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Research Article

Fabrication and characterization of vapor grown carbon nanofiber reinforced flexible polymer composites

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Abstract

In this study, highly flexible polymer nanocomposites that can be stretched more than 9 times their original length were successfully fabricated by using poly [styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) and vapor grown carbon nanofibers (VGCNFs). Two different polymers were used in order to investigate the effects of the polymer molecular weight on viscosity, morphological and mechanical properties of the samples. Mixing was carried out by a planetary high shear mixer for various levels of VGCNFs and SEBS. Nanocomposites were prepared by the combination of solvent casting and compression molding. Viscosity measurements were carried out as a function of filler ratio for both polymers. Higher molecular weight and higher filler ratio led to higher viscosity. Morphological analysis showed homogeneous filler dispersion without any dominant filler orientation throughout the composites with good filler-matrix interface and absence of any pores or voids. Filler content and matrix molecular weight were found significant for mechanical properties. The mechanical strength and elastic modulus of the nanocomposites increased by the addition of VGCNF regardless of the polymer molecular weight. Nanocomposites fabricated by using higher molecular weight polymer showed better mechanical properties. Above mentioned attributes those belong to both polymer composites meet the requirements of flexible electronics and can be used for many applications including micro-electro-mechanical systems, conductive coatings, electromagnetic shielding applications, polymeric sensors and actuators.

1. Introduction

Recent developments in technology, lead to the development of new materials and electronic materials are one of the most popular areas. Since traditional electronic materials are hard and brittle, over the last decades many of the efforts have been focused on flexible electronics because of their potential to provide the multiple requirements. Elastic and stretchable polymer-based materials with electronic capabilities have been referred to as flexible electronics. Depending on the components, type, and application, flexible electronics may be capable of sensing, data processing, actuation, and energy storage or generation. In all these applications flexibility is particularly crucial for micro-electro-mechanical systems (MEMS), sensors and actuators whose basic function is depended on their electromechanical properties. For the flexible electronics various polymers can be used as basic or auxiliary components including inherently conductive polymers [1-5], thermoplastics [6-8], thermosets [9, 10], elastomers [11-13], and thermoplastic elastomers [14-16] or polymer blends [17]. In this case, in addition to electrical character, mechanical character plays an important role during the functioning

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and not only flexible but also stretchable, bendable, twistable materials are required with high resilience and satisfying recoverability after unloading the mechanical effect [18]. Therefore, in the process of designing any the electro-mechanical system; analysis and characterization of the mechanical properties of the materials should be in the first place. As known, for electro-mechanical based systems such as sensors and actuators; electrical property is mostly governed by mechanical properties and response under various internal and/or external conditions [19, 20]. The group of polymeric materials that show all those required functions is called thermoplastic elastomers (TPEs). TPEs are polymers that combine the unique properties of thermoplastics and rubber. TPEs are compatible with a wide range of technologies and they can be used for many applications for a variety of purposes such as sealants, adhesives, rubber bands, protective films, airbag covers, automotive panels, sensors, actuators, electro-mechanical components of MEMS and so on. Processability, mechanical and end-use properties of the TPEs are the most important reasons for being preferred in these applications. While they perform as rubber in terms of elastic behavior; they can be melt-processed as thermoplastics. TPEs are copolymers with two phases as the elastomeric phase and the rigid phase. While the elastomeric phase represents the flexibility of rubber; the rigid phase represents the strength and processability of thermoplastics. Depending on the chemical structure, the ratio of these soft/rigid phases, the molecular weight of the polymer; physical, chemical and morphological properties of the TPEs change. They are named based on the thermoplastic block in the structure such as polyamide-based, olefin-based and styrene-based TPEs. In all, styrene-based thermoplastic elastomers are one of the most common TPEs found in the market due to their superior properties. In this group, poly [styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) stands out because of its superior properties such as higher thermo-oxidative and UV resistance. In SEBS, the polystyrene blocks act as rigid blocks because of physical cross-links between styrene blocks. As seen from Fig. 1, styrene blocks tie the continuous elastomeric phase in a three-dimensional network and minimize the deformation of the TPE system [21-25].

