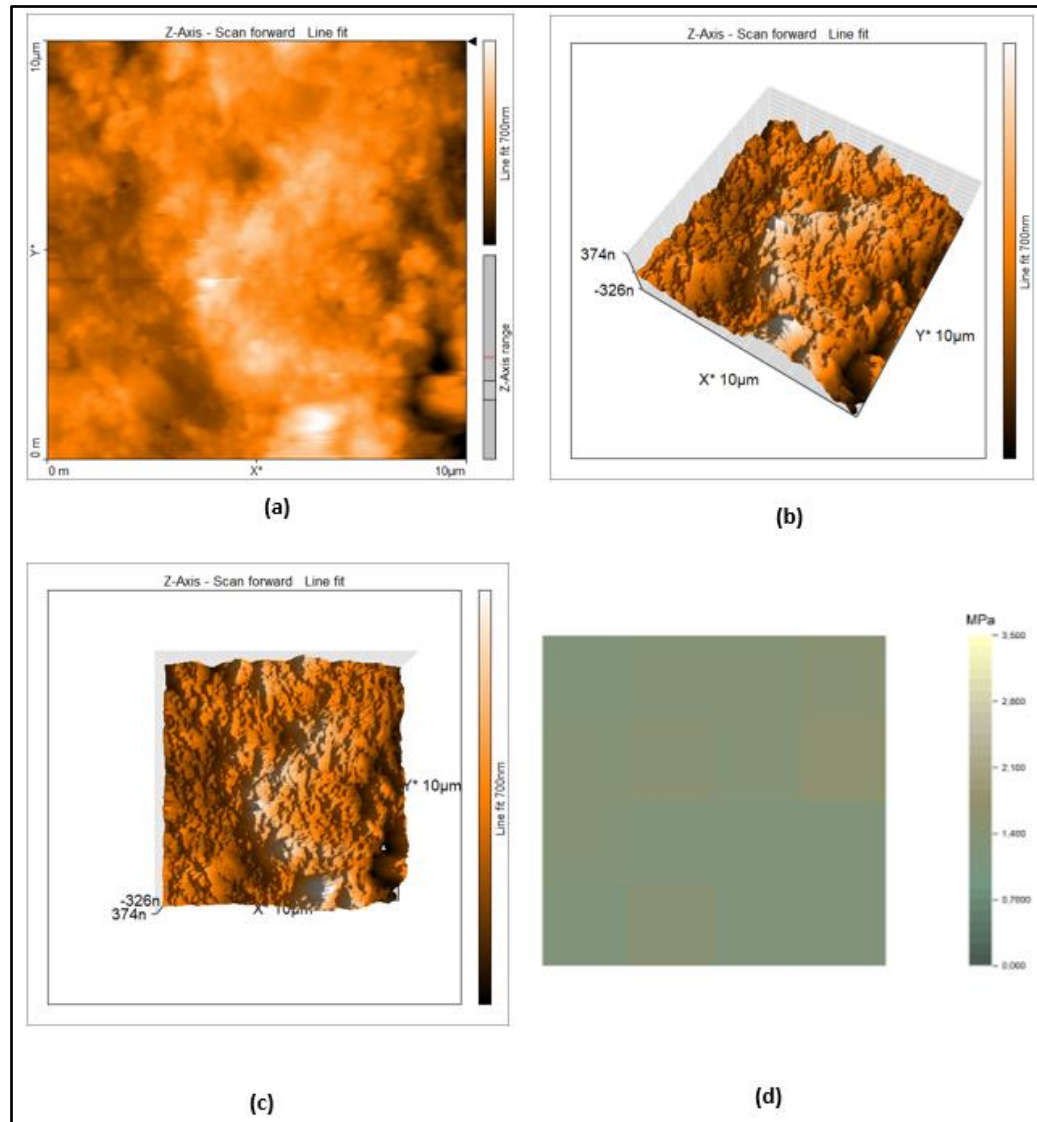


Figure 3.27: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+C60 0.1 composite film.

Topography of ABS/CF+C60 0.1 composite film has been investigated by AFM and the height profile of the surface were shown in Figure 3. 27a. The maximum height

value of the ABS with respect to start point height is obtained as 374nm and the minimum height value of the ABS with respect to start point height is nearly 326nm.

Figure 3. 27d displays the strength of the surface which is shown as a color map. The maximum Young's Modulus (E) value is extracted as 1.5335 MPa, the minimum E is found to be 1.2104 MPa and the average value of Young's Modulus is 1.3236 MPa.

The topography of ABS/CF+GR 0.1 film was investigated by AFM and the height profile of the surface was shown in Figure 3.28.

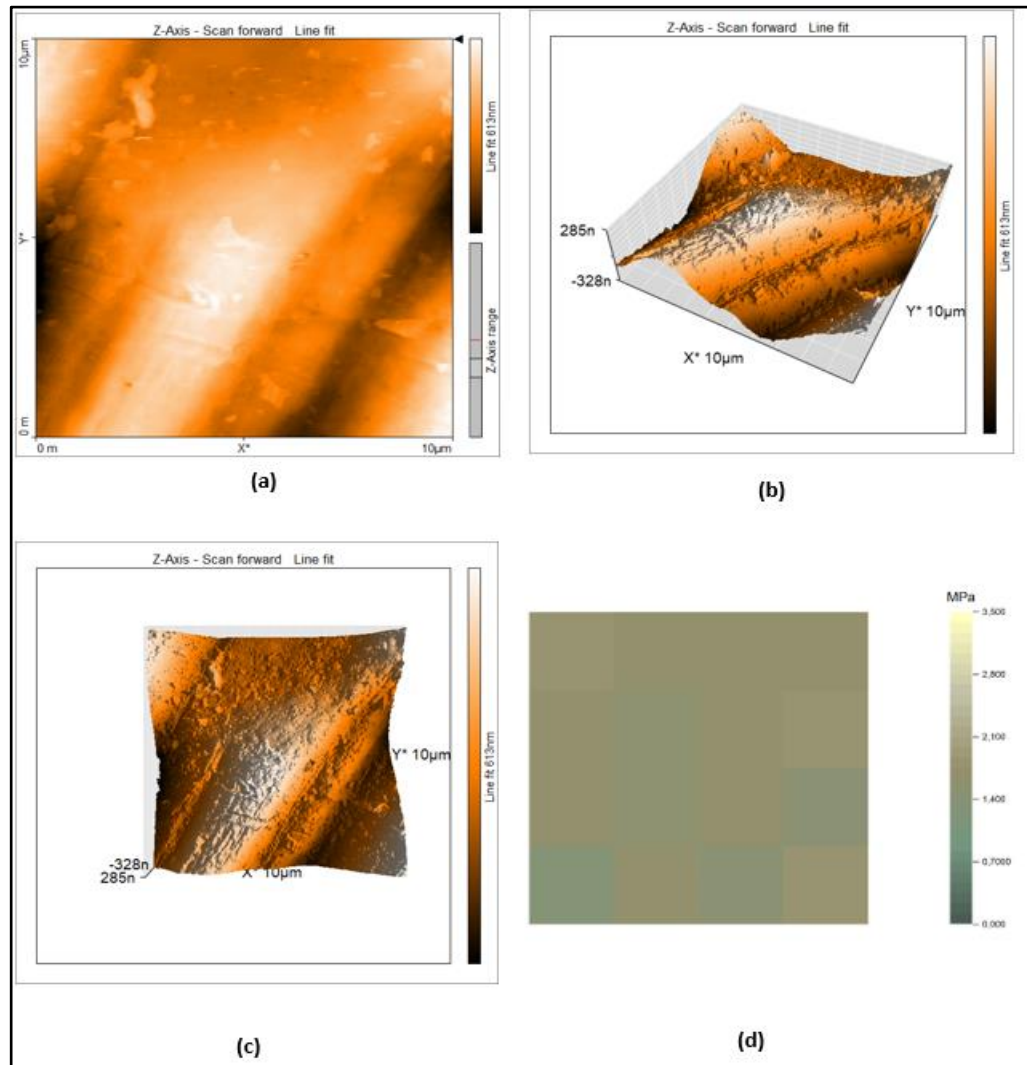


Figure 3.28: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+GR 0.1 composite film.

According to the topography image of ABS/CF+GR 0.1 (Figure 3. 28a) film and height profile of the surface (Figure 3. 28b), the maximum height value of the ABS for

start point height is 285nm and the minimum height value of the ABS for start point height is approximately 328nm.

Figure 3. 28d represents the strength of the surface which is shown as a color map. The maximum Young's Modulus (E) value is extracted as 1.7984 MPa, minimum E is estimated as 1.286 MPa. The average value of Young's Modulus is 1.6345 MPa.

The topography of ABS/CF+CNT 0.5 film was investigated by AFM and the height profile of the surface was shown in Figure 3.29.

