Study on Nanocomposite Thermoplastic Elastomer Gels

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Summary: The effect of several network-forming nanoscale materials such as two different types of graphite and multiwalled carbon nanotube on the property development of thermoplastic elastomer (TPE) gels prepared from microphase-ordered poly(styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer dissolved in paraffin oil was studied. Dynamic rheological measurements of the resultant nanocomposite TPE (NCTPE) gels showed that at temperature between 30 °C to 40 °C below the gel point, the NCTPE gels have dynamic storage modulus greater than loss modulus (G′ and G″), thereby indicating that at ambient temperature a physical network is still present despite the addition of nanoparticles. In general, the nanoparticles lower the gelation temperature. The X-ray diffraction of NCTPE gels showed that EG2 system exhibited intercalation, those with CNTs exhibited exfoliation and EG1 did not change at all.

Keywords: nanoparticles; physical gel; thermoplastic elastomer; viscoelastic properties

Introduction

In recent years, physically associating thermoplastic elastomer (TPE) gels have attracted scientific and technical interest. TPE gels are molecular networks composed of a microphase copolymer swollen to a large extent by a low volatile midblock-selective solvent. One of the most highly investigated thermoplastic elastomer is the commercially available poly [styrene-b-ethylene-co-butylene-b-styrene] (SEBS) triblock copolymer, which is widely used for the modification and compatibilization of blends. The ability of the SEBS TPE gels to establish bridges between micelles can form three-dimensional network in a matrix of solvent and dissolved midblocks. If the micelle forming block is glassy such as polystyrene (PS), then the styrene micelle serve as physical crosslinks sites and copolymer the resultant copolymer/solvents solution behaves as physical gels. Since the formation of the micelles is a thermoreversible process, these gels have a unique network behavior providing high elasticity. The temperature where it shows rubber like behavior can be easily adjusted by changing the polymer concentration. Numerous significant researches have been done in understanding the structural morphologies,[1–3] viscoelastic and thermal properties[4–10] of these systems in mineral oils and n-octane. Although thermoplastic elastomer gels are well-known, there has been a limited study on the properties of nanocomposite TPE (NCTPE) gels. It is the aim of this work to ascertain the effect of nano materials on the properties of thermoreversible physical gels. The linear viscoelastic properties of nanocomposite TPE gels were taken for study and investigated as a function of temperature and frequency. Gelation temperature, mechanical properties and morphological properties of NCTPE gels were also investigated.

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Experimental Part

The poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) triblock copolymers, Kraton G1652 was produced by the Shell Co, Ltd (USA), has been previously characterized in detail[9,10] and is used as received. Two types of expandable graphite (EG) were used: (1) EG1 with nominal size of 100 mesh and expansion ratio of 1:54 and (2) EG2 has nominal size of 20 × 100 mesh having expansion ratio of 1:200. These materials were produced by Anthracite Industries (USA). Multiwalled carbon nanotube (CNTs) was supplied by Iljin Nanotech Co. The CNTs synthesized by the chemical vapor deposition (CVD) process having average diameter of 13 nm and length of 10 μm. The paraffin oil was supplied by Michang Oil Industrial Co, South Korea with molecular weight of 500 g/mol and density of 0.88 g/cm^3. Graphite was sonicated in ethanol bath for 8 hours to break up carbon clusters into flakes before it was added to 20 wt% SEBS concentration. For MWCNTs, no further treatment was done. The amount of nanoparticles were varied from 0.5 to 10 wt%. NCTPE gels were prepared in similar manner in our previous studies[9,10] and elsewhere[11] to permit direct comparison and maintain reproducibility. The resultant hybrid gels were compression-molded without applying much pressure for 10 minutes at 150 °C to yield films measuring 2.0 to 2.5 mm thickness. The specimens were stored between sheet of wax paper under dark and cool condition to avoid degradation prior to analysis. Dynamic measurements were conducted in two different instruments: a stress-controlled rheometer (Rheologica Instruments,USA) and a strain-controlled Rheometrics Mechanical Spectrometer (RMS800, USA), both operated with 25 mm parallel plate geometry and a 1.5 or 2.5 mm gap heights. The elastic storage modulus, G', and loss modulus, G'', were measured at the temperature range 30–140 °C with increments of 10 °C/min and at frequency between 0.1 to 10^2 rad/s at a constant strain (γ_o) of 1% at three different temperatures 30 °C and 70 °C, 90 °C). The X-ray diffraction (XRD) peaks were taken using a D8 Discover with GADDS, Bruker AXS (Germany) using CoK_α radiation in the angular range from 10–60° at an operating voltage of 40 kV and a current of 20 mA with a wavelength of 1.7902 Å. For data acquisition and analysis, Origin 5.0 software was used. The tensile tests were performed on a Lloyd LR10K tensile testing machine (Farehan- Hamsphire, UK). The crosshead speed was 500 mm/min with a load cell of 10 KN and a gauge length of 25 mm.

