MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF EXPANDABLE GRAPHITE FILLED ACRYLONITRILE-BUTADIENE-STYRENE COMPOSITES

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HUSSAM MOHAMMED S. CIRMAD

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Approval of the Graduate School of Natural and Applied Sciences, Atılım University.

____

Prof. Dr. Ali KARA
Director

I certify that thesis satisfies all the requirements as a thesis for the degree of Master of Science.

____

Prof. Dr. Atilla CİHANER
Head of Department

This is to certify that we have read the thesis "Mechanical, Thermal and Morphological Properties of Expandable Graphite Filled Acrylonitrile-Butadiene-Styrene Composites" submitted by "Hussam Mohammed S. Cirmad" and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

____________________	____________________
Dr. Ümit TAYFUN	Assoc. Prof. Dr. Seha TİRKEŞ
Co-Supervisor	Supervisor

Examining Committee Members

Prof. Dr. Ali ÇIRPAN	____________________
Assoc. Prof. Dr. Murat KAYA	____________________
Assoc. Prof. Dr. Seha TİRKEŞ	____________________

Date: 14.07.2017

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Name, Last name: Hussam Mohammed S., Cirmad

Signature:

ABSTRACT

MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF EXPANDABLE GRAPHITE FILLED ACRYLONITRILE-BUTADIENE-STYRENE COMPOSITES

Cirmad, Hussam Mohammed S.

M.Sc., Chemical Engineering and Applied Chemistry

Supervisor: Assoc. Prof. Dr. Seha TİRKEŞ

Co-Supervisor: Dr. Ümit TAYFUN

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In this thesis work, acrylonitrile-butadiene-styrene (ABS) copolymer was loaded with expandable graphite (EG) at four different concentrations of 5%, 10%, 15% and 20%. ABS/EG composite samples were prepared by lab-scale micro-compounder followed by injection molding process. Mechanical, thermo-mechanical, melt-flow and morphological characterizations of composites were done by carried out tensile and impact tests, dynamic mechanical analysis (DMA), melt flow index (MFI) test and scanning electron microscopy (SEM), respectively.

According to tensile, impact and DMA test results, tensile strength and storage modulus of ABS were improved with increase in EG content. However, percent elongation and impact strength values showed decreasing trend with EG additions. MFI test revealed that the EG incorporation caused no dramatic change on MFI value and processability of neat ABS. EG flakes exhibited well-dispersion for all of the filling ratios as the SEM micro-images of composites were examined. 15% and 20% EG containing ABS composites were remarked as more suitable among prepared composites.

Keywords: Acrylonitrile-butadiene-styrene, Expandable Graphite, Mechanical Properties, Polymer Composites, Extrusion.

ÖZ

GENİŞLETİLEBİLİR GRAFİT EKLENMİŞ AKRİLONİTRİL-BÜTADİEN-STİREN KOMPOZİTLERİN MEKANİK, ISISAL VE MORFOLOJİK ÖZELLİKLERİ

Cirmad, Hussam Mohammed S.

Yüksek Lisans, Kimya Mühendisliği ve Uygulamalı Kimya

Danışman: Doç. Dr. Seha TİRKEŞ

Yardımcı Danışman: Dr. Ümit TAYFUN

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Bu tez çalışmasında, akrilonitril-bütadien-stiren (ABS) kopolimeri genişletilebilir grafit (EG) ile %5, %10, %15 ve %20 dört farklı konsantrasyonda karıştırılmıştır. ABS/EG kompozit örnekleri laboratuvar ölçekli mikro-karıştırıcı ve sonrasında enjeksiyonlu kalıplama prosesi ile hazırlanmıştır. Kompozitlerin mekanik, ısısal-mekanik, eriyik-akış ve morfolojik karakterizasyonları, sırasıyla çekme and darbe testleri, dinamik mekanik analiz (DMA), erime akış indisi (MFI) testi and taramalı elektron mikroskopisi (SEM) ile gerçekleştirilmiştir.

Çekme, darbe ve DMA test sonuçlarına göre, ABS'nin çekme dayanım ve depolama modülü EG miktarı ile arttırılmıştır. Ancak, yüzde uzama ve darbe dayanım değerleri EG eklenmesi ile düşme eğilimi göstermektedir. MFI testine göre EG eklenmesi, ABS'nin MFI değeri ve işlenebilirliğini çok fazla etkilememiştir. Kompozitlerin SEM mikro-resimleri incelendiğinde, EG plakalarının bütün yükleme oranlarında iyi dağılım sergilediği görülmektedir. %15 ve %20 EG içeren ABS kompozitleri, hazırlanan kompozitler içinde en uygun olarak belirlenmiştir.

Anahtar Kelimeler: Akrilonitril-bütadien-stiren, Genişletilebilir Grafit, Mekanik Özellikler, Polimer Kompozitler, Ekstrüzyon.

Dedicated to my family

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LIST OF ABBREVATIONS

ABS	-	Acrylonitrile-Butadiene-Styrene
EG	-	Expandable Graphite
T_g	-	Glass Transition Temperature
MFI	-	Melt Flow Index Test
DMA	-	Dynamic Mechanical Analysis
SEM	-	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

Polymer matrix composites have numerous usages in our daily life and their application areas are continue to grow rapidly. Researches dealing with their property enhancement and their adaptation to several application areas have gained importance since polymers have lack of proper characteristics individually. Acrylonitrile-Butadiene-Styrene copolymer (ABS) has become popular due to increase in its application fields especially in 3D printing technology. Melt mixing is the most preferred production method in industrial scale and basically it has very near precessing parameters as compared with 3D printing applications.

Number of research topics based on investigations of properties of ABS and its composites has been extended up remarkably in recent decade. Scientists and research specialists are tuning their properties including mechanical, rheological and morphological investigations as well as examination of processability.

Mineral fillers are the most desired candidate to consider as reinforcing material for plastics because of their low cost and ease of availability. Expandable graphite is naturally occurring filler which has flake-like structure. This mineral gained importance about improvement of thermal and flame resistance of plastics.

ABS is one of the polymers that exhibiting worst fire performance and this means that expandable graphite can be served as a flame retardant for ABS composites. Mechanical properties of polymers are the basic characteristics and addition of any reinforcing material can be changing these properties and they must be evaluated.

Thermo-mechanical response of composite material can be deduced by dynamic mechanical analysis. This method represents changes of mechanical history of material in a specific temperature range. Rheological investigation is also important because it mostly effects application of 3D printing field.