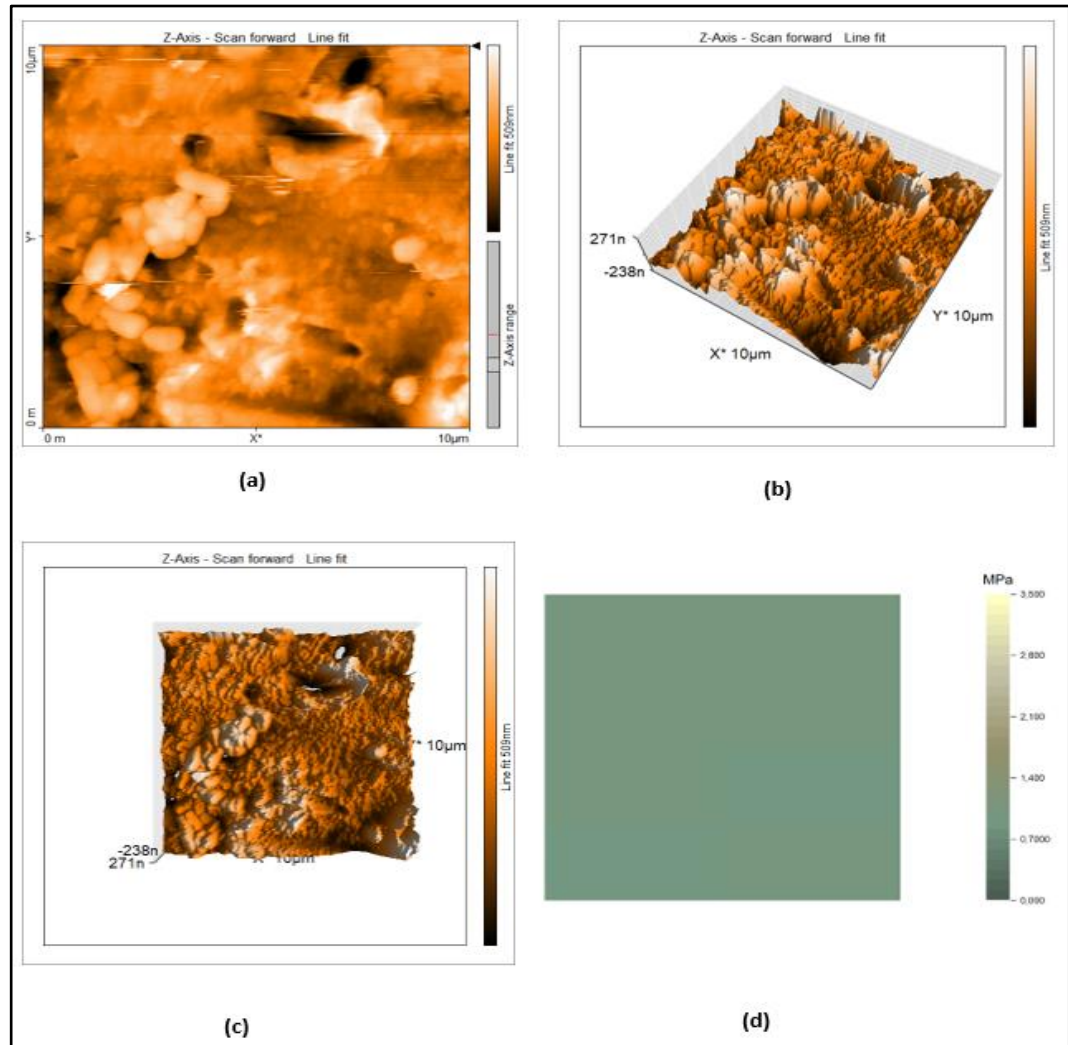


Figure 3.29: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+CNT 0.5 composite film.

The topography of ABS/CF+CNT 0.5 film has been investigated by AFM and the height profile of the surface. According to Figure 3. 29a, the maximum height value of the ABS to the start point height is 271nm and the minimum height value of the ABS with respect to start point height is 238nm.

Figure 3. 29d shows the strength of the surface which is shown as a color map. The maximum Young's Modulus (E) value is obtained as 1.037 MPa, minimum E is found to be 0.8179 MPa. The average value of Young's Modulus is 0.9535 MPa.

The topography of ABS/CF+C60 0.5 film was investigated by AFM and the height profile of the surface was shown in Figure 3.30.

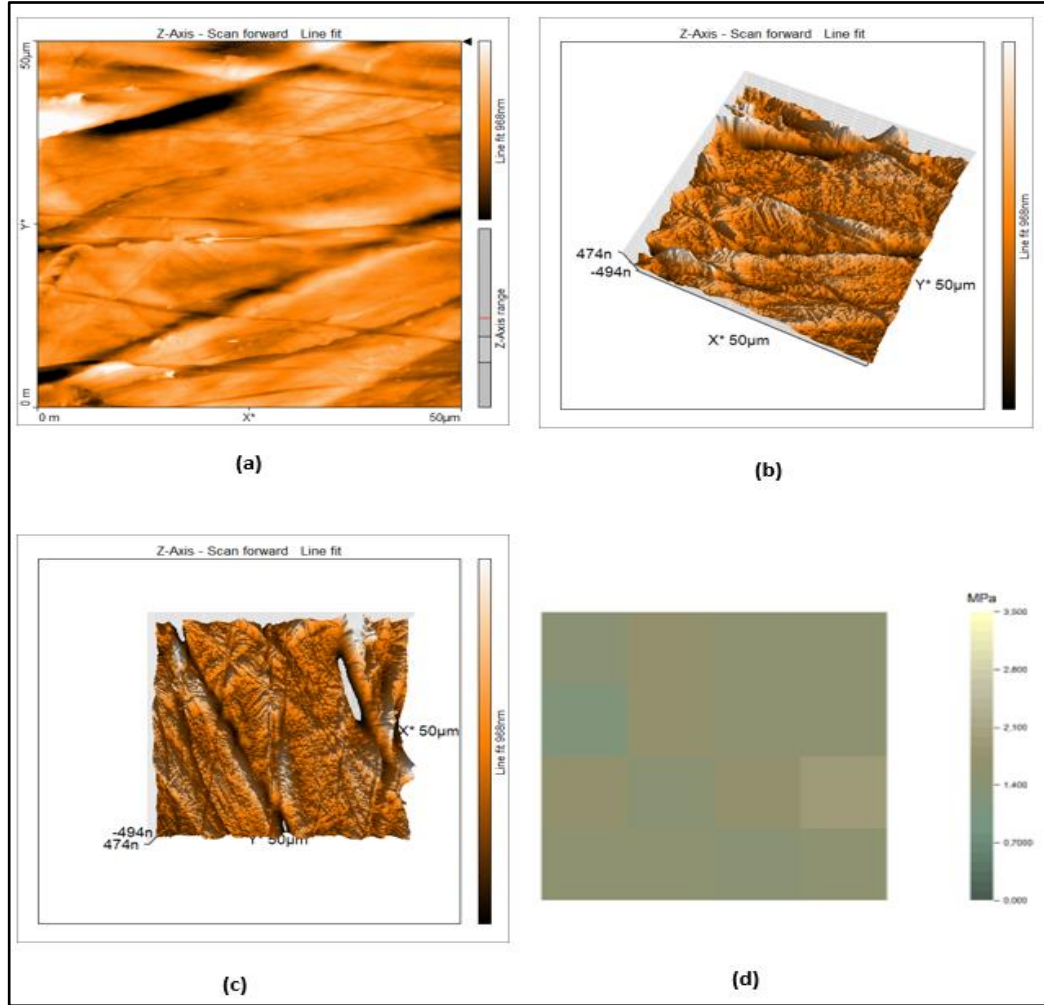


Figure 3.30: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+C60 0.5 composite film.

The topography of ABS/CF+C60 0.5 composite film was investigated by AFM and the height profile of the surface was shown in Figure 3. 30a. According to Figure 3. 30a, the maximum height value of the ABS for start point height is 474nm and the minimum height value of the ABS concerning start point height is 494nm.

Figure 3. 30d shows the strength of the surface which is shown as a color map. From Figure 3. 30d, the maximum Young's Modulus (E) value is extracted as 1.9113

MPa, and the minimum E is estimated as 1.2612 MPa. The average value of Young's Modulus is 1.5832 MPa.

The topography of ABS/CF+GR 0.5 film was investigated by AFM and the height profile of the surface was shown in Figure 3.31.