Results and Discussion

Rheological Observations

Figure 1 shows the change in G' with temperature for NCTPE gels with corresponding parent TPE gels. The parent TPE gel consists of four characteristics region (i) an initial plateau over which G' remains relatively constant or slightly increase with increasing temperature, which means that the rubbery PS domains become glassy (ii) an abrupt reduction in G' attributed to lattice disordering transition in the vicinity of 75 °C (iii) a small second plateau in G' at 100 °C and (iv) a steep decrease in G' signifying the collapse of the copolymer network at ca 108 °C. The existence of second plateau reflects the persistence of a residual, load-bearing nanostructure that either remains intact or develops upon increasing temperature. Montensen and co-workers[12] have demonstrated that similar TPE gels exhibit high temperature body-centered cubic phase that possess in unusually high degree of nanostructured order. Similar results with exception of the second plateau have been reported for the same parent TPE gels in our previous studies[9,10] and other as well.[13] On the other hand, the NCTPE gels consist only three major characteristics region without the second plateau observed in the parent TPE gels, meaning without any morphological change during the heating procedure albeit a very small plateau in EG2 NCTPE gels. An abrupt reduction in G' which is the lattice disordering transition, was reduced in the vicinity of 58 °C for CNTs, 63 °C for

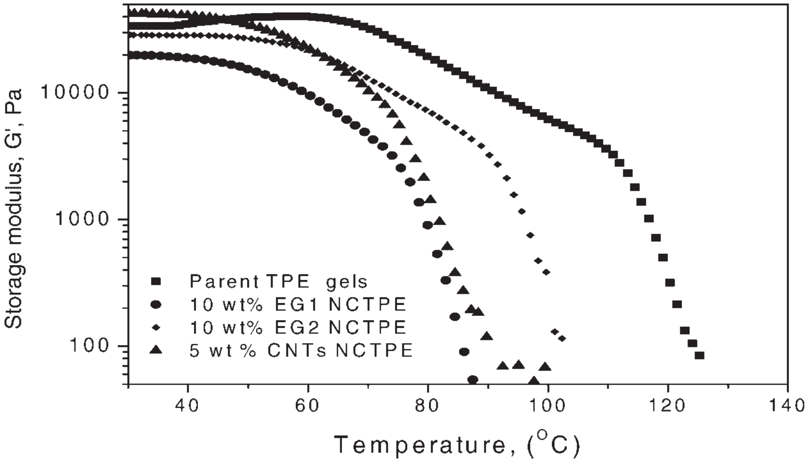

Figure 1.
Dynamic storage modulus, G′, presented as a function of temperature.