Dispersion of graphite flakes can be examined by using scanning electron microscopy and this give realistic evidence for experimental results. Evaluating the effect of concentration of expandable graphite into ABS matrix to basic properties may give opportunity for researchers to conclude which composition of expandable graphite is more suitable for a proper application of ABS based composites in their field.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Polymer Composites

Polymer composites are prepared by blending two different phases, namely matrix and reinforcer phases. Reinforcers or fillers can give to polymeric material additional property or can enhance its property to higher levels. After addition of filler into polymer matrix, resulting polymer composite material can be lower cost, weight and density and can be stronger as well as can gain extraordinary property such as electrical conductivity or fire resistant ability which is depending on the characteristic of added filler [1,2].

Reinforcers are classified based on their distinctive functions like their ability to tune properties. Mechanical, thermal, fire retardancy, electrical, solvent permeability properties are well-known and widely studied examples of these characteristics. According to general consideration, classification of reinforcing materials for polymers is divided into five major categories as:

. Mechanical property modifiers,

. Flame retardants,

. Electrical and magnetic property modifiers,

. Surface property modifiers, and

. Processing aids [1,3].

2.2 Acrylonitrile-Butadiene-Styrene Copolymer

ABS copolymer is consisting of elastomeric polybutadiene groups dispersed in thermoplastic styrene and acrylonitrile phases. This thermoplastic part gives toughness, chemical resistance, dimensional stability and ease of processibility characteristics to ABS. The overall proportions of monomers can be changed from 15% to 35% for acrylonitrile, 5% to 30% for butadiene and 40% to 60% for styrene portions depending on the desired grades [4].

Production of ABS can be made by several polymerization processes including bulk polymerization, emulsion polymerization, suspension polymerization or hybrid method of bulk and emulsion processes [5-7].

ABS copolymer is providing several applications in our daily life. The main applications are including sporting goods, helmets, home appliances, telephone switchboard panels, electronic equipments. Additionally, ABS has found wide usage in the automotive sector thanks to its smooth surface [8].

In recent years, ABS has gained popularity on usage as polymeric monofilament in 3D printing technology field. Rheological parameters of ABS and its composites are important for 3D applications. Melt flow behavior of ABS effects the fabrication of 3D printed product at desired levels [9-11].

Shear thinning and non-Newtonian viscosity characteristics of ABS make viscosity control easier and more flexible for several processing techniques including injection molding, compression molding and 3D printing [12].

2.3 Expandable Graphite

Expandable graphite, also known as intumescent flake is a carbonaceous mineral which can be obtained as naturally and or synthetically. It has a large planar structure including carbon atoms bonded in hexagonal rings. Each carbon layers are joining together with weak interlayer bonds. General structure of expandable graphite is represented in Figure 2.1.

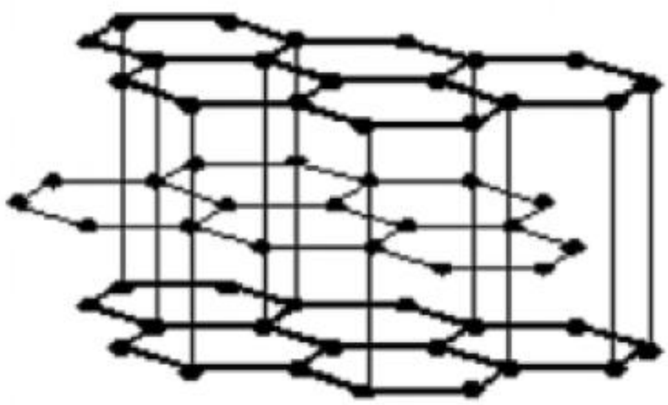

Figure 1. Structure of Expandable Graphite [1].

Graphite is treated with several intercalation reagents such as sulphuric acid, nitric acid and acetic acid in order to donate expansion behaviour. When the expansion occurs by elevating temperatures, it's volume rises up to 300 times. This property of expandable graphite gives opportunity to serve as an effective flame resistance product. In addition to fire retardancy applications, expandable graphite is widely used as conductive additive, barrier filler, lubricate, pigment, electromagnetic reagent, radiation shielding material and insulation product [1, 13,14].

Polymer composites filled with expandable graphite have been studied in previous studies in which mostly dealing with its flame resistance property. In these works, several polymers have been preferred as a matrix including polypropylene [15-17], poly (methyl methacrylate) [18], poly (lactide) [19], ethylene vinyl acetate [20] and polyurethanes [21-23].

2.4 Production Method of Polymer Composites

There are several approaches applied for the production of polymeric composite materials. In-situ polymerization, Solution mixing and casting method, and melt compounding are the main techniques employed for that purpose. The most practical and favoured method is melt compounding since extrusion process is conveniently used in plastic industry. Injection molding is also the common technique to shape polymeric materials in large scale productions.

2.4.1 Extrusion Process

Extrusion process is used efficiently for melting polymeric materials. This process is proper method for thermoplastic composite parts by mixing molten plastics with desired additives.

The main parts of the extruder machine are namely feeder zone, screw, barrel and die. The screws are the basic component of the extruder which has several functions of transporting polymer pellets, melting and conveying the plastics and dispersing additives homogeneously in molten polymer phase. The screw transports the molten polymer as well as mixing additives through barrel. The final destination of molten plastic into extruder is die where polymer is shaped. Resulted material after extrusion process can be tuned as pellet, sheet, film, pipe, tube, rod or chip form depending on the die design.

Compounding operation in extruder carried out with high shear forces in addition to elevated temperature which make mixing more homogeneous. This process is conventional and cost-effective for plastic industry [24, 25].

2.4.2 Injection Molding

Injection molding is the practical technique to shaped plastics. In this process, polymer is molten in barrel component, then it is pushed rapidly and repeatedly into a mold by applying injection pressure. Polymeric material gains desired shape after cooling period and it can be easily released from the mold to outside.

The barrel temperature, holding time, mold temperature and injection pressure are the main parameters of injection molding machine which can be adjusted according to working plastic. These parameters are varied depending on the melt-flow and rheological behaviour of polymer [26].

2.5 Literature Survey

Several researchers postulated the properties of ABS composites containing mineral fillers.

Bai et al. performed the fabrication of calcium carbonate loaded ABS composites [27]. They found that thermal degradation of ABS decreases after calcium carbonate additions. Tang et al examined the tensile, impact and bending properties of calcium carbonate reinforced ABS and they observed that tensile strength and impact strength decreases with increase in filler content while modulus values improves [28].

Taghinejad et al. investigated rheological behaviour titanium dioxide containing ABS and they postulated that the particle dispersion highly effects the rheological properties of composites [29]. Tjong et al. observed the improvement of mechanical and thermal properties of ABS after addition of potassium titanate. However, impact strength decreases with filler content. [30].