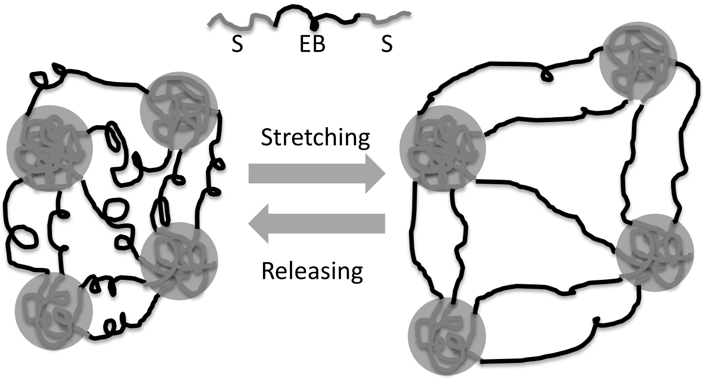

Fig. 1 SEBS under stretch and release

As mentioned above, SEBS is a promising material for flexible electronics because of its low elastic modulus, high degree of stretch ability and good resilience. In order to make it mechanically stronger and electrically conductive, fillers are needed to be incorporated into the structure. Since mechanical properties of the flexible electronics are very critical in terms of stretch ability, bendability and recoverability; filler selection should be done carefully. Surface area, surface properties, geometry and aspect ratio of the fillers have to be considered. In addition to that, if high level of fillers is loaded into the structure, flexibility and resilience of the material will be destroyed. At this point, nanofillers become more important.

Although, SEBS can be filled with various nanofillers [26-29], depending on our experience and previous studies CNFs are one of the most suitable materials [16, 18]. Their contribution to mechanical property improvement stemmed from their unique structure. As known, CNFs are cylindrical, fibrous nanostructures that consist of arranged graphene layers with high elastic modulus that is at least two orders of magnitude higher than the polymeric materials. In addition to that high aspect ratio and high surface area enhance the filler-matrix interface and improves the mechanical properties even at low filler loadings. Since filler loading is relatively low, stretching limits and flexibility of the material can be kept almost in the same range [30-32]. However CNFs have unique properties, mechanical properties of the CNF filled composites might be affected by many factors such as polymer properties, polymer-matrix interface, filler distribution, filler orientation, mixing conditions and composite fabrication [32]. In all these filler dispersions is the most critical one. In the case of nonhomogeneous filler dispersion, many problems might occur including filler aggregation, insufficient filler wetting, decrease in the aspect ratio of fillers, bad filler-matrix interface [32, 33]. As a result of these, stress transfer from matrix to filler might not be sufficient enough and mechanical properties of the composites get worse. In the literature, CNFs were mostly dispersed in the polymeric matrix in various ways such as extrusion compounding [33-35] sonication [17, 36, 37] and so on.

In above-mentioned methods, extrusion compounding has some drawbacks such as filler breakage and/or filler agglomeration. As reported by Al-Saleh [33], depending on the process conditions fillers can break and/or agglomerate and aspect ratio of the filler decreases that leads to change in various properties. Another common method for the dispersion of the CNF is the sonication and in order to obtain good filler dispersion, the viscosity of the solution or polymer-filler mixture has to be low enough. In other words, sonication process cannot be used effectively for highly viscous solutions or mixtures. On the contrary, planetary high shear mixing has no such problems. In this method, the aspect ratio of the fillers is almost the same that is significant for the mechanical properties of the composites. Also, it can be used for both low and high viscosity solutions/mixtures. Another important advantage is relatively short processing time is (1-2 minutes) [18].