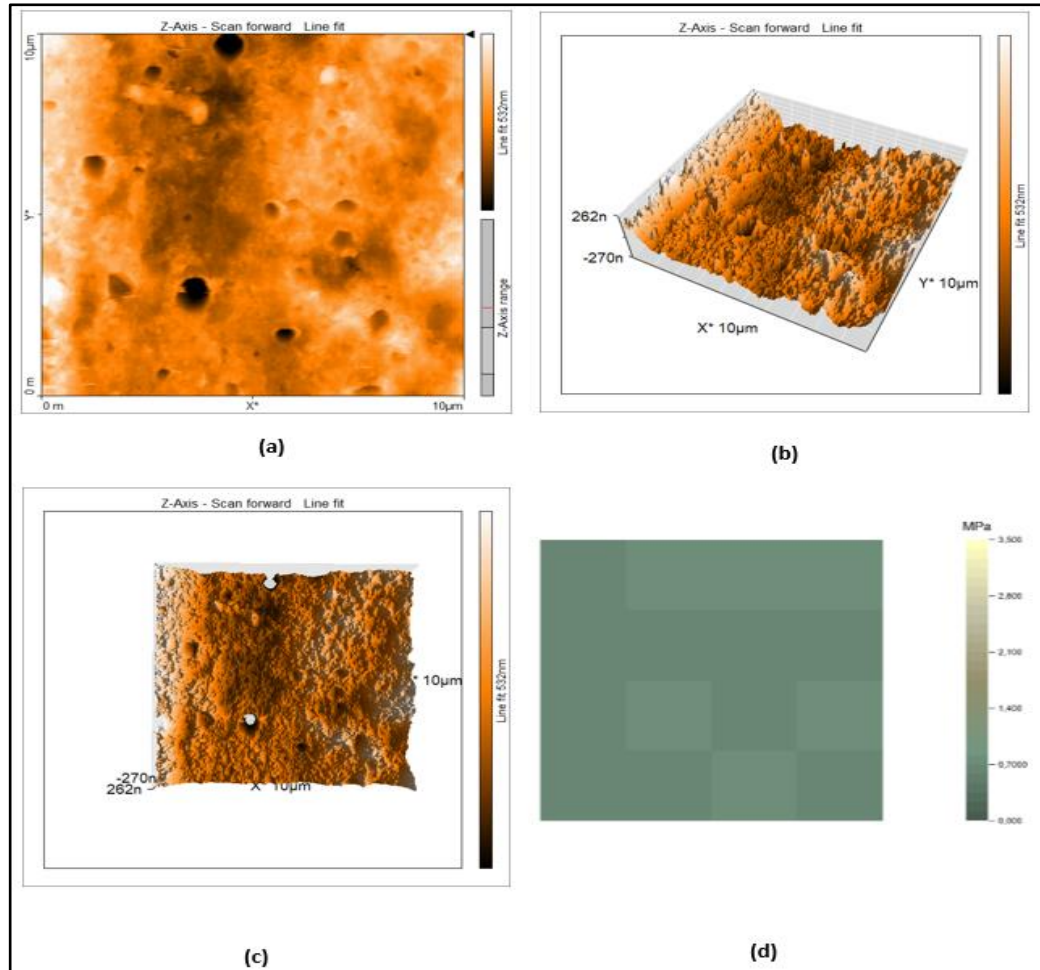


Figure 3.31: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+GR 0.5 composite film.

Figure 3. 31a displays the topography of ABS/CF+GR 0.5 composite film and the height profile of the surface. According to Figure 3. 31a, the maximum height value of the ABS with respect to start point height is obtained as 262nm and the minimum height value of the ABS to the start point height is 270nm.

From Figure 3. 31d, the maximum Young's Modulus (E) value is extracted as 0.781 MPa, and the minimum E is found as 0.5911 MPa. The average value of Young's Modulus is 0.6859 MPa.

The topography of ABS/CF+CNT 1.0 film was investigated by AFM and the height profile of the surface was shown in Figure 3.32.

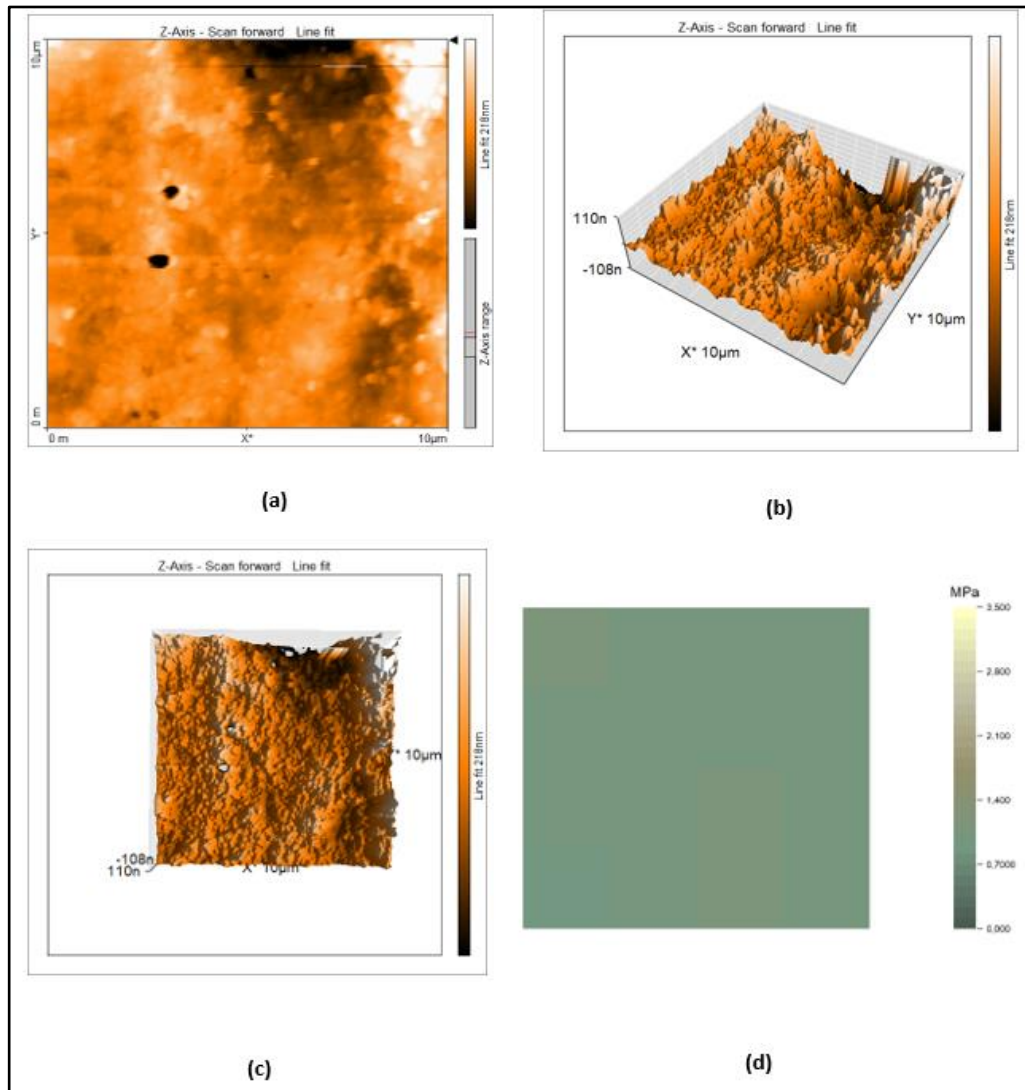


Figure 3.32: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+CNT 1.0 composite film.

Figure 3. 32a represents the topography of CF+CNT 1.0 film investigated by AFM and the height profile of the surface. The maximum height value of the ABS for start point height is 110nm and the minimum height value of the ABS for start point height is nearly 108nm.

Figure 3. 32d shows the strength of the surface which is shown as a color map. From Figure 3. 32d, the maximum Young's Modulus (E) value is extracted as 1.0888 MPa, and the minimum E is found to be 0.8197 MPa. The average value of Young's Modulus is 1.0187 MPa.

The topography of ABS/CF+C60 1.0 film was investigated by AFM and the height profile of the surface was shown in Figure 3.33.