Bigg developed ABS composites filled with several particulate reinforcers including minerals, such as talc and silicon carbide, and metals, such as aluminium flake and stainless steel fibers [31]. He investigated that tensile modulus of composites is related with filling ratio while tensile strength values highly depend on filler-polymer adhesion.

Calderon et al. performed the production of fibrous membrane of natural zeolite containing ABS composites by using electrospinning [32]. and they investigated the homogeneous dispersion of zeolite particles into ABS matrix as morphological characterization.

Basurto et al. evaluated the optimal modification process for sepiolite for ABS matrix by using melt-mixing process. In their study, modification of sepiolite gives the best results for prepared composites [33].

EG reinforced ABS based composites were also studied in the literature. Investigations of these composites mostly dealt with the fire performance.

Pang et al. found that EG shows higher expandable property, thermal stability and flame retardancy for ABS based composites [34]. They also proved that EG exhibits synergistic effect with traditional intumescent flame retardant additives in ABS matrix. Ge et al. also observed synergistic effect between EG and a common flame retardant as they prepared EG filled ABS composites [35]. Zhang et al. demonstrated a novel carbon source derived from biomass for enhancing flame retardancy of ABS by using EG [36]. In other study, Hong et al. found that treated EG displays significant improvement on the fire performance of ABS as compared with untreated EG [37]. Guler et al. observed synergistic interaction between EG and a mineral filler for polyurethane elastomer composites in their study [22]. Zheng et al. also achieved synergistic interaction as they compounded ABS with EG and traditional flame retardants in presence of wood flour [38].

There have been numerous research articles related with several carbonaceous fillers reinforced ABS composites such as carbon black [39,40], carbon nanotube [41,42] and carbon fiber [43-45].

Research efforts focused on 3D applications of ABS and its composites have been also studied in the literature in which basically rheological and mechanical characterizations were examined [46-52].

2.6 Aim of the Study

In this thesis study, effect of concentration of EF to mechanical, thermo-mechanical, melt flow and morphological properties of ABS based composites were investigated. The optimum amount of EG for ABS copolymer was tried to obtain by the help of experimental data.

Melt-mixing technique was used as preparation of composites since this processing method is widely applied in industry. This method is also providing similar processing methodology with 3D printing technology.

ABS and relevant composite samples were characterized by conducting proper test methods. Mechanical and thermo-mechanical properties which are considered as the common characteristics of composites materials were evaluated and these data were supported with morphological analysis by SEM micrographs in this work.

Additionally, the changes on melt flow behaviour of ABS after EG inclusions were studied in order to examine processability of prepared composites for conventional applications as well as for 3D printing applications.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

In this study, ABS copolymer was compounded with four different concentrations of EG using extrusion process.

3.1.1 Acrylonitrile-Butadiene-Styrene Copolymer

ABS copolymer used in this study was supplied from Lanxess, USA under the trade name of Lustran ABS M203FC. It has a density of 1.05 g/cm^3 and easy flowing specification.

3.1.2 Expandable Graphite

Expandable graphite used in this study was purchased from Minelco Ltd, Italy with the commercial name of name of LKAB-Firecarb TEG 315. It has appearance of free flowing black flakes with a metallic lustre. The basic characteristics of this EG sample are shown listed in Table 1.

Table 1. Properties of Expandable Graphite

Characteristics	**Specification**	**Unit**
Moisture (105^{o}C)	1 max	%
Volatiles	12 max	%
Expansion onset temperature	170	^{0}C
Loose bulk density	0.4 -0.50	kg/l
Expansion at 1000^{o}C	220	ml/g
Expansion at 250^{o}C	100	ml/g
pH value	5-7	-

3.2 Processing Methods of Composites

Laboratory scale of compounder and injection molding devices were used for the production of ABS/EG composites. Details of processing parameters of production of composites are given.

3.2.1 Extrusion

ABS copolymer and EG flakes were dried at 100˚C for a period of 12 hours to avoid possible moisture before processing. Composites were prepared using lab-scale counter rotating twin screw extruder (15 ml micro-compounder, DSM Xplore, Netherlands). Processing parameters applied during fabrication of composites by are listed in Table 2 and photograph of micro-compounder machine is displayed in Figure 2.

Table 2. Compounding Parameters of Composites

Parameters	Specification	Unit
Process temperature	230	^{0}C
Mixing time	5	min
Screw speed	100	rpm

Figure 2. Lab-scale Compounder

3.2.2 Injection Molding

The samples obtained from extrusion process were cut to chip form and shaped using lab-scale injection molding instrument (Microinjector, Daca Instruments, UK). Parameters applied during injection molding process are listed in Table 3. Representative photograph of injection molding device is given in Figure 3.

Table 3. Molding Parameters of Composites

Parameters	**Values**	**Unit**
Barrel temperature	210	^{0}C
Mold temperature	50	^{0}C
Injection pressure	8	Bar
Holding time	5	min

Figure 3. Injection Molding Machine.

Test specimens were obtained from injection molding as dog-bone shape with dimensions of 7.6×2.0×80 mm^3 as represented in Figure 4. Gauge length of dog-bone shaped samples is 5 cm.

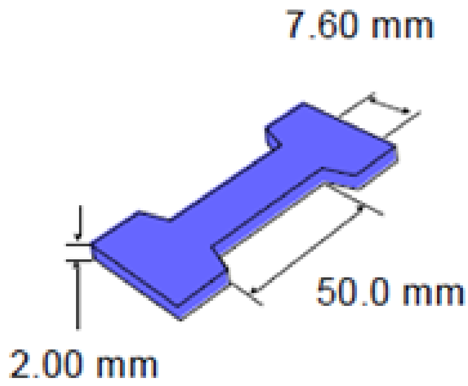

Figure 4. Tensile Test Specimen

3.3 Characterization Techniques

Characterization techniques were applied to samples according to related standards. All of the experimantal data were recorded as an avarage of minimum required number of samples. Experimental details used during tests are given in their sections.

3.3.1 Tensile Test

Tensile test measurements of ABS and its composites were carried out in accordance with the ASTM D-638 standard using Instron 5565A tensile testing apparatus. 5 kN load cell and 5 mm/min crosshead speed were used during test. Tensile strength, percentage elongation at break and tensile modulus parameters were recorded as an average of five samples. Photograph of tensile testing machine is shown in Figure 8.

