

The Effect of Inclusion of Nanoparticles on the Rheological and Morphological Properties of Triblock Copolymer Gels

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ABSTRACT

Nanocomposite materials were prepared by embedding nanosized particles into triblock copolymer gels. The properties related to morphology, viscoelasticity and thermal stability were explored and discussed. Dynamic rheological measurements of the resultant NCTPE gels showed that at temperature between 30 °C to 40 °C below the gel point, the nanocomposite thermoplastic elastomer gels (NCTPEGs) have dynamic storage modulus greater than loss modulus (G' and G''), thereby indicating that at ambient temperature a physical network was still present despite the addition of nanoparticles. Storage modulus slightly increases as the nanoparticles increases. The morphology revealed that nanoparticles used to generate nanocomposite triblock copolymer gels are dispersed generally within the swollen copolymer and or solvent. Thermal degradation was improved with addition of nanoparticles. This research hopefully gives new advancement in the field of nanocomposite polymer gels with wider application.

Keywords: nanocomposite, triblock copolymer, nanoparticles, MWCNT, nanographite platelets

1 INTRODUCTION

Most studies of polymer nanocomposites utilize a homopolymer matrix to which nanofiller is added. In recent years, the colloidal properties of nanocomposite polymer clay gels and solutions have also received considerable attention in the literature. Unusual properties are induced by the physical presence of the nanoparticle and by the interaction of the polymer with the particle and the state of dispersion. Silva et al. [1] have examined the rheological properties of intercalated nanocomposites based on a poly(styrene-*b*-isoprene) (SI) diblock copolymer and a dimethyl/dioctadecyl-substituted montmorillonite (silicate). While numerous fundamental studies on the rheological and morphological properties of molecular networks composed of a microphase-separated multiblock copolymer swollen to a large extent by a low-volatility midblock-selective solvent, [2-6] few comparable efforts have extended studies

to thermoplastic elastomer gels in the presence of nanoparticles. The aim of this paper is to determine the effect of these nanoparticles on the rheological, thermal, and morphological properties of nanocomposite thermoplastic elastomer gels (NCTPEGs). The results obtained here further add to the insight gleaned from previous experiment studies of triblock copolymer [7-9] and hopefully gives new advancement in the field of nanocomposite polymer gels with wider application.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

The poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (SEBS) triblock copolymers with number molecular weight of 79,000 and 29 wt% S (Kraton G1652) was used as received. Two types of exfoliated Graphite Nanoplatelets (xGnP) were used, xGnP1 which has thickness of ~10nm and an average diameter of 1 μ m and and xGnP-15 with the same thickness and diameter of 15 μ m. Details on the exfoliation process as well as on the morphology of xGnP can be found elsewhere [10]. The MWCNTs was purchased from Iljin Nanotech Co., Korea, synthesized by the chemical vapor deposition (CVD) process with average diameter of 13 nm and length of 10 μ m. Purity of the pristine MWCNTs, as received, was 97%. The paraffin oil with molecular weight of 480 g/mol and density of 0.88 g/cm³ was used, which was supplied by Michang Oil Industrial Co., South Korea.

2.2 Preparation of Nanocomposite Triblock copolymer Gels

Nanoparticles were sonicated in ethanol bath for 8 hours, dried and dispersed in chloroform before it was added to the mixture. Nanocomposite triblock copolymer gels composed of 20% SEBS, 1% Irganox antioxidant, 80 % Paraffin Oil, and 0.5 to 5 wt% nanoparticles were prepared in similar in our previous manner except the temperature is reduced to 130°C [5-6]. The resultant hybrid gels were compression-molded without applying much pressure for 5 minutes at 130 °C to yield sample measuring 2.0 to 2.5 mm thickness.

2.3 Characterization

The elastic storage modulus, G' and loss modulus, G'' were measured at a temperature range 30–140 °C with increments of 10 °C/min with constant strain (γ_0) of 1% using a strain-controlled Rheometrics Mechanical Spectrometer (RMS800, USA). Parallel plate geometry with 25 mm and with 1.5 or 2.5 mm gap heights was used for measurement.

The transmission electron microscopy (TEM) measurements were carried out with a Bio-TEM transmission electron microscope applying an acceleration voltage of 120 kV. The specimens were cut at -100 °C by an ultra microtome (Ultra cut E, Reichert & Jung) equipped with a diamond knife. Ultra thin sections of approximately 50 nm thickness were stained with the vapor of 0.5% RuO_4 (aq) gas phase for 5 min, i.e. the PS blocks are stained selectively.