EG1 and 70 °C for EG2. This indicates the collapse of the triblock copolymer network. At temperature between 30 to 40 °C below the gel point the NCTPE gels have the property of elastic moduli, where $G' > G''$. This phenomenon was found at every nanoparticle composition as shown in Figure 2 for loss modulus (G'') of (a) 10 wt % EG1, (b) 10 wt% EG2 and (c) 5 wt% CNTs. This indicates that at ambient temperature a physical network is still present despite with addition of nanoparticles. One other unexpected feature of the data shown is that at the highest concentration examined (10 wt% for EG1), G' decreases sharply at very low temperature, which an indicative of limited network alteration. Eventually plummeting of G' was observed as the network ultimately collapses. At higher concentration, this particular graphite type is probably flocculated into large-scale aggregates and thus may not diffuse within the swollen polymer network. In the case of EG2 and CNTs nanoparticles, the behavior of G' is almost the same. At low concentration, G' drastically drops at lower temperature. However increasing the nanoparticle content for EG2, G' slightly decreases then eventually a liquid-like structure occurred upon further heating. Similar behavior was seen in CNTs with higher concentration. Values of the plateau G' extracted from the data between 30 °C to 40 °C in Figure 2 are displayed in Figure 3 as a function of nanoparticle concentrations. The parent TPE gel with 20 wt% SEBS was included here as reference material for comparison. The G' value is 33.8 kPa. The EG1 nanoparticle system yields a markedly lower G' in all concentrations range, which suggests that these nanoparticles may interfere with the connectivity of the underlying copolymer network. Another possible explanation is due to sulfuric acid content of EG1 that may not be totally removed during sonication with ethanol. Uhl and Wilkie[14] observed that the tensile strength for nanocomposite prepared from graphite containing acid and nylon show a significant reduction in tensile strength. At higher concentrations, the nanoparticles are probably flocculated into large-scale aggregates and hinder to a lesser extent the bridging efficacy of individual copolymer molecules. On the other hand, addition of CNTs at low concentration yields low G' values with their parent TPE gels, which possibly dictated by dispersion problems encountered. With further addition of 3 to 5 wt% concentrations to SEBS/oil gel likewise promotes a modest increase in G' which may be due to high aspect ratio nature of this material.

One of the most important characteristics of TPE is the gelation temperature (T_{gml}), defined as here as the temperature

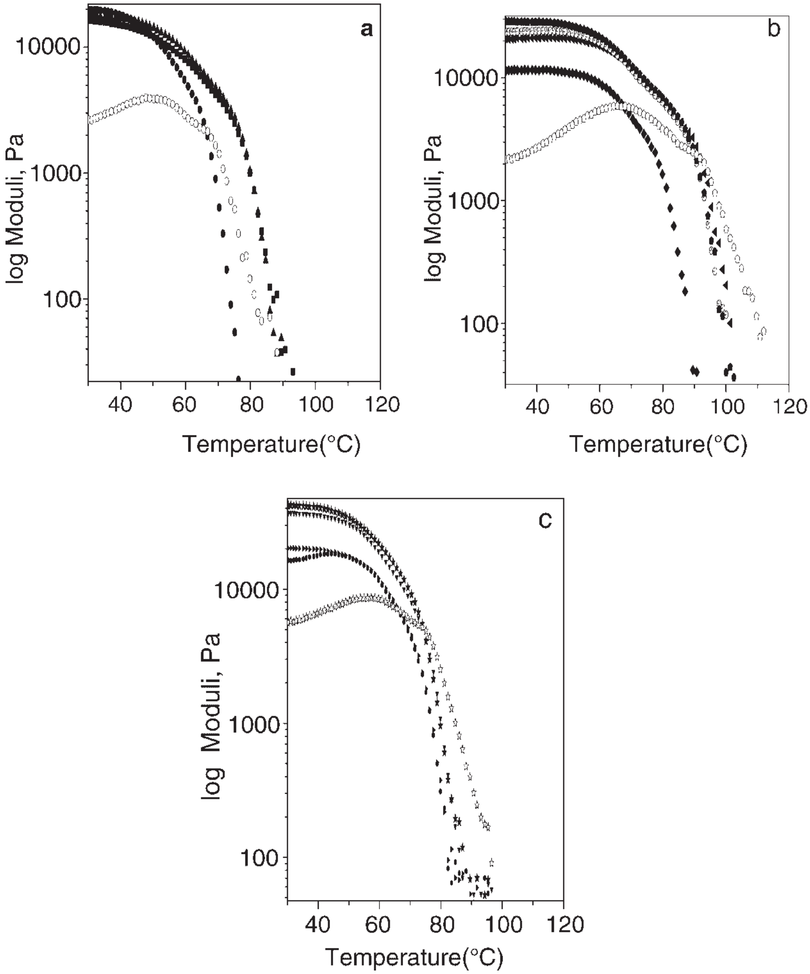

Figure 2.