In the literature there is a very limited number of studies regarding CNF/SEBS nanocomposites. In one of these studies, polypropylene/maleated SEBS (PP/SEBS-g-MA) blends were reinforced with CNFs. Polymer and fillers were compounded by a twin-screw Brabender extruder and granules were injection molded. Injection-molded samples were analyzed in terms of morphological, thermal and mechanical properties. It was reported that mechanical properties were enhanced by the addition of CNFs [30]. In another study, CNF/PP/SEBS composites were fabricated; the toughness and ductility of the composites were reported to be improved [38]. In another study, Huang et al, fabricated CNF decorated flexible and super-hydrophobic polyurethane (PU)/SEBS composite nanofiber membranes. In this study, the nanofiber mat was immersed into the CNF suspension in order to cover the surface of the mat by the fillers. Although the aim of the study was to develop a piezoresistive gas sensor, mechanical properties were also analyzed. Even though CNFs were not compounded with the matrix, attachment of the CNFs on the mat surface was reported to improve the tensile strength and elastic modulus of the flexible nanofibers. This was attributed to the alignment of CNFs and nanofiber mat to the direction of applied force and increase in interfacial area between both phases. As a result of this load transfer and mechanical strength was found to increase [39]. However, in the studies mentioned above, SEBS was not the only matrix and also it was used in order to modify the impact resistance properties of thermoplastics or to tune the spinnability of other thermoplastic elastomers. On the other hand, Dios et al. fabricated SEBS based composites by using various carbonaceous fillers including CNF. CNF/SEBS nanocomposites were prepared by the combination of sonication and solvent casting. Unlike the studies mentioned above, mechanical strength and elastic modulus of the samples were reported to decrease after the addition of the CNFs. Even though the reason for that was not mentioned in the study, this was probably caused by the solvent casting process. As known, the thickness of the film is very crucial for this process and for thicker films there might be some pores in the structure and those pores lead to the worsening of mechanical properties. The mechanical characterization was also carried out after the annealing of composites and as expected lower tensile stress values were obtained [17]. In another study, Turgut *et al.*, developed CNF/SEBS nanocomposites and investigated their piezoresistive strain sensing behavior. In this study two different SEBS polymers with different block ratios were used. Mechanical and electromechanical properties were investigated. Mechanical properties were reported to increase by the addition of CNFs [16].

In the present study, we have designed, fabricated and characterized the VGCNF filled SEBS nanocomposites. Two different polymers were used in order to investigate the effects of the molecular weight of the polymer on viscosity, morphological and mechanical properties of the samples. VGCNFs at various concentration levels were mixed with SEBS matrix by the high shear mixer in order to obtain good dispersion. Solvent cast samples were compression molded in order to obtain a homogeneous film. Viscosity, morphology and mechanical properties were found to be affected by VGCNF ratio, and matrix molecular weight.

2. Materials and Methods

Two SEBS block copolymers (linear) with S/EB ratio of 30/70 were used. Low molecular weight is shown as SEBS-1 (180 kDa), medium molecular weight is shown as SEBS-2 (250 kDa). White mineral oil (MO) manufactured as Merlot 261 with a molecular weight of 567 g/mol by Petroyag ve Kimyasallar San. Tic. A.Ş/Petroyag Lubricants (Gebze, Kocaeli, TURKEY), was used as received. Toluene (Merck, Germany) was used as a solvent. VGCNFs were purchased from Sigma–Aldrich, USA. The average diameter of VGCNFs is 130 nm and the length of the fibers changes from 20 to 200 µm.