To discern the effect of SEBS/and or hydrocarbon oil on the morphology of the platelets, the spatial atomic arrangements of the neat MWCNTs and NCTPEGs were characterized using a Bruker AXS X-ray Diffractometer (Type D8 Advance), Germany and a Siemens generator (Kristalloflex 760). X-ray diffraction (XRD) profiles were recorded using CoK_α radiation in the angular range from 10°–60° (2 θ) at an operating voltage of 40kV and a current of 20mA with a wavelength of 1.7902 Å.

The thermal stability of NCTPE gels was evaluated by TG-DTA. TG measurements were carried out on 10 mg sample in a DuPont TA2100 TGA in the temperature range of 30–700 °C at a heating rate of 20 °C/min and a nitrogen flow of 50 ml/min. For determining the degradation temperature of TPE and NCTPE gels, thermogravimetric analysis (TGA) was carried out.

3 RESULTS AND DISCUSSION

3.1 Rheological Properties

All NCTPEGs with hybrid of nanoparticles have been subjected to dynamic mechanical studies to discern the effect of nanoparticles on the rheological behavior of NCTPEGs. The oscillatory shear measurements were focused on the variations of elastic (in-phase) G' and viscous (out-of-phase) G'' , as a function of temperature and frequency. Figure 1(a,b & c) show the change in G' with temperature heated throughout the melting range for NCTPEGs containing different amounts of nanoparticles. At a temperature between 30 °C to 40°C, an initial plateau over which G' remains relatively constant or slightly increases with increasing temperature is observed, which means that the rubbery PS domains become glassy below the gel point. Also at this temperature, the NCTPEGs have the property of elastic moduli, where $G' > G''$. This indicates that at ambient temperature physical network is still present despite with addition of nanoparticles. As the

temperature increases, an abrupt reduction in G' , which attributed which an indicative of limited network alteration. Eventually plummeting of G' was observed as the network ultimately collapses. The most common feature observed for all NCTPEGs at low concentration between 0.5 to 1 wt%, G' values are lesser and drops at lower temperature. It was observed that the magnitude of G' slightly increases at low concentration. The minimal increase in G' is probably due poor dispersion that tend the particles to flocculate into large-scale aggregates and thus may not diffuse within the swollen polymer network. Also, the nanoparticles have less connectivity to the underlying copolymer network and weak bonding between the nanoparticles and swollen SEBS/oil system. However, with further addition of 3 to 5wt % concentrations to SEBS/oil gel likewise promotes a modest increase in G' , which is due to high aspect ratio nature of the material.

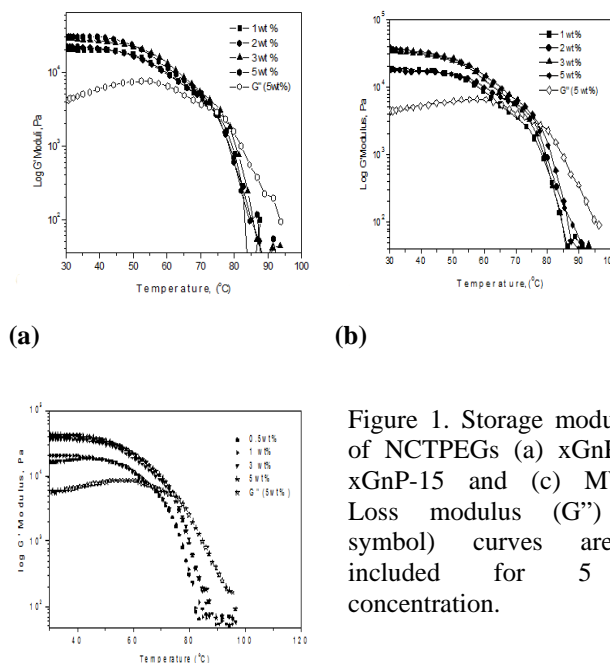


Figure 1. Storage modulus, G' of NCTPEGs (a) xGnP-1, (b) xGnP-15 and (c) MWCNT. Loss modulus (G'') (open symbol) curves are also included for 5 wt% concentration.