Figure 5. Tensile Testing Apparatus

3.3.3 Impact Test

Unnotched Izot impact energy energy values of ABS and its composites were measured using Coesfeld-Material impact tester with pendulum of 4J according to ASTM D256 standard. Recorded results represent an average value of at least five samples with standard deviations. Photograph of impact tester is given in Figure 6.

Figure 6. Impact Tester

3.3.4 Dynamic Mechanical Analysis (DMA)

DMA analysis was performed for thermo-mechanical investigations of ABS and composites. For this purpose DMA 8000, Perkin Elmer dynamic mechanical thermal analyser was used. Test specimens obtained from injection molding with dimensions of 7.6x2.0x50 mm^3 were conducted. DMA analysis was carried out at temperatures ranging from -120°C to 140°C in dual cantilever bending mode at a constant frequency of 1 Hz and heating rate of 5 °C/min. Figure 7 displays the DMA analyzer used in this study.

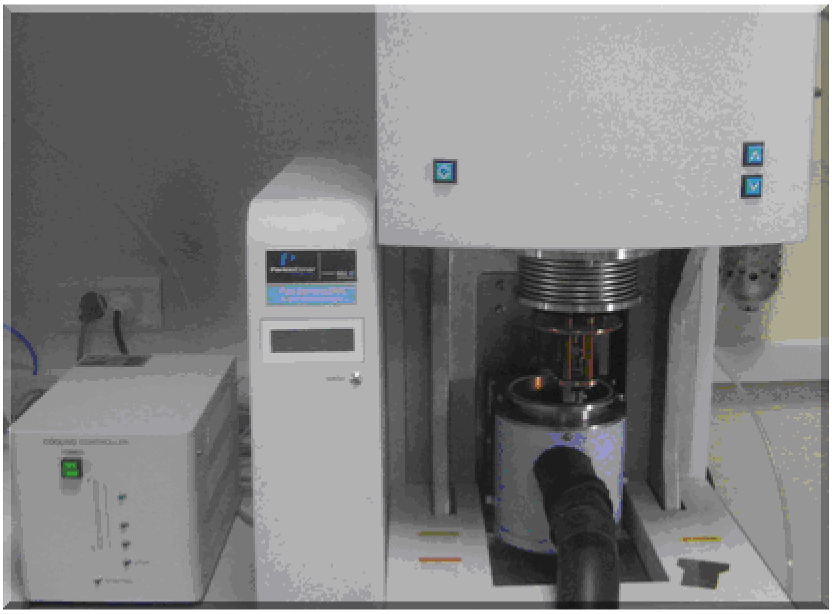

Figure 7. DMA Aalysis Equipment

3.3.5 Melt Flow Index Test (MFI)

MFI values of neat ABS and relevant composites were examined using Coesfield Meltfixer LT. Test measurements were carried out under a standard specified load of 2.16 kg at processing temperature of 230 ^{o}C. Weighted melt flow rate results represent an average value of at least ten samples with standard deviations. Photograph of melt flow indexer is represented in Figure 8.

Figure 8. Melt Flow Indexer

3.3.6 Scanning Electron Microscopy (SEM)

Morphological characterizations of EG filled ABS composites were examined by field emission scanning electron microscope device (JSM-6400 Electron Microscope). Surfaces of fractured samples obtained from impact test were coated with a thin layer of gold in order to obtain conductive surface. SEM micro-graphs were taken at magnifications of x500 and x5000.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Tensile Test

Tensile test data of test samples including tensile strength, elongation at break and elastic modulus are listed in Table 4. Additionally, strength–elongation curves of ABS/EG composites were shared on Appendix as Figure A.1, Figure A.2, Figure A.3 and Figure A.4.

Table 4. Tensile Test Data of ABS and Composites

Samples	**Tensile Strength** (MPa)	**Elongation at Break** (%)	**Tensile Modulus** (GPa)
ABS	35.4±1.7	7.1±0.8	0.92±0.3
ABS/5 EG	34.5±0.9	4.4±0.9	1.50±0.2
ABS/10 EG	37.1±0.8	4.2±0.7	1.52±0.3
ABS/15 EG	39.0±1.3	3.9±0.6	1.97±0.5
ABS/20 EG	39.6±0.6	3.0±0.4	2.29±0.2

According to Table 4, tensile strength and modulus values of ABS were improved with increase in EG concentration. 15% and 20% EG filled composites gave remarkably higher strength and modulus values.

Percent elongation of neat ABS was drop down about its one-half after EG addition. 20% EG compounded ABS composite exhibited the maximum tensile strength value.

4.2. Impact Test

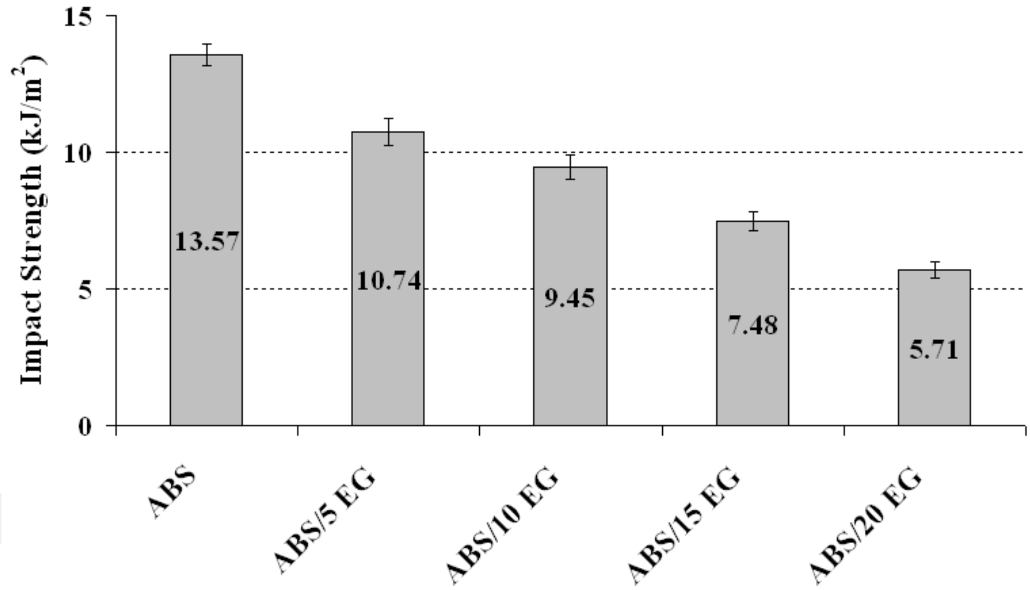

Figure 9. Impact Test Results of ABS and Composites

As the impact strength results of ABS and ABS/EG composites in Figure 9 were examined, it was found that EG additions caused almost proportional reductions for impact strength of ABS. Impact strength decresed with increase in EG content in neat ABS.