Nanocomposites were fabricated in 3 main steps as shown in Fig. 2. In the first step polymer and mineral oil (MO) were mixed with a ratio of 30:70 (Polymer: MO). Then toluene was added into this mixture with the ratio of 1:2 ((Polymer+MO): toluene). Stirring was performed until complete dissolution was achieved with a magnetic stirrer at 200 rpm for 12 hours at room temperature (25°C). In order to obtain nanocomposites, the relevant amount of VGCNF solution was mixed by a planetary high shear mixer (Kurabo-Mazerustar-KK250, Japan) for 90 sec. After that, the polymer solution was added and mixed for another 90 sec. by a high shear mixer at 1600 rpm. Following that step, the mixture was solution cast in a petri dish and placed in a vacuum oven at 50°C for 12 hours. In the final step, cast films were compression molded into 0.8-0.9 mm thick films by using a laboratory type hot press at 190°C for 15 min. under 0,3 MPa of pressure.

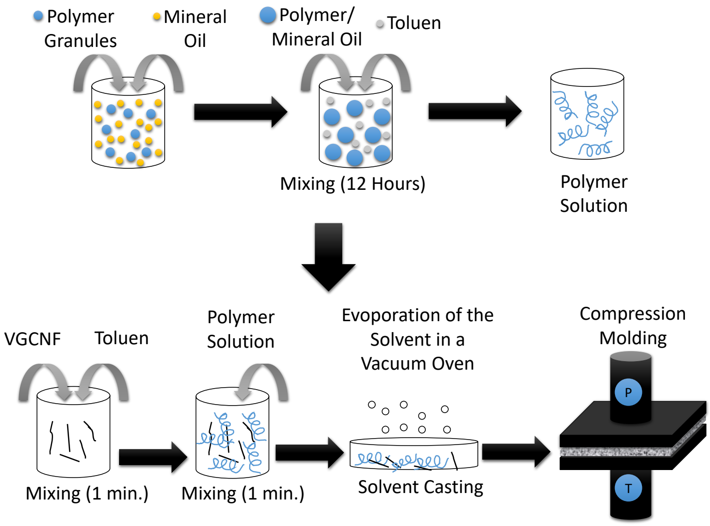

Fig. 2 Preparation of nanocomposites

Viscosity measurements were carried out by a Brookfield DV2T viscometer just after the high-shear mixing. All the measurements were done at 200 rpm with the spindle # 7 at room temperature (25°C). The morphology of nanocomposites was analyzed by scanning electron microscope (FESEM) (5 kV, METU Central Research Laboratory). The stress-strain behavior of the composite films was characterized by a universal load frame (Devotrans, DVT GPU/RD). The test speed was 50 mm/min. For each composite type, 3 specimens with the dimensions of 25 mm x 5mm (length x width) were prepared and tested for load-extension behavior. This test is a modified version of the ASTM 1708 Standard Test Method for Tensile Properties of Plastics by Use of Microtensile Specimens. Since thermoplastic elastomers are highly stretchable, we have used small-sized samples. Otherwise, the maximum jaw distance of the device will be exceeded and complete set of data may not be obtained. The stress-strain graphs were given as true stress vs true strain. Engineering stress and strain were calculated by using the Eq(1) and Eq (2), true stress and strain were calculated by using the Eq (3) and Eq (4):

$$\sigma_E = F/A_0 \tag{1}$$

where σ_E : Engineering stress (MPa), F: Force (N), A_0 : Initial cross sectional area (mm^2)

$$\varepsilon_E = (L - L_0) / L_0 = \Delta L / L_0 \tag{2}$$

where ε_E: Engineering strain (mm/mm), L: Final length of sample (mm), L_0 : Initial length of sample (mm), ΔL : Change in length (mm)

$$\sigma_T = \sigma_E(\varepsilon_E + 1) \tag{3}$$

where, σ_T: True stress, σ_E : Engineering stress (MPa), ε_E : Engineering strain (mm/mm)

$$\varepsilon_T = \ln(1 + \varepsilon_E) \tag{4}$$

where, ε_T **:** True strain ε_E : Engineering strain (mm/mm)