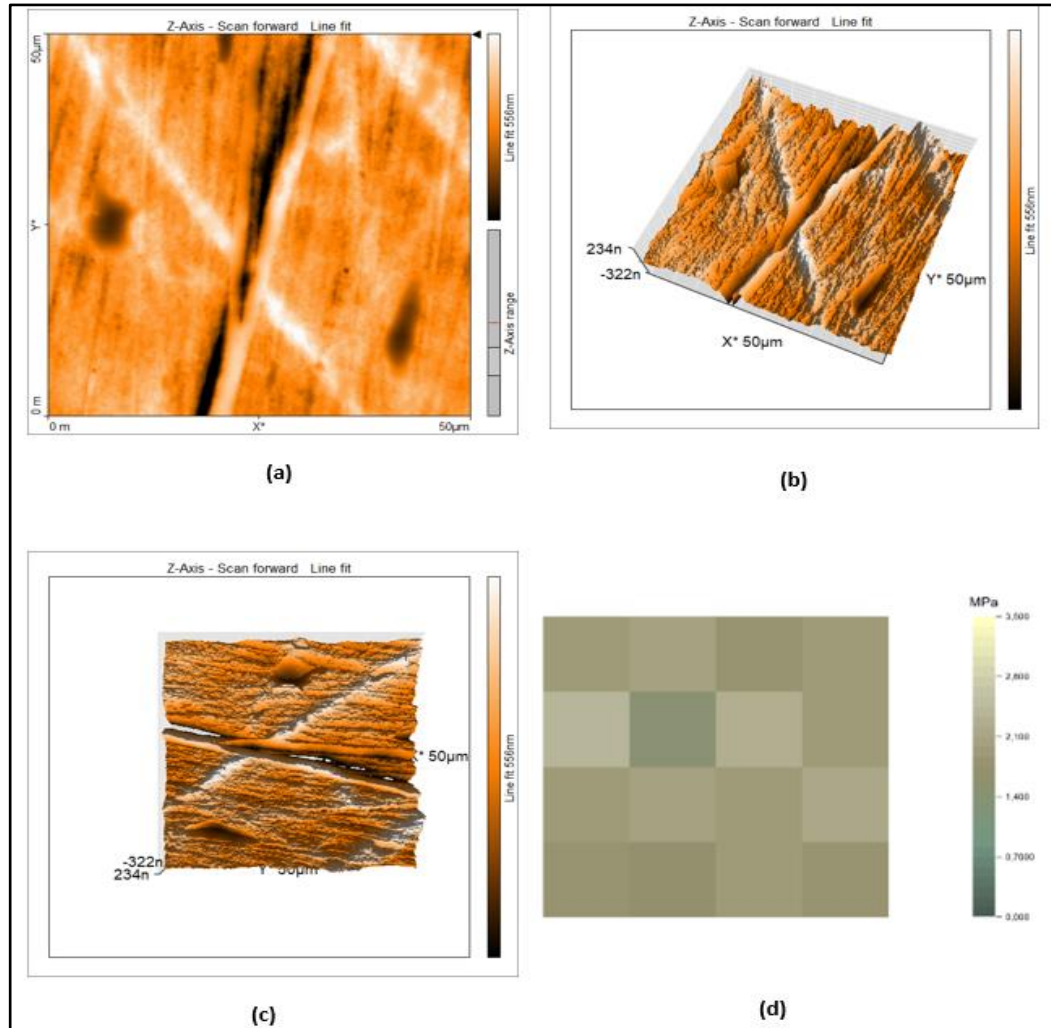


Figure 3.33: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+C60 1.0 composite film.

The topography of ABS/CF+C60 1.0 polymer was investigated by AFM and the height profile of the surface was shown in Figure 3. 33a. The maximum height value of the ABS concerning start point height is 234nm and the minimum height value of the ABS for start point height is 322nm.

Figure 3. 33d displays the strength of the surface which is shown as a color map. The maximum Young's Modulus (E) value is extracted as 2.3621 MPa, minimum E is obtained as 1.4506 MPa. The average value of Young's Modulus is 1.9477 MPa.

The topography of ABS/CF+C60 1.0 film was investigated by AFM and the height profile of the surface was shown in Figure 3.34.

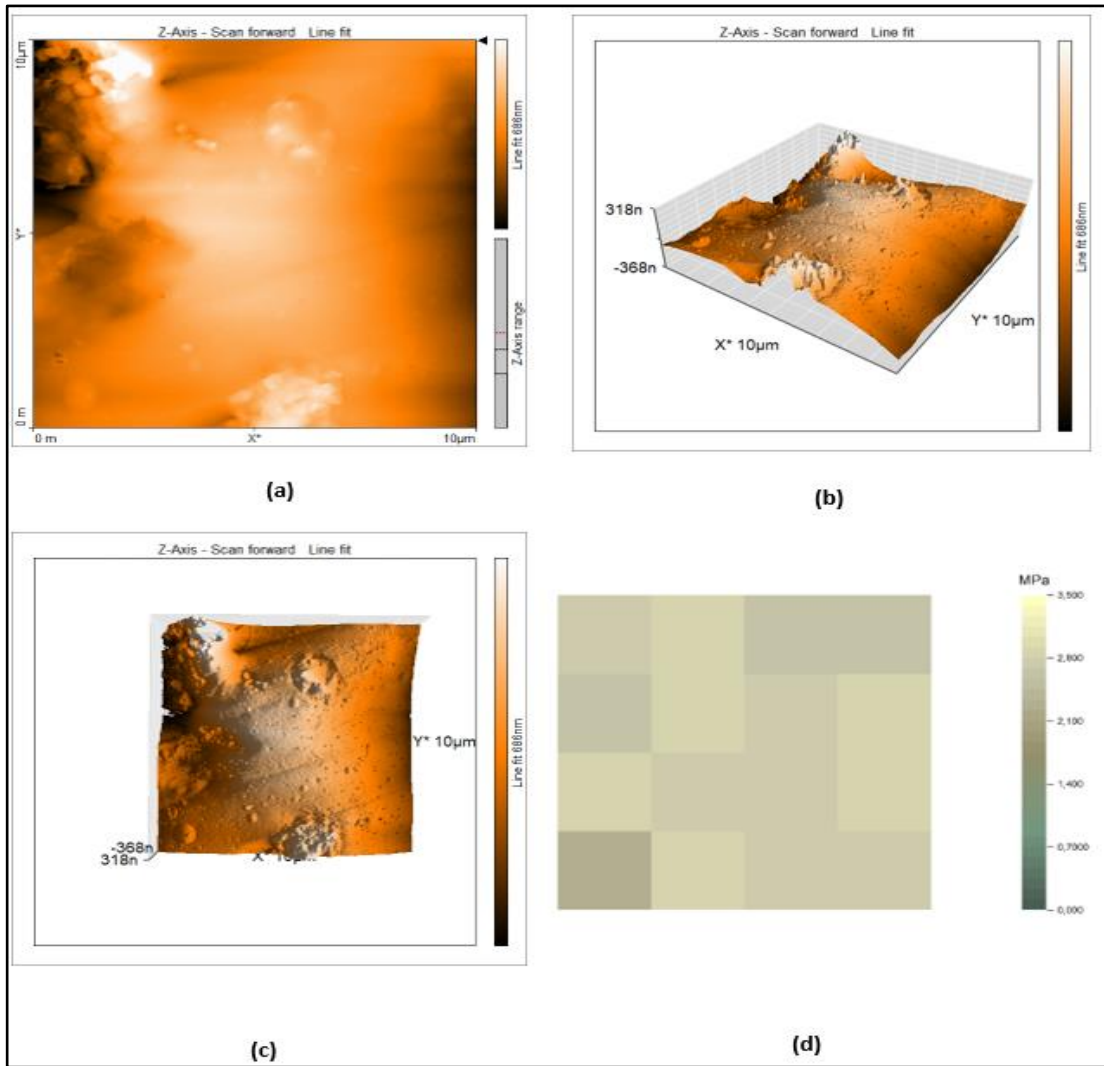


Figure 3.34: a) 2D Topography, b) 3D Topography, c) 3D Topography Top View, d) Young's Modulus mapping of ABS/CF+GR 1.0 composite film.

The topography of ABS/CF+GR 1.0 composite film and the height profile of the surface were shown in Figure 3. 34a. The maximum height value of the ABS to start point height is 318nm and the minimum height value of the ABS with respect to start point height is 368nm.

The strength of the surface is shown as a color map in Figure 3. 34d. The maximum Young's Modulus (E) value is extracted as 2.8642MPa, minimum E is found as 2.3303 MPa. The average value of Young's Modulus is 2.732 MPa.

3.7.5. Electrical Conductivity Investigations of Film Samples

Figure 3. 35 displays the nano-electrical characterization of ABS, ABS/CF, and ABS/CF+CNT composite films.

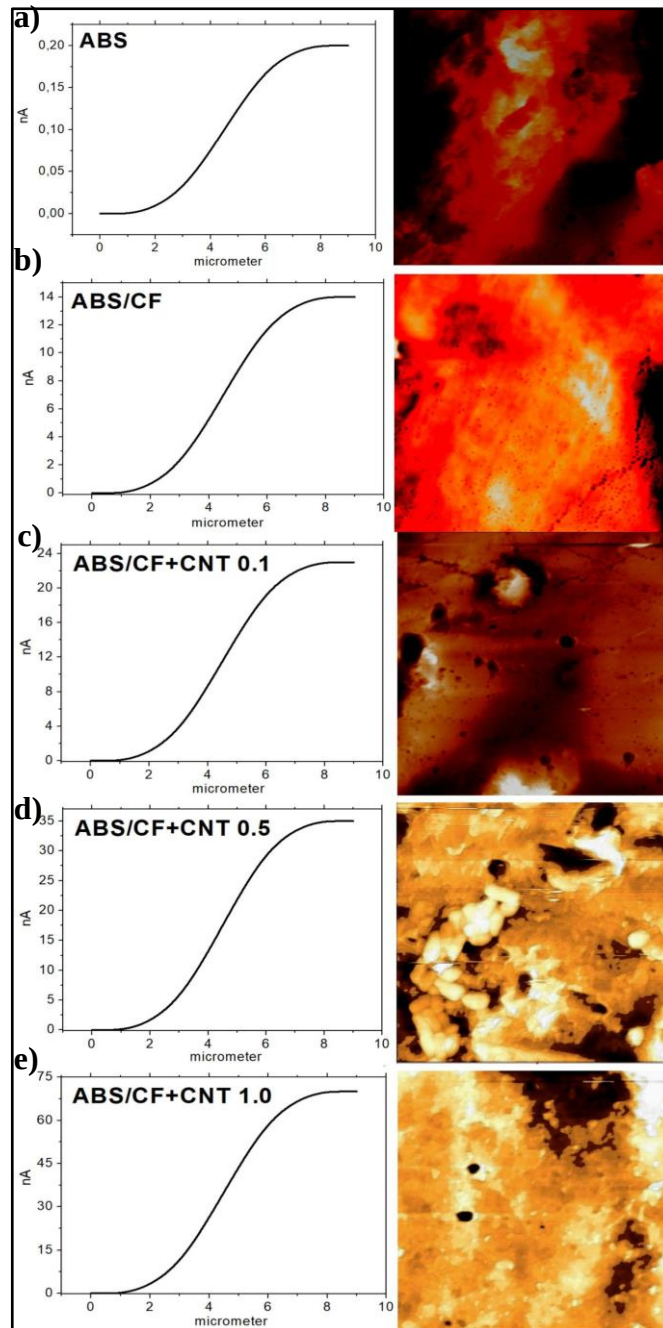


Figure 3.35: Electrical conductivity of a) ABS, b) ABS/CF, c) ABS/CF+CNT 0.1, d) ABS/CF+CNT 0.5, and e) ABS/CF+CNT 1.0 composite films.