3.2 Morphological Properties

Figure 2 displays a pair of TEM images collected from NCTPEGs modified with 5 wt % of, (a) xGnP1, (b) xGnP15 and MWCNT. The images of NCTPEGs exhibit morphology composed of a micellar of SEBS in hydrocarbon oil and nanographite. The irregularity shaped, dark features identify the nanoparticles. It is clear that these nanoparticles are flocculated into large-scale aggregates due to high solvent content and hinder to a lesser extent the bridging efficacy of individual copolymer molecules which possibly dictated by poor dispersion. It was observed by Kalaitzidou [11] that xGnP15 has a tendency to roll together and to form some agglomeration during mixing due the intrinsic van der Waals attractions between the individual nanoplatelets. The relatively high magnification

image in all the figures of NCTPEGs confirm that the matrix consists of SEBS micelles measuring ca.20 nm in core diameter uniformly dispersed throughout the hydrocarbon oil, which agrees well with our previous studies [12]. It is clear from these related images that the micelles do not exhibit discernible indication of long-range order a face- or, more likely, body-centered cubic lattice. This indicates that addition of nanoparticles didn't reduce the intermicellar distance. Moreover, the nanoparticles are formed within the swollen polymer network and not on PS styrene endblock. This finding was also observed in expandable graphite (EG) with the same parent TPE gels [12].

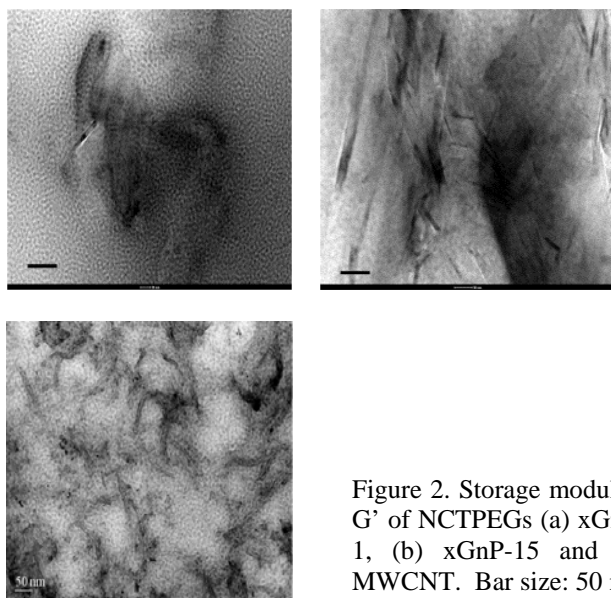


Figure 2. Storage modulus, G' of NCTPEGs (a) xGnP-1, (b) xGnP-15 and (c) MWCNT. Bar size: 50 nm

X-ray diffraction is valuable tool in discerning the extent to which the SEBS/oil matrix alters the layering of the MWCNTs and possibly modify their intrinsic morphology. Figure 3(a & b) represent the X-ray data for NCTPEGs in comparison with parent TPE gels and their neat nanoparticles. From X-ray diffraction (XRD) the 002 peak was observed at $2\theta = 25.95^\circ$ for xGnP (Figure 3a). This xGnP exhibited a clearly discernible basal reflection corresponding to layer spacing 3.40\AA . The d-spacing for NCTPEGs containing 1 wt% and 5 wt% is 26.31° , while xGnP15 is 26.05° for 1 wt % and 26.69° for 5 wt %. The shift in xGnP15 and xGnP1 to higher angles is similar to NCTPEGs with EG [12]. This phenomenon was also seen in PP-g-MA layered EG [13]. Cheng reported that the shift to higher angles indicates tighter packing in the crystal unit cell in directions perpendicular to the chain direction [14]. This can be concluded that the xGnP did not intercalate into the gallery of the carbon layers of graphite during mixing. The NCTPEGs with xGnP is a typical conventional microcomposite. This can be explained that even after the expansion or exfoliation process of the intercalated graphite flakes, it is practically not possible to obtain ideally or

completely exfoliated graphite layers. The inner layers of the exfoliated platelets may have a graphene nanostructure consisting of multiple graphene sheets [15-16]. As a result, the NCTPEGs consist of multi-layered xGnP which is dispersed within the swollen triblock network on the nanoscale, as seen in TEM (Figure 2 (a & b)). On the other hand, the structure of MWCNTs is similar to the hexagonal close-packed lattice of graphite with the interplanar spacing of the diffraction peak 002 at $2\theta = 25.55^\circ$, which corresponds to interlayer spacing 3.45\AA . Due to extensive layer separation (beyond the resolution of Bragg-Brentano geometry), it is not possible to observe basal reflection peak, leading to intensity loss and disappearance of the unintercalated basal reflection. This behavior was observed for NCTPEGs with MWCNTs (Figure 3b), indicating that TPE gels is successfully exfoliated within the nanoparticles of MWCNTs, which is well supported in TEM images. The XRD patterns also show a broad, but distinct peak at low 2θ , confirming the existence of the intrinsic micellar network of TPE gels. The broadened peak is attributed to the heterogeneous distribution of styrene micelles.