3. Results and Discussions

3.1 Viscosity

The results of the viscosity measurements are given in Table 1 and Fig. 3 as a function of VGCNF for both polymers. As seen from Table 1, SEBS-2 showed higher viscosity. While SEBS-1 polymer solution had a viscosity value of 2.18 cP, SEBS-2 had a value of 16.76 cP. As known higher molecular weight leads to higher molecular chain entanglements and resistance to flow. In addition to that increase in filler concentration resulted in higher viscosity for both polymers. As seen from Fig. 3, viscosity values are 2.26, 2.38, 2.76 cP for 2, 4 and 6 wt % VGCNF/SEBS-1, respectively. Similar to that, other set of samples showed an increase in viscosity and 18.14, 18.9, 19.64 cP are the values for 2, 4 and 6 wt % VGCNF containing SEBS-2 samples respectively. As known, VGCNFs are rigid fillers with high elastic modulus. Addition of those rigid materials into the polymer solution increases the rigidity of the system and causes an increase in the viscosity [40, 41]. In order to understand the response of the two sample sets and to provide a better comparison, normalized viscosity (NV) was also calculated for the samples by dividing the viscosity of VGCNF filled sample to the viscosity of polymer solution (η/η_0). NV of the samples are 1.036, 1.092, 1.26 for 2, 4 and 6 wt % VGCNF/SEBS-1, respectively and 1.082, 1.127, 1.171 for 2, 4 and 6 wt % VGCNF/SEBS-2, respectively. As seen in Fig. 4, while SEBS-2 showed a linear fit, SEBS-1 showed a polynomial fit and 6 wt % VGCNF/SEBS-1 sample showed a drastic change in NV around 27 %. This is explained as rheological percolation. Rheological percolation is the value at which VGCNF bundles come very close to form the percolation network. Similar to the electrical percolation, at this point fillers form a continuous network throughout the sample and the change in viscosity is not linear anymore. Since SEBS-2 has relatively high viscosity, rheological percolation was not observed at 6 wt%. It will be probably observed at higher filler concentrations. In addition to that, as will be explained in SEM results, agglomeration of the fillers and cluster formation might also retard this region to higher filler concentrations [41].

Table 1. Viscosity and normalized viscosity values of the samples

Polymer	Filler Ratio (wt%)	Viscosity (cP)	Normalized Viscosity ($\eta/\eta0$)
SEBS-1	0	2.18	1
	2	2.26	1.036
	4	2.38	1.091
	6	2.76	1.266
SEBS-2	0	16.76	1
	2	18.14	1.082
	4	18.9	1.127
	6	19.64	1.171

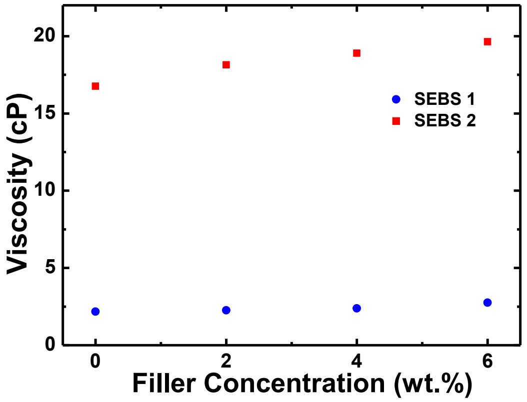

Fig. 3 Viscosity values as a function of VGCNF concentration for SEBS-1 and SEBS-2

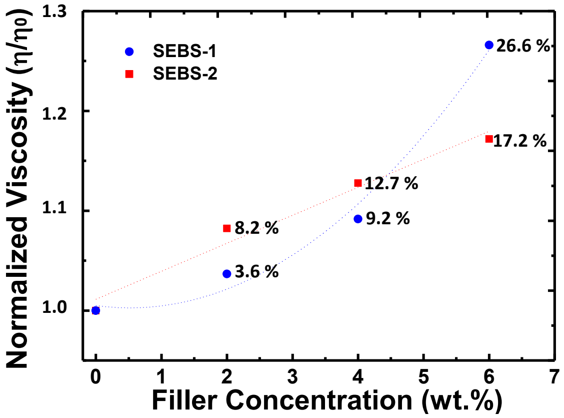

Fig. 4 Normalized viscosity values and the % increase in normalized viscosity as a function of VGCNF concentration for SEBS-1 and SEBS-2