Dynamic storage modulus (G′) (closed symbols) of NCTPE gels with different nanoparticles as a function of temperature (a) EG1: 1 wt% (square), 3 wt% (up triangle), 10 wt% (circle); (b) EG2: 1 wt% (diamond), 3 wt% (left triangle), 5 wt% (sphere), 10 wt% (pentagon) (c) CNTs: 0.5 wt% (hexagon), 1 wt% (right triangle), 3 wt% (down triangle), 5 wt% (star). Illustrative dynamic loss modulus (G″) (open symbols) data are also included for only one concentration for each nanoparticle to maintain figure clarity (a) 10 wt% EG1 (circle); (b) 10 wt% EG2 (pentagon); (c) 5 wt% CNTs (star).

corresponds to region (iv), i.e the onset of liquid-like behavior. This temperature is also considered as maximum operating temperature (MOT).[15] In this report, the temperature at which $G' = G''$ was considered as T_{gml} since it marks the transition from solid-like state to a viscoelastic liquid state.[8–13,16] While the nanoparticle slightly increases in magnitude of G′ as the concentration increases as previously shown in Figure 3, however in the presence of nanoparticles (Figure 4) appears to have a deleterious effect on gelation temperature. EG1 and CNTs based TPE gels resulted to much lower gelation temperature than EG2. If the 15 wt% SEBS TPE gels is considered as the reference material as also shown in the Figure, then a TPE gel with 20 wt% SEBS, for example, will contain 5 wt% nanoparticle additives. The gelation temperature of CNTPE gels with different amounts of CNTs and EG1 show a little

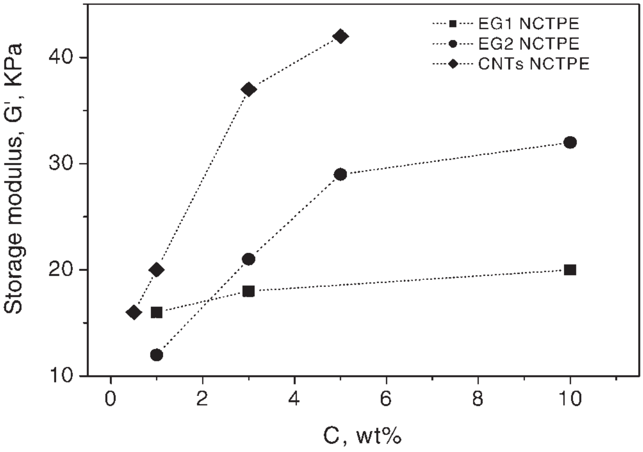

Figure 3.
G′ of NCTPE gels with different nanoparticles and parent TPE gels.

change compared to 15 wt% SEBS, but much lower than their parent TPE gels with 20 wt% SEBS. The NCTPE gels system with EG2 at different concentrations showed higher T_{gml} compared with 15 wt% TPE gels. However T_{gml} is much lower compared with their parent SEBS TPE gels (20 wt%). In general, the nanoparticles lowers the gelation temperature of the gels.

The effect of frequency at different amounts of EG2 for NCTPE gels is shown in Figure 5a and different nanopartcles having the highest nanoparticles concentrations (10 wt% for both EG1 and EG2 and 5 wt% for CNTs) measured at 30 °C (Figure 5b). In these figures, all NCTPE gels were confirmed to behave as physical gels. Here, we mean physical gels as a liquid-rich system exhibiting solid-like behavior, which the characteristics of showing flat mechanical spectrum in an oscillatory shear experiment.[17] The results show G′ exceeds G″ over the entire experimental frequency range, and G′ is dependent of frequency at this 1% strain. The slight increase in G′ as the frequency increases may still be considered as negligible. The onset of gelation temperature