Solely ABS has no electrical response to applied bias and the total current was found to be 0.2 nA. The conductivity of films has significantly increased as the CF and CNT component increases in composite films. The ABS/CF composite has yielded

14 nA current over the scanned area (100 μm^2). The CNT component has provided a substantial contribution to the overall conductivity of the ABS/CF/CNT. The total conductivity has been developed to the 20 to 30 and finally 60 nA for ABS/CF+CNT 0.1, ABS/CF+CNT 0.5, and ABS/CF+CNT 1.0 respectively. This may be attributed to the network formation of CNT through the samples and the formation of conductive pathways. The random orientation of the high aspect ratio of CNT as well as CNT may generate homogeneous distribution in the polymer matrix thereby causing an enhancement in total conductivity at contact points. This also confirms that suggested processing (compression molding) exhibits advantages in terms of total conductivity as compared to other processing methodologies.

Figure 3. 36 shows the nano-electrical characterization of ABS, ABS/CF, and ABS/CF+C60 composite films.

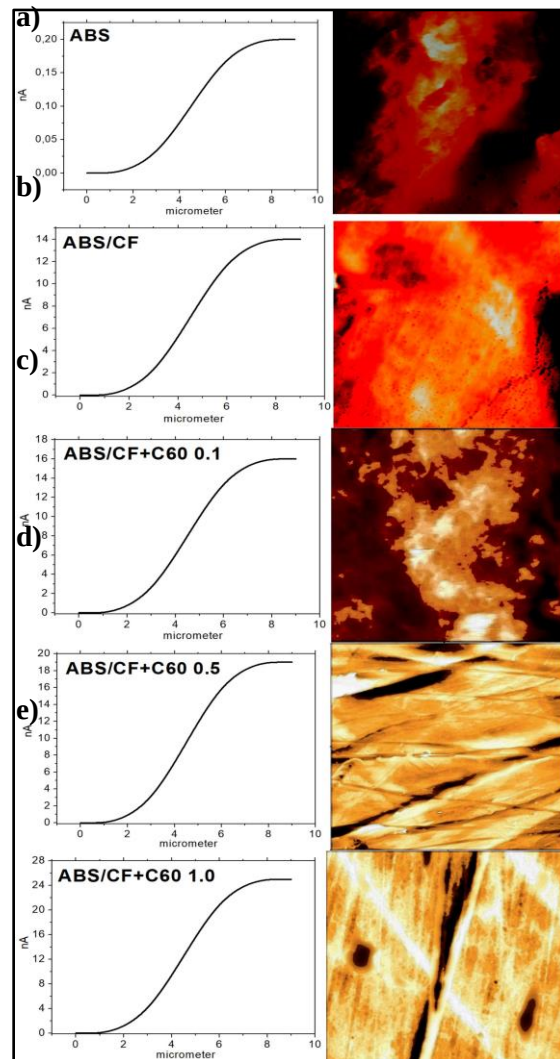


Figure 3.36: Electrical conductivity of a) ABS, b) ABS/CF, c) ABS/CF+C60 0.1, d) ABS/CF+C60 0.5, and e) ABS/CF+C60 1.0 composite films.

The conductivity of ABS/CF composite films was remarkably improved with the addition of fullerene. C60 component has provided a moderate contribution to the overall conductivity of the ABS/CF+C60. From Figure 3. 36, Total conductivity was found to be in narrow range between 16 to 18 and finally 24 nA for ABS/CF+C60 0.1, ABS/CF+C60 0.5 and ABS/CF+C60 1.0 respectively. This may refer to the random and independent formation of C60 islands or agglomerates through the samples and without conductive pathways. This confirms that conductive pathway formation requires high aspect ratio carbon materials rather than C60. As seen in conductive AFM images of ABS/CF/C60 0.5 and ABS/CF/C60 1.0, CF caused major paths over the samples which contribute to a total conductivity of more than C60.

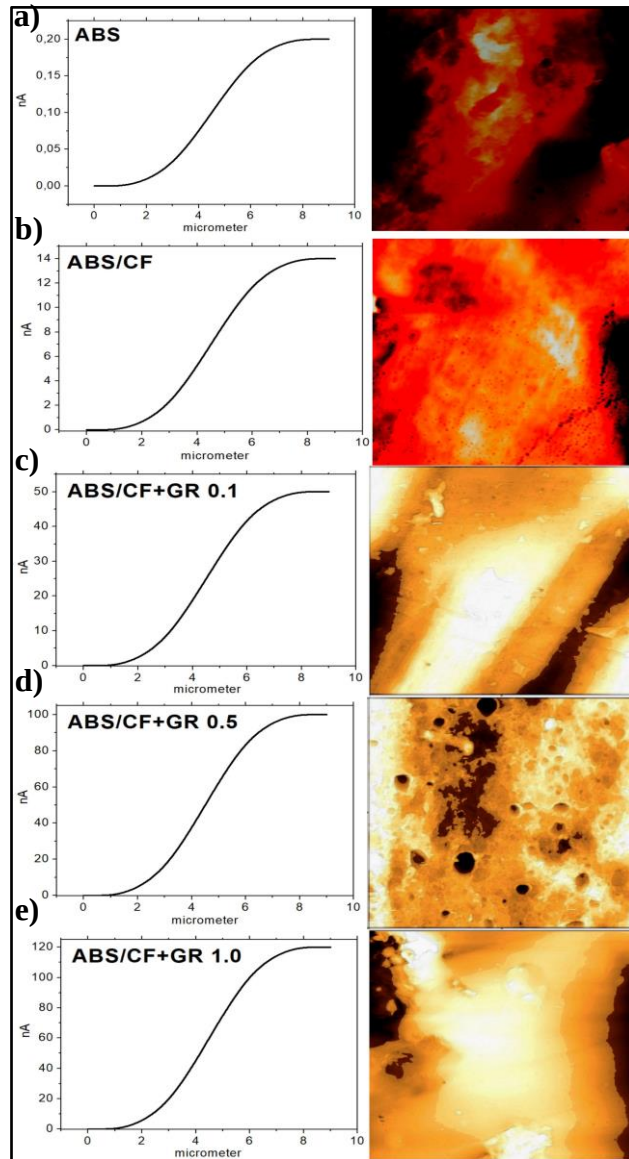


Figure 3.37: Electrical conductivity of a) ABS, b) ABS/CF, c) ABS/CF+GR 0.1, d) ABS/CF+GR 0.5, and e) ABS/CF+GR 1.0 composite films.

Figure 3. 37: represents the nano-electrical characterization of ABS, ABS/CF, and ABS/CF+GR composite films.

The conductivity of films has slightly increased as the CF and GR components increased. The integration of GR nanostructures displayed a substantial contribution to the overall conductivity of the ABS/CF composites. The total conductivity of composite films exhibited an increasing trend as the loading amount of GR increased. The electrical conductivities of ABS/CF+GR 0.1, ABS/CF+GR 0.5, and ABS/CF+GR 1.0 samples reached 50, 100, and 120 nA, respectively. The inclusion of GR led to a jump up to higher levels in the conductive network of ABS/CF structure thanks to the synergistic action of GR along with the CF phase in terms of the formation of conductive pathways in the composite structure. The plate-like structured geometry of graphene plays an important role in the establishment of conductive paths between high aspect ratio CF and the high surface area of GR layers.

4. CONCLUSIONS

In this thesis study, we aimed the establishment synergistic interactions between two carbon-based additives in the ABS phase by means of mechanical, thermal, and electrical behaviors. One of those additives is in micron size and fiber form while the other is nano-sized with a tubular shape. The influence of the working mechanism of these two different scales (micron and nano size) was investigated in hybrid form compared with the individual addition of CF. It was aimed to confer electrical conductivity with the incorporation of CNT, GR, and C60 while attaining higher mechanical characteristics thanks to the achievement of synergistic interaction between CF and carbon-based conductive additives.

Tensile test findings revealed that nano-filler inclusions led to higher strength values with respect to ABS/CF, especially for an increasing amount of C60. An increasing tensile strength trend was observed with lower loading amounts of CNT and GR (0.1% and 0.5%). Further addition of these nanoparticles yields a remarkable reduction in strain values which is stem from the formation of agglomerates for 1.0% content. ABS/CF/carbonaceous ternary composites showed a remarkable improvement in tensile modulus compared to ABS/CF binary composites as a general trend. As an overall result, nano-dimensional carbon additives donated a multi-functional character to the CF-reinforced ABS composite system, while increasing both tensile strength and strain values.