3.2 Morphological Characterization

In order to examine the morphology of the samples; both SEBS films and VGCNF filled nanocomposites were cryo-fractured in liquid nitrogen and cross-sections of the samples were analyzed by FESEM. Fig 5 a and e are SEBS-1 and SEBS-2 films, respectively. As seen, both SEBS-1 and SEBS-2 showed classical fractured surface morphology. It can also be inferred from the images that both samples were melted completely under determined processing conditions. In order to understand the VGCNF dispersion, orientation and filler-matrix interface all nanocomposites were analyzed. SEBS-1 based nanocomposites (Fig. 5 b-d) showed homogeneous filler dispersion for all concentrations. In addition to these, no pores, pulled out VGCNFs, or matrix discontinuity were observed. VGCNF/SEBS-1 composites were found to show a good filler-matrix interface. The good matrix-filler interaction is probably due to well-dispersed fibers (high-shear mixing), high-temperature processing (melt processing), and nanoscale surface roughness of the VGCNF particles.

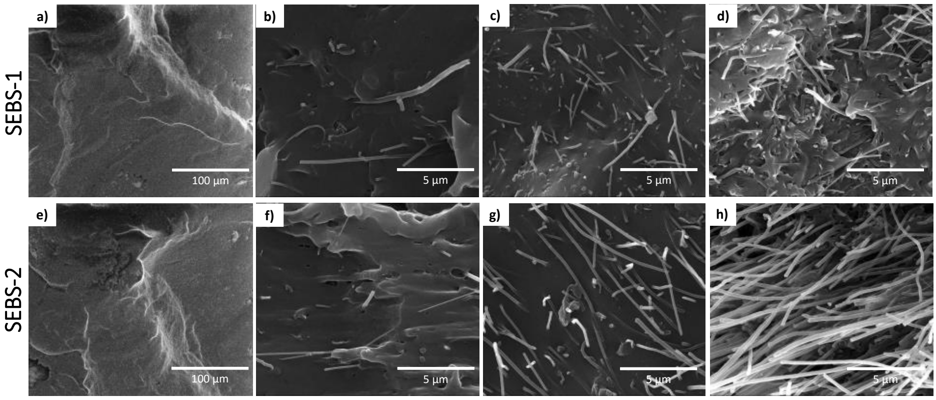

Fig. 5 Cross-sectional SEM images of a)SEBS-1 film b) 2 wt % VGCNF/SEBS-1 c) 4 wt % VGCNF/SEBS-1 d) 6 wt % VGCNF/SEBS-1 e)SEBS-2 film f) 2 wt % VGCNF/SEBS-2 g) 4 wt % VGCNF/SEBS-2 h) 6 wt % VGCNF/SEBS-2

High shear mixing is a one-step, easy and effective way of dispersing nanofillers in a polymeric matrix. Also, it lowers the matrix viscosity during the process by which the matrix-filler interaction is enhanced [18]. SEBS-2 nanocomposites (Fig. 5 f-g) showed almost same behavior as SEBS-1. On the other hand, at high filler concentrations such as 6 wt% VGCNF/SEBS-2 composite, some filler clusters were observed. In Fig. 5h one of those clusters is shown. As obvious from the image the wetting of VGCNFs was not completed. That was probably caused by not only high filler concentration but also higher solution viscosity of SEBS-2 polymer. As previously mentioned in the viscosity analysis, the higher molecular weight causes higher interaction between polymer macromolecules and interlocking of the macromolecular chains will increase the viscosity of the polymer solution [18]. In our case, as shown in Fig. 6, higher viscosity of the SEBS-2 polymer solution led to nonhomogeneous filler dispersion throughout the matrix. This is also parallel with the mechanical data shown in Fig. 8. In other words, under the same processing conditions, solution of the low molecular weight polymer can be mixed more efficiently with the fillers and that leads to better wetting and filler dispersion [18].