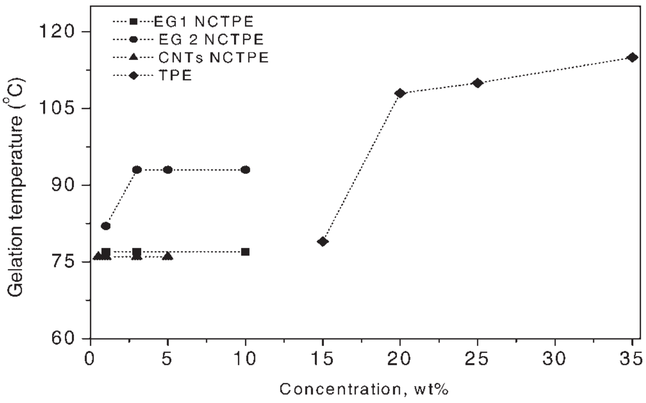

Figure 4.
Gelation temperature of NCTPE gels and TPE gels. The data of TPE gels were taken from our previous study using P3 paraffin oil[9,10] for comparison. This type of oil was used in the preparation of NCTPE gels.

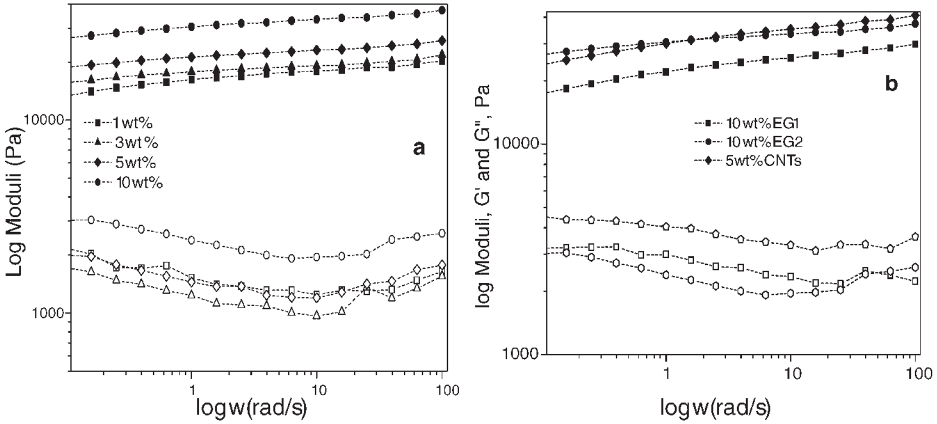

Figure 5.
Storage modulus, G′, (closed symbols) and loss modulus, G″, (open symbols) presented as a function of ω at a γ_o of 1% at 30 °C.

such as 70 °C for all nanoparticles and 90 °C for parent TPE gels, as shown in Figure 2, was chosen to investigate the effect on frequency. As further increase in temperature causes moduli to become frequency dependent with increasing ω for all NCTPE gels with 10 wt % EG1, 10 wt% for EG2 and 5 wt% CNTs respectively, (see