Both unfilled ABS and ABS/CF composite gained impact resistance after the inclusion of carbon-based additives. GR and CNT-containing samples exhibited higher impact strength compared to composites involving C60. The shore hardness parameter of ABS was slightly increased with the highly filled CNT, GR, and C60 inclusions. The best wear performance was observed for FR-filled composites due to their plate-like geometry. C60 and CNT additions caused no positive effect on the tribological property of neat ABS.

DMA analysis implied that the storage modulus and loss factor of unfilled ABS was remarkably improved after the loadings of additives. Similarly, the highest results were obtained for composites involving CNT, GR, and C60 with 0.5% content. Glass transition temperature of ABS shifted to a lower temperature after being incorporated with CF and nano-additives.

Improvement of thermal stability of ABS with the help of synergistic interactions of CF and carbon fillers was investigated from TGA curves in which the decomposition rates of composites declined after the integration of additives. Additionally, the char yield of composites was found to be higher compared to pristine ABS.

According to AFM studies of composite samples, the maximum value and more homogeneous distributions for Young's modulus were reached as ABS/CF samples were loaded with 0.5% of nano-additives. Additionally, the maximum pull-out force displayed enhancement by the increase in CNT, GR, and C60 compositions. Based on the conductivity characterizations by AFM, an ohmic behavior was obtained in the current-voltage characteristics of ABS thanks to the incorporation of CNT, GR, and C60 into the non-conductive ABS structure.

AFM characterization of film samples revealed that the maximum electrical response was achieved for GR-loaded composites thanks to the plate-like structure of graphene nano-sheets. GR layers promoted the electrical conductivity in composite structure by the formation of a conductive network. ABS/CF+CNT composite films also gave remarkable electrical properties since high aspect ratio CF and CNT exhibited synergistic interactions with the help of their random distribution in the ABS phase in film form in contrast to bulk form in which they oriented in one direction. The dispersion efficiency of additive structures increased as the addition rate of additives increased. The aggregation rate decreased with the increase in the amount of CNT and C60, and the additives followed a homogeneous dispersion approach in the polymer phase. The GR additive material is well adapted to the surface, and it can be understood from the topography images that it improved the surface in the material topography.

Additionally, as Young's Modulus values from AFM measurements were investigated, CF caused a serious decrease in strength for ABS polymer. In addition, when the mechanical performance of the additives was examined, it was understood that GR was found to be a successful strength enhancer. The strength enhancement of the CNT additive material was obtained as a lower performance compared to the C60 and GR additives. CNT inclusions adversely affected the surface quality and uniformity compared to other additives since similar strength values could not be read at every point of the material.

As the SEM micrographs of composites were examined, the high filling ratio of carbonaceous fillers resulted in a decrease in the homogeneity of dispersion due to the formation of bundles and agglomerates. Composites containing CF and low amounts of CNT, GR, and C60 exhibited morphologies with homogeneous dispersion of added fillers into the ABS phase. ABS/CF+ 0.5 CNT, ABS/CF+ 0.5 C60, and ABS/CF+ 0.5 GR samples yielded the optimum results in the case of investigated properties since the synergistic action between CF and nano-additives was achieved for this loading level.

CF reinforced ABS composites containing carbonaceous additives have the potential to be the option for the development of automotive composite parts having thermally stable, easily processable, mechanically strong, and electrostatic behaviors.

According to investigated findings, the overall performances of CF-reinforced ABS composites were enhanced with the additions of carbon-based nano-fillers in the order of plate-like GR (2D) > tubular CNT (1D) > spherical C60 (0-D) structural geometries.

The targeted application of the optimum formulations would be the automotive sector since it has multifunctional performance. [72]

REFERENCES

- [1] Kulshreshtha A.K., (1993), “A review of commercial polyblends based on PVC, ABS, and PC. Polymer-Plastics Technology and Engineering”, 32 (6), 551-578.
- [2] Moore J.D., (1973), “Acrylonitrile-butadiene-styrene (ABS)-a review. Composites”, 4 (3), 118-130.
- [3] Olivera S., Muralidhara H.B., Venkatesh K., Gopalakrishna, K. and Vivek, C.S., (2016), “Plating on acrylonitrile–butadiene–styrene (ABS) plastic: a review. Journal of materials science”, 51 (8), 3657-3674.
- [4] Kim H. and Woo S.S., (1995), “Recent Developments and Perspectives in ABS Resin”, Polymers and Other Advanced Materials, 185-188.
- [5] Mazumdar K., (2002), “Composites Manufacturing Materials Product and Process Engineering”, CRC Press LLC, Boca Raton.
- [6] Eberhardt C., Clarke A., Wincent M., Giroud T., Flouret S., (2001),” Composite Science and Technology”, 61, 1961.
- [7] Woodhoms R.T., Xanthos M., (1978), “In Handbook of Fillers and Reinforcement for Plastic”, Katz, H. S. J.V., Milewski, J. V. Eds., Van Nostrand Reinhold, New York.
- [8] Sabu T., Kuruvilla J., Malhotra K., Koichi G., Sreekala M., (2012),” Introduction to Polymer Composites”, Wiley VCH, Weinheim, Germany.
- [9] Visakh M., Thomas S., Chandra K., Mathew P., (2013), “Advances in Elastomers II: Composites and Nanocomposites”, Springer, Heidelberg, Berlin.
- [10] Thwe M.M., Liao K., (2003), “Preparation and Properties of Kenaf Bast Fiber Filled (Plasticized) Poly (Lactic Acid) Composites”, Composite Science and Technology, 63, 375.
- [11] Huang J. C. Wang M. S., (1989), “Recent Advances in ABS/PC Blends, Advances in Polymer Technology”, John Wiley & Sons, Inc., Vol. 9 (4), 293-299.
- [12] Polli H., Pontes L. A. M., Araujo, A. S., Barros J. M., F. Fernandes Jr. V. J., (2009), “Degradation Behavior and Kinetic Study of Abs Polymer, Journal of Thermal Analysis and Calorimetry”, 95 (1), 131-134.
- [13] Wang S., Hu, Y., Song L., Wang Z., Chen Z. Fan Z., (2002), “Preparation and thermal properties of ABS/montmorillonite nanocomposite, Polymer Degradation and Stability”, 77, 423-426.
- [14] Aoki Y., (1981), “Dynamic Viscoelastic Properties of ABS Polymers in the Molten State. II. Relaxation Spectra”, J. Rheol. 25, 351 – 357.

- [15] Huang C.Y., Wu C.C., (2000), "The EMI shielding effectiveness of PC/ABS/nickel-coated carbon-fibre composites", *European Polymer Journal*, 36, 2729-2737.
- [16] Krache R. Debbah I., (2011), "Some Mechanical and thermal properties of PC/ABS blends", *Materials Sciences and Applications*, 2, 404-410.
- [17] Cheng F. Li, H. Jiang W., Chen D., (2006), "Properties of Compatibilized Nylon 6/ABS Polymer Blends", *Journal of Macromolecular Science, Part B: Physics*, 45:4, 557-561.
- [18] Tzeng S. S., Chang F. Y., (2001), "EMI shielding effectiveness of metal-coated carbon fiber-reinforced ABS composites", *Materials Science and Engineering A302* 258-267.
- [19] Liang X., Ling L., Lu C., Liu L., (2000), "Resistivity of carbon fibers / ABS resin composites", *Materials Letters*, 43, 144-147.
- [20] Lu C., Xiaotian L., Jianc H., Xiancjun M., (1996), "Electrical Conductivity of Carbon Fibers/ABS Resin Composites Mixed with Carbon Blacks", *Journal of Applied Polymer Science*, John Wiley & Sons, Inc., 62, 2193-2199,
- [21] Lu G., Li L., Jiang H., (1996), "Electrical and shielding properties of abs resin filled with nickel-coated carbon fibers", *Composites Science and Technology*, Elsevier Science Limited, 56, 193-200.
- [22] Ogi K., Nishikawa T., Okano Y., Taketa I., (2007), "Mechanical properties of ABS resin reinforced with recycled CFRP", *Adv. Composite Mater.*, 16 (2), 181-194.
- [23] Yao S. S., Jin F. L., Rhee K. Y., Hui D., Park S. J., (2018), "Recent advances in carbon-fiber-reinforced thermoplastic composites: A review", *Composites Part B*, 142, 241-250.
- [24] Singh R., Sandhu G. S., Penna R., Farina I., (2017), "Investigations for thermal and electrical conductivity of ABS-graphene blended prototypes", *Materials*, 10, 881.
- [25] Wang X., Jiang M., Zhou Z., Gou J., Hui D., (2017), "3D printing of polymer matrix composites: A review and prospective", *Composites Part B*, 110, 442-458.
- [26] Al-Saleh M. H., Al-Anid H. K., Husain Y. A., El-Ghanem H. M., Jawad S. A., (2013), "Impedance characteristics and conductivity of CNT/ABS nanocomposites", *Journal of Physics D: Applied Physics*, 46, 305-385.
- [27] Pang H., Xu L., Yan D. X., Li Z. M., (2014), "Conductive polymer composites with segregated structures", *Progress in Polymer Science*, 39, 1908-1933.
- [28] Schmitz d. P., Silva T. I., Ramona S. D. A. S., Barra G. M. O., Pegoretti A., Soares B. G., (2018), "Hybrid composites of ABS with carbonaceous fillers for

electromagnetic shielding applications”, *Journal of Applied Polymer Science* 315, 46546.