4.3. Dynamic Mechanical Analysis (DMA)

Thermo-mechanical properties of ABS and relevant composites were determined by DMA analysis. Storage modulus and Tan δ curves as a function of temperature were displayed in Figure 10 and Figure 11, respectively.

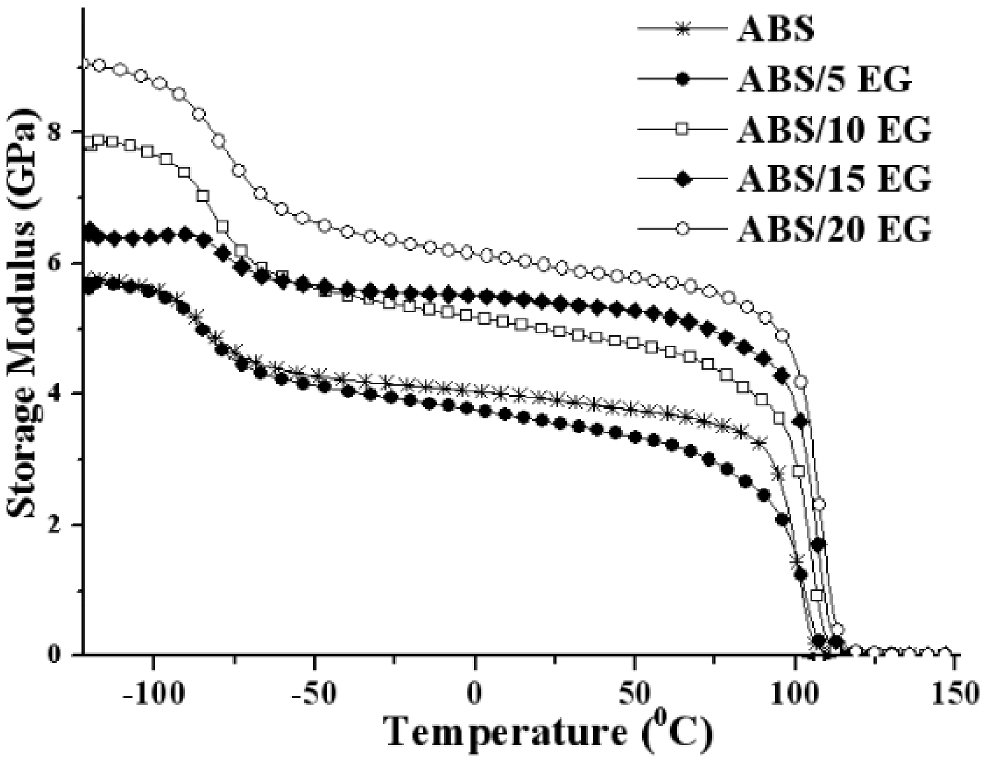

Figure 10. Storage Modulus vs. Temperature Curves

According to Figure 10, all of the composites exhibited higher storage modulus values with an exception of ABS/5 EG. The highest storage modulus was observed for 20% EG loaded composite. ABS/ 5 EG composite yields nearly identical storage modulus with neat ABS.

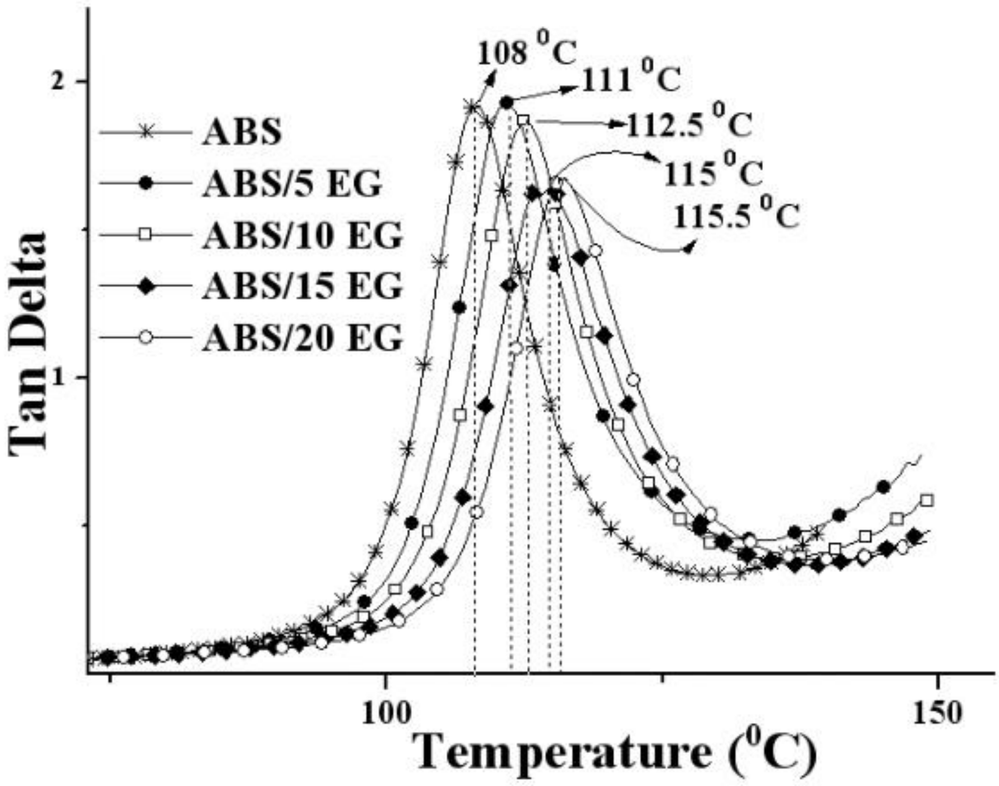

Figure 11. Tan δ vs. Temperature Curves

Figure 11 represents the**.** Tan δ curves of ABS and composites. EG additions caused shifting for glass transition temperature (T_g) of ABS to higher temperatures. Nearly 7 units improvement on T_g of ABS is observed for higher amount of EG. 15% and 20% EG containing composites display remarkably higher values than 5% and 10% filled composites.

The shifting of T_g to higher temperature indicates that material gained vibration-damping and sound-deadening property owing to sliding flakes of layered structure of EG during the deformation of composite on DMA analysis [53,54].

4.5. Melt Flow Index Test (MFI)

Melt flow rates of neat ABS and composites was evaluated by MFI test which provides important information about viscosity changes of molten polymer and processability of polymeric composites.