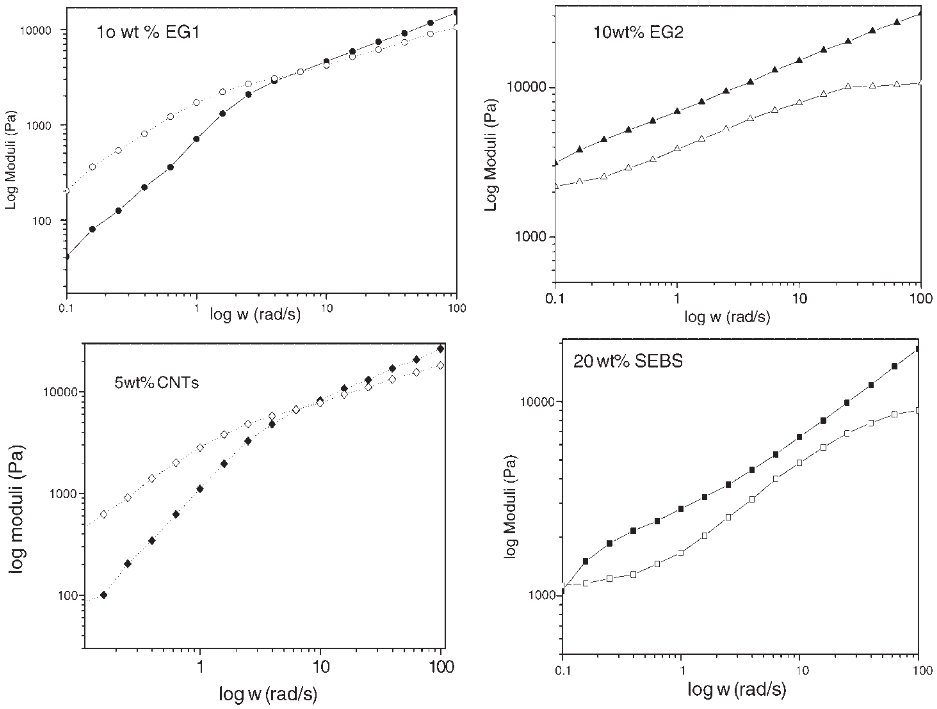

Figure 6.
Storage modulus, G′, (closed symbols) and loss modulus, G″, (open symbols) presented as a function of ω at a γ_o of 1% at 70 °C for NCTPE and 90 °C for SEBS TPE gels.

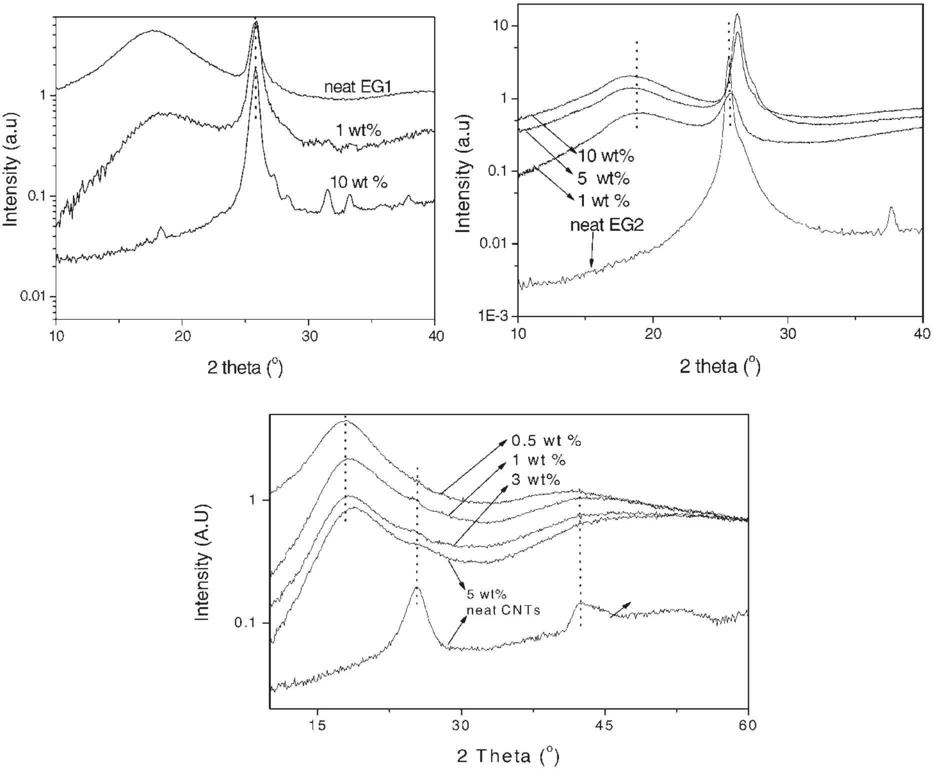

Figure 7.
XRD peaks for NCTPE gels.