- [29] Jyoti J., Singh B. P., Aryaa A. K., Dhakatea S. R., (2016), “Dynamic mechanical properties of multiwall carbon nanotube reinforced ABS composites and their correlation with entanglement density, adhesion, reinforcement and C factor”, *RSC Advances*, 6, 3997-4006.
- [30] Jogi B. F., Sawant M., Kulkarni M., Brahmanekar P. K., (2012), “Dispersion and Performance Properties of Carbon Nanotubes (CNTs) Based Polymer Composites: A Review”, *Journal of Encapsulation and Adsorption Sciences*, 2, 69-78.
- [31] Srinivas G., Zhu Y., Piner R., Skipper N., Ellerby M., Ruoff R., (2010). “Synthesis of graphene-like nanosheets and their hydrogen adsorption capacity”, *Carbon*, 48 (3), 630-635.
- [32] Shinar J., Vardeny Z.V., Kafafi Z.H., (2000), “Optical and electronic properties of fullerenes and fullerene-based materials”, Marcel Dekker, New York.
- [33] Langa F., François J., (2012), “Fullerenes: Principles and applications”, 2nd edition, RCS Publishing, Cambridge.
- [34] Nierengarten J.F., (2004), “Fullerene-containing macromolecules for materials science applications”, *Carbon*, 42, 1077–1083.
- [35] Wang C., Guob Z. X., Fua S., Wub W., Zhu D., (2004), “Polymers containing fullerene or carbon nanotube structures”, *Progress in Polymer Science*, 29, 1079-1141.
- [36] Burchell T.D., (1999), “Carbon materials for advanced technologies”, *Material Science and Technology*, Pergamon, Amsterdam.
- [37] Badamshina E.R., Gafurova E.R., (2008), “Characteristics of fullerene C60-doped polymers”, *Polymer Science Series B*, 50, 215-225.
- [38] Liu H., Song P., Fang Z., Shen L., Peng M., (2010), “Thermal degradation and flammability properties of HDPE/EVA/C60 composites”, *Thermochemica Acta*, 506, 98-101.
- [39] Zhao L., Guo Z., Cao Z., Zhang T., Fang Z., Peng M., (2013), “Thermal and thermo-oxidative degradation of high-density polyethylene/fullerene composites”, *Polymer Degradation Stability*, 98, 1953-1962.
- [40] Wan D., Wang Y., Wen X., Qiu J., Jiang Z., Tan H., Tang T., (2012), “The rheological, thermostable, and mechanical properties of polypropylene/fullerene C60 composites with improved interfacial interaction”, *Polymer Engineering and Science*, 52, 1457-1463,

- [41] Fang Z., Song P., Tong L., Guo Z., (2008), "Thermal degradation and flame retardancy of polypropylene/C60 composites", *Thermochemica Acta*, 473, 106-108.
- [42] Zuev V. V., Ivanova Y. G., (2012), "Mechanical and electrical properties of polyamide-6-based nanocomposites reinforced by fulleroid fillers", *Polymer Engineering & Science*, 52 (6), 1206-1211.
- [43] Ouyang J., Goh S.H., (2012), "Crystallization, morphology, and dynamic mechanical behavior of supramolecular [60] fullerene-containing poly (ethylene-co-acrylic acid)", *Fullerenes Nanotubes Carbon Nanostructures*, 10, 183-196.
- [44] Akhanova N., Yerlanuly Y., Batryshev D., Kulsartov T., Chikhray Y., Ramazanov T., Veziroglu A., Schur D., Kang W., Gabdullin M., (2021), "The study of deuterium permeability of film-forming inhibitors with the addition of fullerenes", *International Journal of Hydrogen Energy*, 46 (10), 7426-7431.
- [45] Shi S., Khemani K. C., Li Q., Wudl F., (1992), "A polyester and polyurethane of diphenyl C61: retention of fulleroid properties in a polymer", *Journal of the American Chemical Society*, 114 (26), 10656-10657.
- [46] Tayfun U., Akar A.O., (2021), "The use of fullerene in thermoplastic matrices on polymeric composites applications", *Advances in Materials Science Research*, Nova Science Publishers, 48, 187-211.
- [47] Alekseeva O. V., Bagrovskaya N. A., Noskov A. V., (2018), "Effect of C60 filling on structure and properties of composite films based on polystyrene", *Arabian Journal of Chemistry*, 11, 1160-1164.
- [48] Hassanien A., Atta A. A., Ward A., M. A. Ahmed. E., Alsubaie A., El-Nahass, M. M., & Altalhi T., (2019), "Investigation of structural, electrical, and optical properties of chitosan/fullerene composites", *Materials Research Express*.
- [49] Roy, N., Sengupta, R. and Bhowmick, A. K., (2012), "Modifications of carbon for polymer composites and nanocomposites", *Progress in Polymer Science*, 37, 781-819.
- [50] Tayfun U., Kanbur Y., Abaci U., Guney H.Y., Bayramli E., (2015), "Mechanical, flow, and electrical properties of thermoplastic polyurethane/fullerene composites: Effect of surface modification of fullerene", *Composites Part B: Engineering*, 80, 101-107.
- [51] Kanbur Y., Tayfun U., (2019), "Development of multifunctional polyurethane elastomer composites containing fullerene: Mechanical, damping, thermal, and flammability behaviors", *Journal of Elastomers & Plastics*, 51(3), 262-279.
- [52] Zhang M., Wang X., Bai Y., Li Z., & Cheng B., (2017), "C60 as fine fillers to improve poly (phenylene sulfide) electrical conductivity and mechanical property", *Scientific Reports*, 7 (1).

- [53] Gerasin V.A., Antipov E.M., Karbushev V.V., Kulichikhin V.G., Karpacheva G.P., Talroze R.V., & Kudryavtsev Y.V., (2013), “New approaches to the development of hybrid nanocomposites: from structural materials to high tech applications”, *Russian Chemical Reviews*, 82, 303.
- [54] Marom G., Fischer S., Tuler F.R., Wagner H.D., (1978), “Hybrid effects in composites: conditions for positive or negative effects versus rule-of-mixtures behaviour”, *Journal of Materials Science*, 13(7), 1419-1426.
- [55] Sanusi O.M., Benelfellah A., & Hocine N.A., (2020), “Clays and carbon nanotubes as hybrid nanofillers in thermoplastic-based nanocomposites – a review”, *Applied Clay Science*, 185, 105408.
- [56] Szeluga U., Kumanek B., & Trzebicka B., (2015), “Synergy in hybrid polymer/nanocarbon composites”, A review. *Composites Part: A Applied Science and Manufacturing*, 73, 204–231.
- [57] Ozdil N., Kayseri G.O., Menguc G.S., (2012), “Analysis of abrasion characteristics in textiles”, In: Adamiak, M. (Eds) *Abrasion Resistance of Materials*. Intech, Rijeka.
- [58] Polat S., Sun Y., Çevik E., Colijn H., Turan M. E., (2019), “Investigation of wear a corrosion behavior of graphene nanoplatelet-coated B4C reinforced Al–Si matrix semi-ceramic hybrid composites”, *Journal of Composite Materials*, 53 (25), 3549-3565.
- [59] Mohamed S., Tirkes S., Akar A., Tayfun U., (2020), “Hybrid nanocomposites of elastomeric polyurethane containing halloysite nanotubes and POSS nanoparticles: Tensile, hardness, damping and abrasion performance”, *Clay Minerals*, 55 (4), 281-292.
- [60] Brown R., (1999), “Handbook of Polymer Testing-Physical Methods”, Shawbury: Rapra Technology.
- [61] Wang S., Capoen L., D’hooge D.R., Cardon L., (2018), “Can the melt flow index be used to predict the success of fused deposition modelling of commercial poly (lactic acid) filaments into 3D printed materials?”, *Plastics, Rubber and Composites*. 47(1), 9-16.
- [62] Nidzad M., Masood S.H., Sbarski I., Groth A., (2009), “Study of melt flow analysis of an ABS-iron composite in fused deposition modeling process”, *Tsinghua Science & Technology*, 14(S1), 29-37.
- [63] Alhallak L.M., Tirkes S., Tayfun U., (2020), “Mechanical, thermal, melt-flow and morphological characterizations of bentonite-filled ABS copolymer”, *Rapid Prototyping Journal*, 26 (7), 1305-1312.