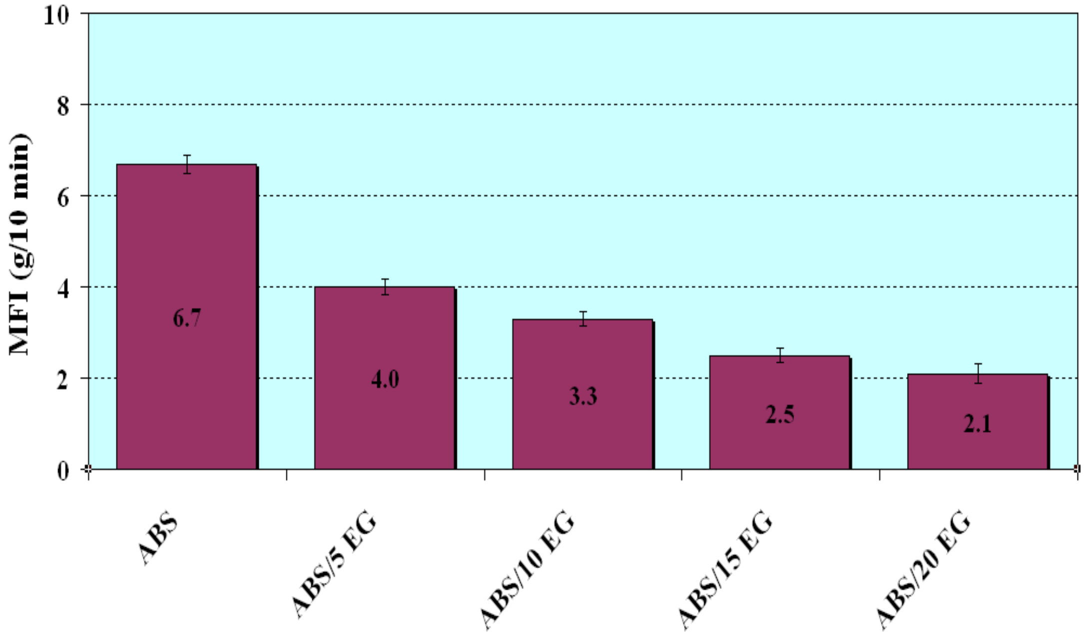

Figure 12. MFI Values of ABS and Composites

As shown in Figure 12, EG containing composites resulted in slightly lower MFI values as compared with unfilled ABS. Reduction on MFI was observed as the amount of EG increases. Similar results were obtained in literature that calcium carbonate, carbon black and potassium titanate inclusions resulted in reductions for melt flow rate of ABS copolymer [30, 55,56].

It can be deduced from these results that EG addition caused no dramatic changes on melt flow behaviour of ABS although slight reductions were observed. This means processability of ABS would not much affected as the fabrication of ABS/EG composites is considered.

4.6. Scanning Electron Microscopy (SEM)

Test samples obtained from impact test were used in SEM analysis. Fractured surfaces of samples were coated with gold and photographed at x500 and x5000 magnifications.

SEM micro-images of ABS/5 EG, ABS/10 EG, ABS/15 EG and ABS/20 EG are shown in Figure 13, Figure 14, Figure 15 and Figure 16, respectively.