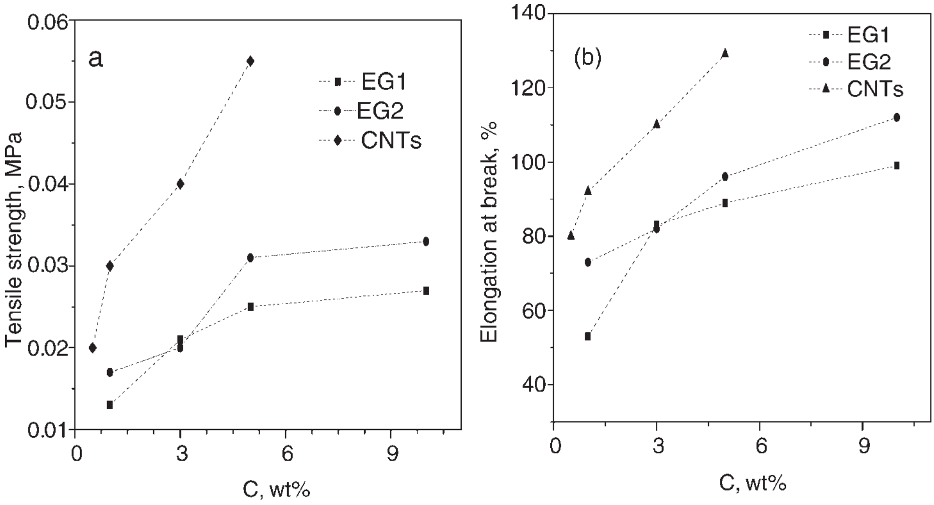

Figure 8.
The mechanical properties of NCTPE gels: (a) tensile strength (closed symbols) and (b) elongation at break.

Figure 6a, b, c) and the parent TPE gels (Figure 6d). This only implies that the gel is no longer a physical gel at these temperatures and the system loses its elasticity. In some instances such as in EG1 and CNTs CNTPE gels, G′ is lower than G″ at lower frequency. As the frequency increases crossover of G′ and G″ is also observed, thereby indicating the gels become viscous liquid. The value of G′ for NCTPE gels with 10 wt% EG2 remains higher than G″ but becomes strongly dependent on ω with increasing ω. Comparable behavior is observed in the TPE gels with 20% SEBS concentration. Such behavior suggests that just below this temperature, the gel network reinforcing TPE gels undergoes some of supramolecular rearrangement, perharps similar to an order-disorder transition (ODT).[6] Note that the loss of gel behavior (i.e., the onset of frequency dependence in G′) is most pronounced at low frequencies, as is typically observed for physical gels.

Morphological Analysis

Different types of interactions take place between polymeric systems and nanoparticles as revealed by X-ray diffraction. When intercalation takes place, there is a finite layer expansion that results into a layer gallery height; obtaining a new basal reflection. Intercalation systems can be either ordered or disordered. A new basal and higher order reflection peak can be seen for ordered intercalated system. On the other hand, diordered intercalated systems exhibit peak broadening and intensity loss due to a decrease in the degree of cohorent layer stacking. For those exfoliated systems, due to extensive layer separation (beyond the resolution of Bragg-Brentano geometry), is not possible to observe a new basal reflection peak. This leads to intensity loss and disappearance of the unintercalated basal reflection.[18] All the three NCTPE gels modified with EGs and CNTs exhibit different behavior as shown in Figure 7 for (a) EG1, (b) EG2 and (c) CNTs and their composites. It can be seen that the basal reflection peak of EG1 with d-spacing of 3.37 Å does not change upon blending with SEBS/oil. The system filled with EG2 exhibits intercalation wherein the small shift on the basal reflection peak to the right indicates an increase in the gallery height. Whereas, NCTPE gels filled with CNTs exhibit exfoliation as indicated by intensity loss and disappearance of unintercalated basal reflection.

Mechanical Properties

Increasing the nanoparticle concentration definitely increases the tensile strength and elongation at break in all NCTPE gels (Figure 8). NCTPE gels filled with CNTs gave higher mechanical properties with all other NCTPE gels maybe due to high aspect ratio nature of this material. As expected, the EG1 based NCTPE gels resulted to much lower mechanical properties as also observed in their G′ modulus. Despite the nanoparticle slightly increases in mechanical properties as the concentration increases, however the value is still far from the parent TPE gels. Since the tensile strength and elongation at break of TPE gels are 0.067 MPa and 82% respectively.[10]

Conclusions

It has been shown in this study that NCTPE gels containing different nanoparticles have the characteristics of physical gels at ambient temperature and G′ remains independent of frequency and consistently greater than G″. All the three types of nanoparticles investigated slightly increases the value of G′ as the concentration increases, however it has deleterous effect on gelation temperature. Different types of interactions took place between polymeric TPE gels systems and nanoparticles. The area of polymer gels/nanoparticles composites are still in infancy stage and much more needs to be done to fully appreciate the systems.

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