- [64] Kasgoz A., Akın D., Durmus A., (2014), “Rheological and electrical properties of carbon black and carbon fiber filled cyclic olefin copolymer composites”, *Composites Part B: Engineering*, 62, 113-120.
- [65] Taghinejad S.F., Behrouzi M., Asiaban S., (2012), “Investigation of the rheological behavior of titanium dioxide pigmented acrylonitrile–butadiene–styrene polymer”, *Journal of Applied Polymer Science*, 124 (3), 2016-2021.
- [66] Suzuki M., Wilkie CA., (1995), “The thermal degradation of acrylonitrile–butadiene–styrene terpolymer as studied by TGA/FTIR”, *Polymer Degradation and Stability*, 47, 217-221.
- [67] Yang MH., (2001), “The thermal degradation of acrylonitrile–butadiene–styrene terpolymer under various gas conditions”, *Polymer Testing*, 19, 105-110.
- [68] Polli H., Pontes L., Araujo A., Barros J., Fernandes V., (2009), “Degradation behavior and kinetic study of ABS polymer”, *Journal of Thermal Analysis and Calorimetry*, 95, 131-134.
- [69] Ahmed S.A., Tirkes S., Tayfun U., (2020), “Reinforcing effect of polyurethane sizing on properties of acrylonitrile–butadiene–styrene composites involving short carbon fiber”, *SN Applied Sciences*, 22-24.
- [70] Dul S., Fambri L., Pegoretti A., (2016), “Fused deposition modelling with ABS–graphene nanocomposites”, *Composites Part A: Applied Science and Manufacturing*, 85, 181-191.
- [71] Rahman A., Ali I., Al Zahrani S. M., Eleithy R. H., (2011), “A review of the applications of nanocarbon polymer composites”, *Nano*, 6 (3), 185-203.
- [72] Akar A.O., Yildiz U.H., Tirkes S., U. Tayfun., Hacıvelioğlu F., (2022), “Influence of carbon nanotube inclusions to electrical, thermal, physical and mechanical behaviors of carbon-fiber-reinforced ABS composites”, *Carbon Letters* 32 987-998.

BIOGRAPHY

Alinda Öykü Akar received her bachelor's degree from the Chemical Engineering Department of Middle East Technical University (METU), in the year 2013. That same year, she began the graduate program of Polymer Science and Technology at METU. She graduated with an M.Sc. degree with thesis work named "Characteristics of Poly(lactide) Composites Involving Montmorillonite and Boron Compounds". Her Ph.D. studies, under the Micro & Nanotechnology priority area of the Council of Higher Education, examine the improvement of electrical, thermal, and mechanical properties of acrylonitrile butadiene styrene (ABS)/carbon fiber composites. She took part in various R&D projects based on innovation, related to new product formulations and new applications while giving technical support to sales & marketing teams for her product range in Ravago (as an R&D Engineer) since 2015 and in Eczacıbaşı (as a Senior Development Specialist) since 2018. Since 2022, she is a part of the BASF team, as a Technical Sales Manager, where she is responsible for technical development and application of construction business and technical and commercial aspects of furniture business, in Türkiye.

APPENDICES

Appendix A: DMA Graphs of ABS/CF+CNT Composites Below Room Temperature

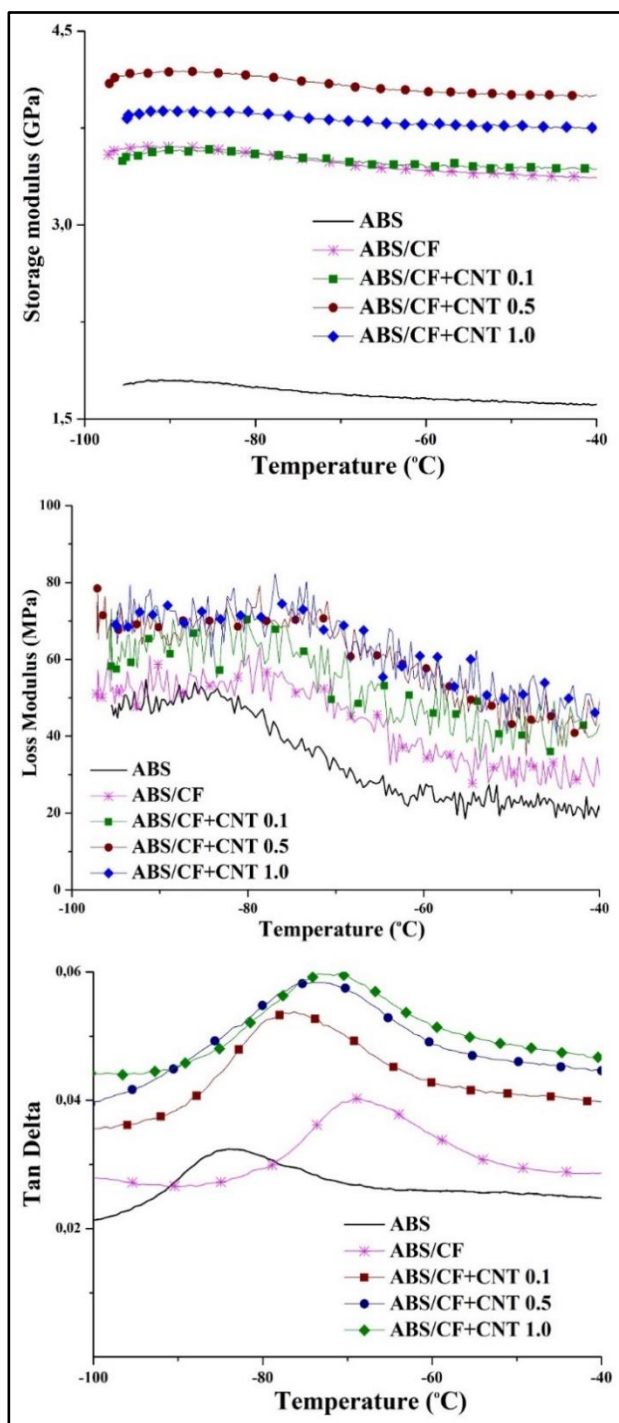


Figure A.1: DMA curves of ABS/CF+CNT composites between the temperature range of -40 and -100 °C.

Appendix B: The Supporting Information of Mechanical Data in AFM Analysis

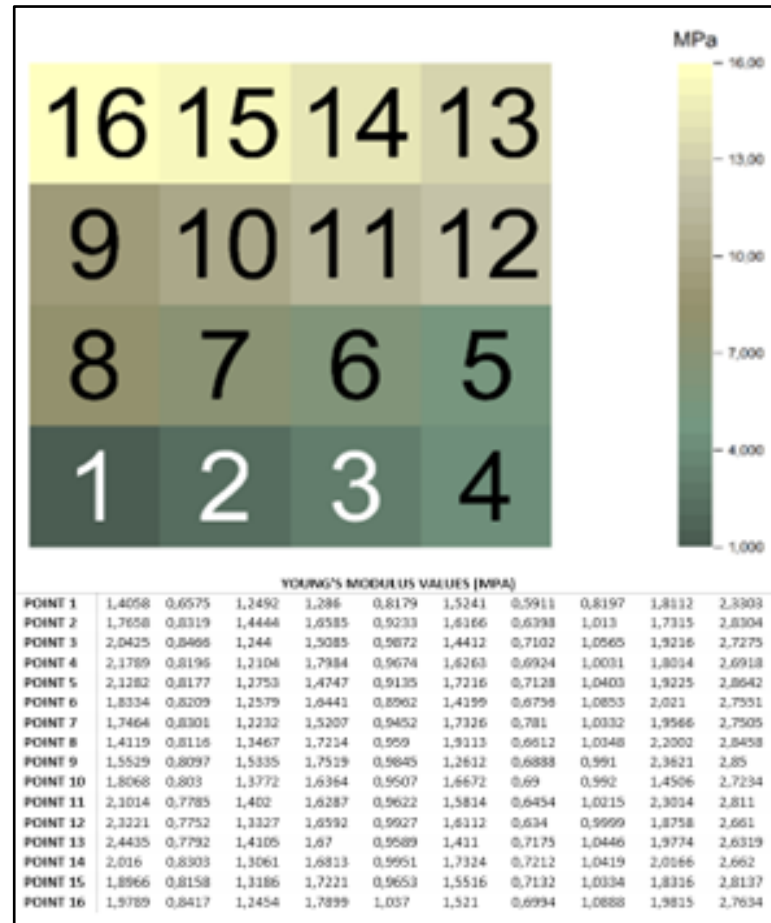


Figure B.1: The structure and test data of Young's modulus mapping.

Appendix C: The Publishments in The Scope of the Thesis Study

Akar A.O., Yildiz U.H., Tirkes S., Hacivelioglu F., Tayfun U., (2021), "Preparation and characterizations on short carbon fiber reinforced acrylonitrile-butadiene-styrene hybrid nanocomposites involving fullerene", Conference of the Polymer Processing Society (PPS36), Montreal, Canada.

Akar A.O., Yildiz U.H., Tirkes S., Hacivelioglu F., Tayfun U., (2021), "Preparation and characterizations on short carbon fiber reinforced acrylonitrile-butadiene-styrene hybrid nanocomposites involving carbon nanotubes", Carbon Chemistry & Materials (CCM-2021), Rome, Italy.

Akar A.O., Yildiz U.H., Tirkes S., Tayfun U., (2022), "Hacivelioglu F., Influence of carbon nanotube inclusions to electrical, thermal, physical and mechanical behaviors of carbon-fiber-reinforced ABS composites", Carbon Letters, 32, 987-998.