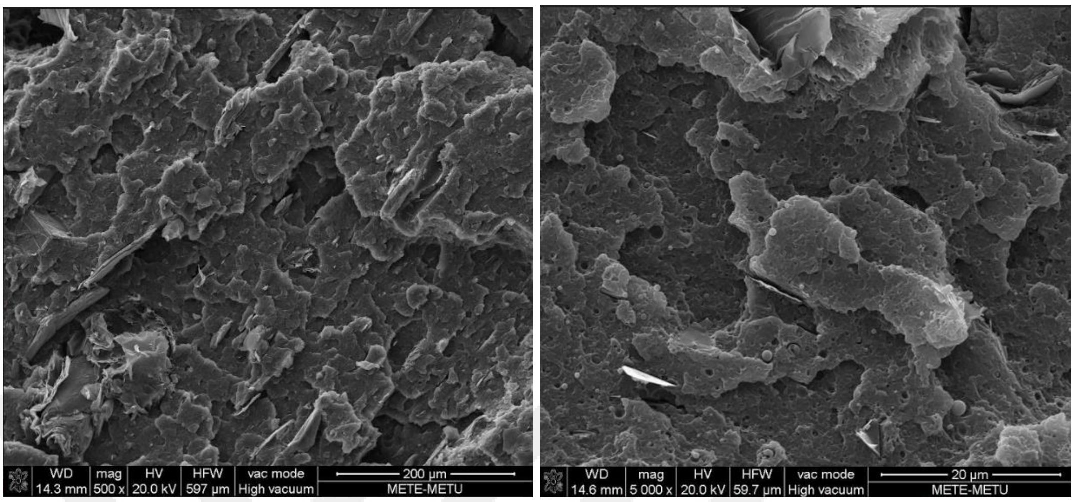

Figure 13. SEM Micrographs of ABS/ 5 EG Composite

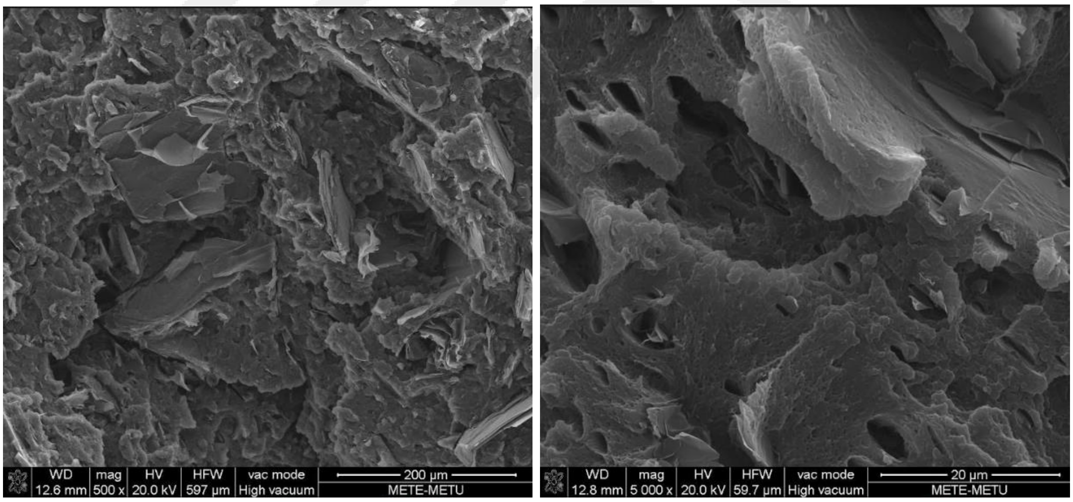

Figure 14. SEM Micrographs of ABS/ 10 EG Composite

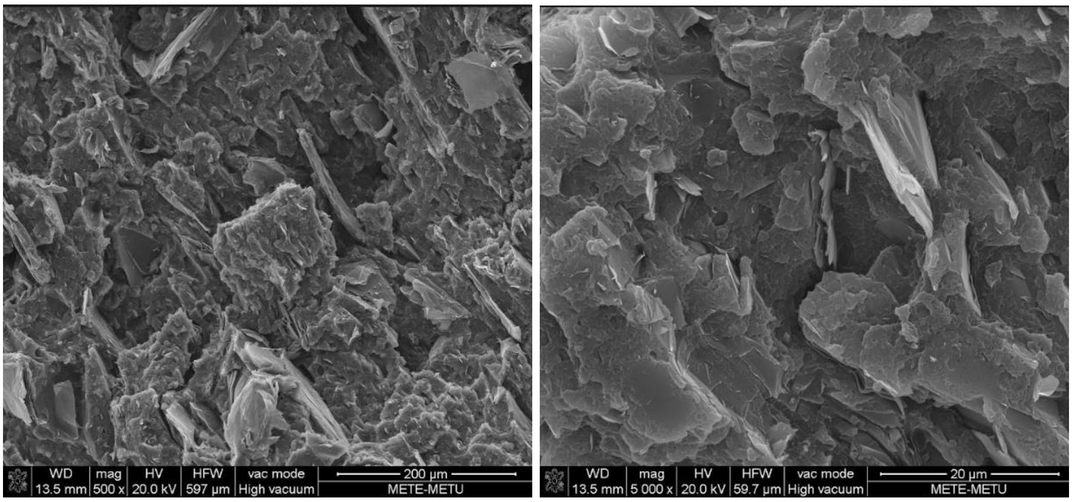

Figure 15. SEM Micrographs of ABS/ 15 EG Composite

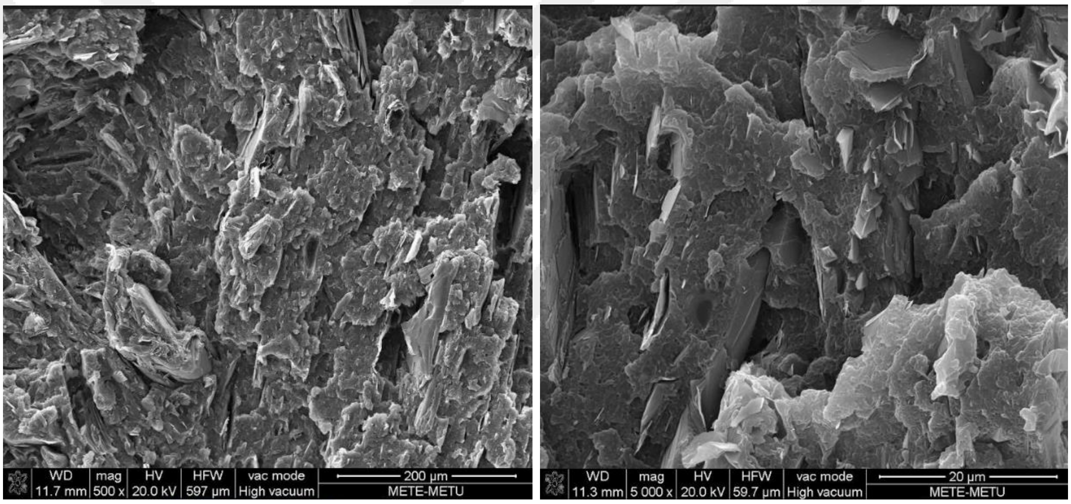

Figure 16. SEM Micrographs of ABS/ 20 EG Composite

As the SEM micrographs of selected composites examined, it can be seen that EG plates dispersed uniformly into ABS matrix even at their higher concentrations because of commercially acid treated surface of EG may cause increase its compatibility with ABS copolymer.

EG flakes displayed dispersion homogeneity in micro-images of all composites. Homogeneity of their mixing in ABS matrix is the reason of improvements of tensile strength and storage modulus discussed in earlier sections.

CHAPTER 4

CONCLUSION

In this current study, EG which is a carbonaceous material was used as additive for ABS matrix. Conventional production techniques of polymeric composite materials, melt compounding and injection molding processes were preferred thanks to their cost-effective and practical characteristics. The mechanical, thermo-mechanical, melt-flow and morphological properties of produced composites were postulated by conducting tensile and impact tests, DMA analysis, melt flow index test and scanning electron microscopy (SEM) methods, respectively.

Mechanical tests reveal that tensile strength and modulus of ABS increases with the incorporation of the EG at higher filling ratios. 15% and 20% concentrations of EG displayed higher values relative to lower contents. EG additions cause remarkable reductions for elongation and impact strength values of ABS.

According to DMA analysis, storage modulus and glass transition temperature of neat ABS are enhanced with addition of EG at higher amounts. As similar with tensile test data, loading levels of 15% and 20% EG give higher results.

EG additions cause slight reductions for MFI of ABS. However, these reductions are found as not huge changes in the case of their processability.

Almost no agglomaration formations are observed on SEM micro-images of composites. EG flakes exhibit homogeneous dispersion even at higher loading levels which may arise from compatible interfaces between acid treated EG between ABS matrix.

As an overall conclusion, generally 15% and 20% EG loaded composites show remarkably higher mechanical and thermo-mechanical properties. These concentrations would be suitable for most of the ABS applications.