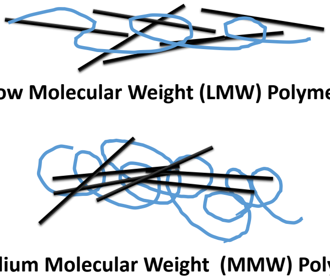

Fig. 6 Dispersion characteristics of VGCNF in LMW and MMW SEBS

3.3 Mechanical Characterization

True stress-strain and elastic modulus values of SEBS films, VGCNF/SEBS-1, and VGCNF/SEBS-2 nanocomposites can be seen from Table 2 and Fig.7 and 8.

Table 2. Mechanical properties of the samples

Polymer	Filler Ratio (wt%)	Maximum True Stress (MPa)	Maximum True Strain (mm/mm)	True Elastic Modulus (MPa)
SEBS-1	0	4.558	2.3	0.164
	2	4.887	2.3	0.241
	4	6.095	2.3	0.341
	6	7.770	2.3	0.534
SEBS-2	0	8.847	2.3	0.197
	2	10.369	2.3	0.254
	4	12.255	2.3	0.407
	6	11.626	2.3	0.726

All samples showed a linear elastic deformation behavior at low strain. As seen in Fig. 7-8, SEBS-2 film showed better mechanical properties and elastic modulus compared to SEBS-1. This is caused by the higher molecular weight of SEBS-2. Longer macromolecular chains increase the interlocking and that leads to better mechanical properties. As clearly seen from both figures, an increase in the VGCNF wt % content leads to an increase in stress values. The incorporation of filler increases the load-bearing capacity of the composites. As previously reported in the literature VGCNF has relatively high elastic modulus when compared with polymeric materials. In the case of homogeneous mixing of VGCNF and SEBS, the mechanical properties of the nanocomposites enhanced. VGCNF increases the mechanical properties not only because of its rigid structure but also surface properties.

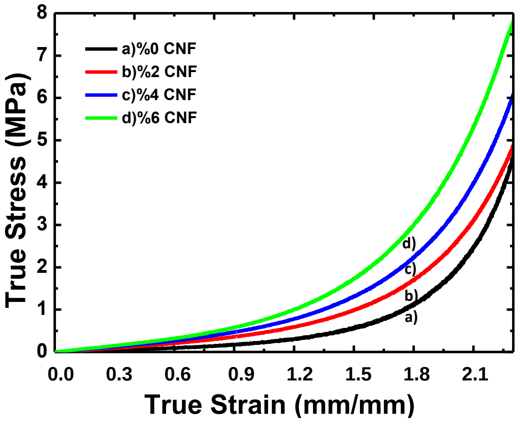

Fig. 7 True stress-strain graphs SEBS-1 film and VGCNF/SEBS-1 nanocomposites

As known, VGCNFs have a nano-scale surface roughness that helps to increase filler-matrix interaction and mechanical interlocking that leads to a good filler-matrix interface [18, 30]. On the other hand, 6 wt % VGCNF filled SEBS-2 composite showed a decrease in stress value at high level of strain. That is probably caused by the formation of some filler clusters at this concentration which is consistent with the FESEM images included in Fig. 5 h. As previously mentioned, that is probably caused by higher viscosity of the SEBS-2 polymer solution. Viscosity of the SEBS-2 is around 8 times higher than SEBS-1 solution and the viscosity of 6% VGCNF/SEBS-2 mixture is 6 times higher than of 6% VGCNF/SEBS-1.