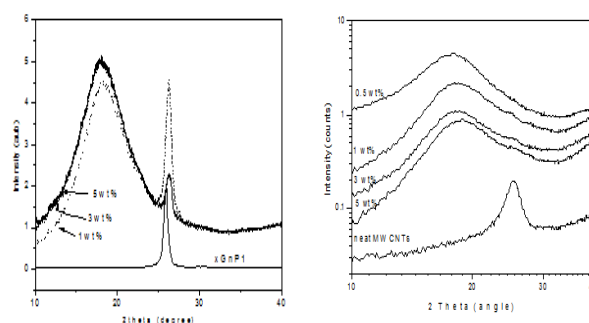


Figure 3. XRD patterns of NCTPEGs (a) xGnP-1 (b) MWCNTs.

3.3 Thermal Stability

The thermograms of NCTPEGs shift towards higher temperature as the heating increases. This shift of thermograms to higher temperature depends primarily on the type of nanoparticles. For each sample, the thermogram revealed that the DTG plot shows a maximum rate of weight loss, so the peak temperatures of degradation (T_p) can be determined. The onset temperatures of degradation (T_{onset}) can be calculated from the TG curves by extrapolating from the curve at the peak of degradation to the initial weight of the polymer. Similarly, the end temperature of degradation can be calculated from the TGA curves by extrapolating from the curve at the peak of degradation forward to the final weight of the polymer. The difference of the peak temperatures and the onset temperatures of degradation is D_T , which represents the temperature range of thermal degradation. These characteristic temperatures are listed in Table 1. The bonding state of EB middle block which dissolves by high

content of oil in SEBS/oil system and microstructure features of the matrix and nanoparticles may play an important role in determining the degradation temperature of the nanocomposites. It appears that the particles reside in the region of EB block swollen by high content of oil thereby increasing the distinct region of oil degradation temperature. However, the second peak that appears at higher temperature remains constant with addition of nanographites. Due to this, the weight loss for swollen EB containing oil and SEBS matrix remains constant with inclusion of nanoparticles. However, the residual yields increase with increasing nanoparticle content, indicating that thermal decomposition of the polymer matrix was retarded in the NCTPEGs/nanoparticles with higher residual yield. This result may be attributed to a physical barrier effect due to the fact that nanoparticles would prevent the transport of decomposition products in the polymer nanocomposites. Comparing the residue of TPE gels without MWCNTs, there is a little residue because the component of the gels consists only of carbon and hydrogen element.

Table 1. Characteristics of thermal stability.

Code NCTPE gels	Onset temperature, °C T _{onset}		Peak temperature, °C T _{peak}		Residue at 600°C, %
	1 st	2 nd	1 st	2 nd	
Parent TPEG	141	413	231	455	0.269
xGnP1-1	163	403	256	454	1.74
xGnP1-5	172	412	273	463	4.95
xGnP15-1	160	410	268	450	0.98
xGnP15-3	167	412	274	453	2.14
xGnP15-5	174	421	291	459	3.20
MWCNT-1	169	410	270	452	0.95
MWCNT-5	174	412	279	464	3.1

4 CONCLUSIONS

The nanocomposite triblock copolymer gels can be generated by addition of nanoparticles such as xGnP and MWCNT into a triblock copolymer of poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene) (SEBS) which is selectively swollen in a midblock-selective solvent. The nanoscale additive can be used to modify the dynamic properties of nanocomposite thermoplastic elastomer gels. Although xGnP did not intercalate nor exfoliated, while MWCNT exfoliated, both dynamic modulus increase to some extent. Thermal degradation was improved with addition of nanoparticles. The area of polymer gels with nanoparticles composites is still in infancy stage and much more needs to be done to fully appreciate the systems.

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