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CHAPTER 5

APPENDIX

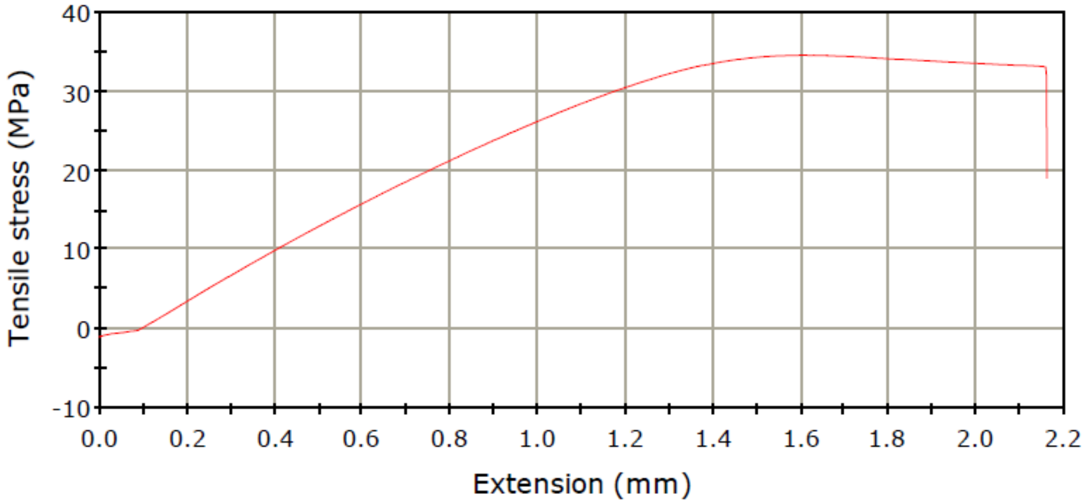

Figure A1. Stress-Strain Curve of ABS/ 5 EG Composite

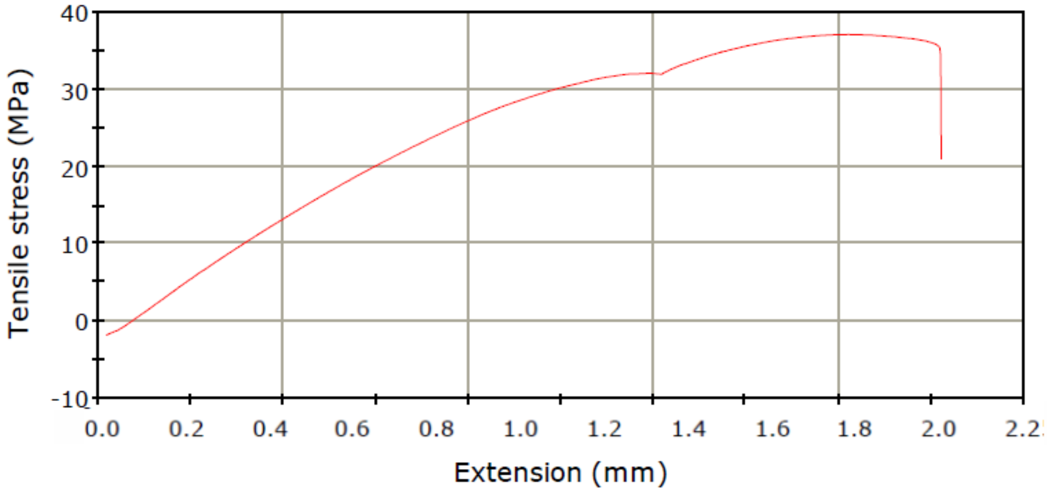

Figure A2. Stress-Strain Curve of ABS/ 10 EG Composite

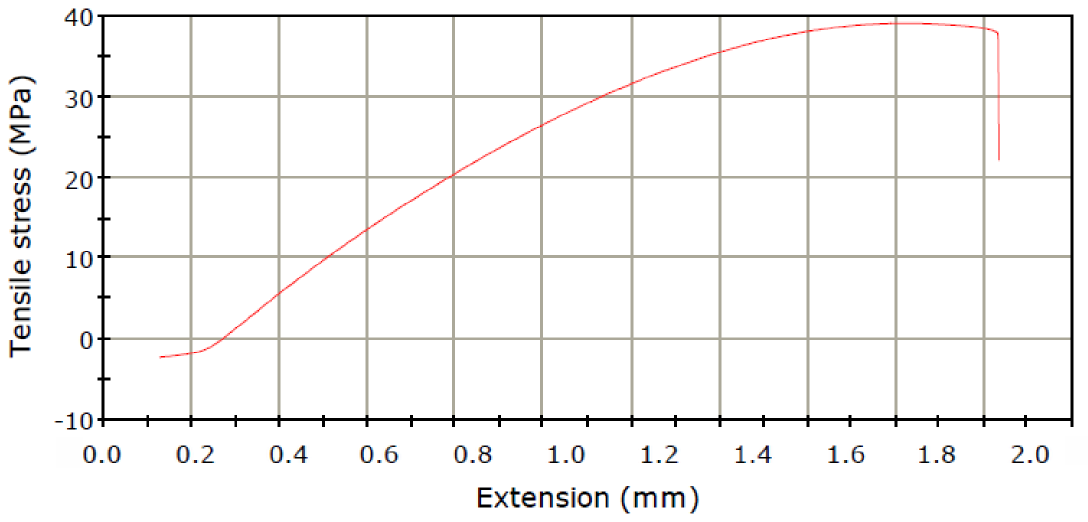

Figure A3. Stress-Strain Curve of ABS/ 15 EG Composite

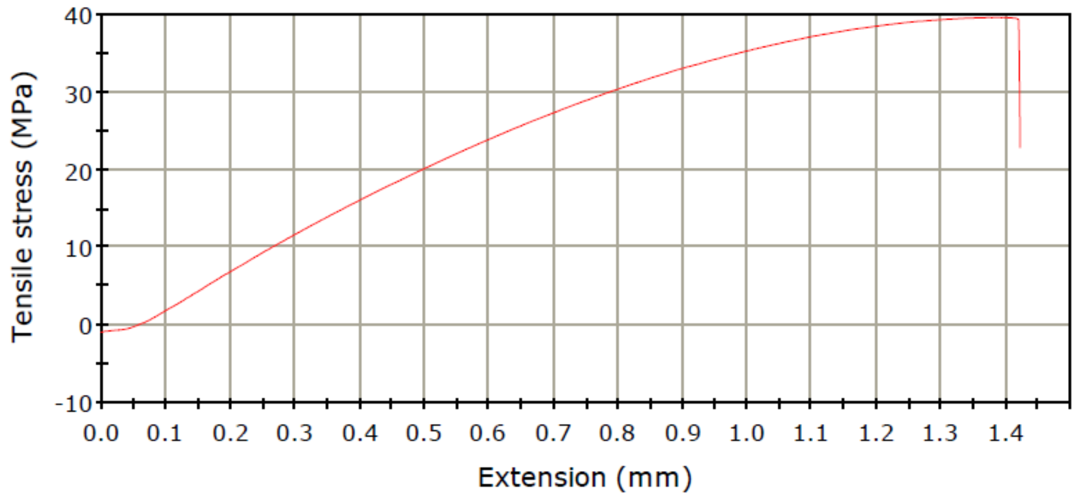

Figure A4. Stress-Strain Curve of ABS/ 20 EG Composite