Incorporation of fillers led to higher viscosity that prevents effective mixing and filler dispersion at a given time. This might be prevented by addition of more solvent or increased mixing time.

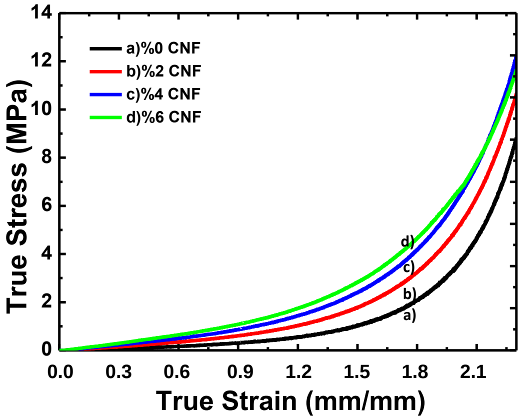

Fig. 8 Stress-strain graphs of SEBS-2 film and VGCNF/SEBS-2 nanocomposites

In addition to stress values and mechanical strength, strain values can also be analyzed from stress-strain curves. SEBS-1, SEBS-2 films can be more than 9 times their original length. No difference was observed between two polymers in terms of strain levels. These strain values are very high when compared to traditional vulcanized rubber or thermoplastics. It is also obvious that the addition of nanofillers did not affect the strain values. In other words, regardless of the polymer type, all nanocomposites can be stretched more than 9 times compared to their initial length.

4. Conclusions

In this study, flexible polymer nanocomposites were prepared by using poly[styrene-b-(ethylene-co-butylene)-b-styrene] and vapor grown carbon nanofibers that can be stretched more than 9 times their original length. Nanocomposites were prepared at various levels of VGCNFs 0, 2, 4 and 6 wt % by using two different SEBS. SEBS-1 and SEBS-2 have the same block ratio (S/EB : 30/70) and they have different molecular weights (SEBS-1: 180 kDa; SEBS-2: 250 kDa). In order to obtain homogeneous VGCNF dispersion, a planetary high shear mixer was used. Composites were prepared by the combination of solvent casting and compression molding. Morphological characterization showed homogeneous filler dispersion without any dominant filler orientation throughout the composites with good filler-matrix interface and absence of any pores or voids. That was caused by two-step fabrication method. High shear mixing is a very effective method for dispersion of the VGCNFs. In addition to that, pressure application during compression molding led to the removal of the solvent completely and increase the filler-matrix interface. Nanofiber clusters were observed for only 6 wt % VGCNF filled SEBS-2 nanocomposite. Mechanical properties were characterized by a mechanical testing system as a function of VGCNF and polymer type. SEBS-2 film showed higher stress values compared to SEBS-1. This is caused by the higher molecular weight of SEBS-2. For both systems, incorporation of filler increases the load-bearing capacity of the composites. VGCNF increases the mechanical properties of the composite system not only because of its rigid structure but also its surface properties. As known, VGCNFs have nano-scale surface roughness that helps to increase filler-matrix interaction and mechanical interlocking that leads to a good filler-matrix interface.

From the outcomes of the present study, the following conclusions can be drawn:

- Highly flexible polymer nanocomposites that can be stretched more than 9 times compared to their initial length were successfully fabricated,
- Molecular weight of polymer directly affects the solution viscosity and filler dispersion,
- Increased polymer molecular weight and filler ratio led to increase in viscosity,
- Homogeneous filler dispersion was obtained for almost all nanocomposites,
- At higher VGCNF concentrations, filler dispersion was not very homogeneous for the polymer with higher molecular weight,
- Films and nanocomposites fabricated by using higher molecular weight polymer showed better mechanical properties,
- Mechanical strength of the nanocomposites increased by the addition of VGCNF regardless of the polymer molecular weight,
- Depending on the requirements, both systems can be used for many applications including, conductive coatings, electromagnetic shielding applications, flexible electronics, wearable electronics and polymeric sensors.

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