

Morphology Evolution, Conductive and Viscoelastic Behaviors of Chemically Reduced Graphene Oxide Filled Poly(methyl methacrylate)/Poly(styrene-*co*-acrylonitrile) Nanocomposites during Annealing^{*}

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Abstract The effect of chemically reduced graphene oxide (CRGO) on the phase separation behavior of poly(methyl methacrylate)/poly(styrene-*co*-acrylonitrile) (PMMA/SAN) blends and the simultaneous response of rheological and conductive behavior of PMMA/SAN/CRGO nanocomposites upon annealing above the phase-separation temperatures were investigated. The introduction of CRGO causes the decrease of binodal temperature and the increase of spinodal temperature for PMMA/SAN blends and then enlarges their metastable regime. During annealing, the well-dispersed CRGO in the homogeneous blend matrix tends to be selectively located in the SAN-rich phase with the evolution of phase separation and then the CRGO further agglomerates effectively in the SAN-rich phase to form the conductive pathway. Thermal-induced dynamic percolation is observed for both the resistivity ρ and dynamic storage modulus G' as a function of annealing time. The resistivity variation is ascribed to the agglomeration of CRGO in the SAN-rich phase, while the modulus evolution is attributed to the combined contribution of phase separation for blend matrix and the agglomeration of CRGO in the SAN-rich phase.

Keywords: Phase separation; Chemically reduced graphene oxide; PMMA/SAN blend; Electrical conduction; Dynamic modulus.

INTRODUCTION

It is well-known that the electrical volume resistivity (ρ) of insulating common polymers can be varied greatly through incorporating some conductive fillers and the conductive polymer composites (CPCs) would display a fierce transition from the insulator to the conductor when the first conductive path is built at a critical concentration^[1]. Up to date, CPC materials have been widely used in antistatic, electromagnetic shielding, microwave adsorption and so on, due to their advantages, such as light weight, easy processing, corrosion resistance, low cost, adjustable electrical and mechanical performance in a large range^[2–4]. Typically, the incorporation of a large amount of conductive fillers into the insulating polymer matrix may endow the materials superior electrical performance. However, their processability and mechanical properties may be also destroyed at the same time^[5–8]. Hence, the loading of conductive fillers should decrease to ensure the processability and mechanical performance and the dispersion of conductive fillers in the polymer matrix should be also improved to achieve the superior electrical performance.

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The incorporation of conductive fillers into multiphase polymer blends can achieve the optimization of electrical performance and the reduction of conductive filler loadings simultaneously. For example, carbon black (CB), carbon nanotubes (CNTs) were introduced into some immiscible polymer blends, such as polyamide-6/acrylonitrile-butadiene-styrene (PA6/ABS)^[9–11], polyethylene/polycarbonate (PE/PC)^[12, 13], polypropylene/PE (PP/PE)^[14–16], poly(ethylene terephthalate)/PE (PET/PE)^[13, 17–19] to obtain the CPC materials with low percolation values. Without doubt, the phase separation of binary blend matrix in CPC materials may be a useful tool for controlling the dispersion of conductive fillers in the blend matrix and further improving their electrical property^[15]. In general, CPC materials are always multiphase/multi-component systems and their properties are mainly affected by their morphology and structure. Hence, CPC materials with desired ultimate properties can be obtained by controlling the formation and evolution of their morphology and structure. In order to achieve the better regulation of morphology and structure for CPC materials, it is of great academic and applied value to investigate the miscibility and phase-separation behavior of blend matrixes with critical phase behavior.

It can be found that the nano-fillers, such as carbon black (CB), layered silicates, calcium carbonate (CaCO_3), may improve the compatibility of polymer blend matrices and stabilize their morphology^[20]. Besides the excellent electrical performance, the introduction of conductive filler may bring much complexity to the miscibility/compatibility and the morphology evolution of polymer blend matrices as they can alter the free energy of the system and lead to a redistribution of polymer molecules between the particle surface and the bulk, depending on the affinity of the polymers for the particles^[21–24].

The potential of graphene as filler in polymeric nanocomposites has widely been explored for designing novel materials owing to their extraordinary combination of properties, such as high intrinsic mobility, high Young's modulus and thermal conductivity, excellent electrical conductivity and optical transmittance^[25–29]. It is envisaged that its large specific area and the oxygen functionalities in graphene allow the enhanced interactions with the polymeric matrix and consequently the better thermal, mechanical, conductive properties^[30]. Although there are some reports addressing structure-property relations in polymeric blends/nanocomposites containing graphene^[31], the effect of graphene on the phase separation of polymer blends has received limited attention^[32].

Dynamic rheological measurement (DRM) is sensitive to the morphology change of multiphase/multi-component systems during phase separation process^[33]. Furthermore, DRM is also sensitive to the filler dispersion in polymers^[34, 35]. Simultaneous measurements of conductive and rheological properties may be used to investigate the real-time viscoelastic and conductive behaviors induced by the variation of microscopic condensed structure in the different external field (thermal field, shear field). Such method has been performed in CB-filled natural rubber^[36], vulcanizates^[37] or electrorheological suspensions^[38] under shear actions. We have proposed a novel method for simultaneous measurement of resistivity ρ and dynamic storage modulus G' for conductive polymer composites^[39]. By using this method, we have investigated the simultaneous variations of ρ and G' for CB-filled semicrystalline polymers undergoing shear deformation^[40], isothermal crystallization^[41], or nonisothermal ramp^[42]. In the present article, we focus our attention on the simultaneous measurement of ρ and G' as a function of time for chemically reduced graphene oxide (CRGO) filled LSCT-type poly(methyl methacrylate)/poly(styrene-co-acrylonitrile) (PMMA/SAN) blend to investigate their evolution of structure and morphology subjected to annealing above the phase separation temperature and the effect of CRGO on the phase separation behavior of PMMA/SAN blend matrix. We also attempt to clarify the influence of temperature and CRGO content, morphology variation of blend matrix on CRGO agglomeration and the resultant evolution of conductive and dynamic rheological behaviors. The correlation among the morphology, viscoelastic response and conductive properties of such conductive polymeric composites during annealing will be established to provide a theoretical guidance for the development and preparation of high performance conductive polymer nanocomposites. Furthermore, the annealing-induced phase separation of blend matrix can be used as an effective tool for improving their electrical properties.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) (IF850, $M_n = 5.0 \times 10^4$, $M_w/M_n = 1.5$, LG Co. Ltd, South Korea) and poly(styrene-co-acrylonitrile) (SAN) (PN-127H, AN content of 32 wt%, $M_n = 5.2 \times 10^4$, $M_w/M_n = 1.7$, Chimei Co. Ltd, Taiwan, China) were dried in vacuum oven at 100 °C for 24 h before use to remove any moisture. Natural graphite (99.8% pure grade, 325 mesh) was obtained from Alfa Aesar Co. Ltd., UK.

Sample Preparation

Graphene oxide (GO) was synthesized from natural graphite powder *via* a modified Hummers' method^[43–45]. Hydrazine hydrate (85%) was used as a reductant in the conversion of GO to CRGO^[46]. GO aqueous solution (10 mL, 1 mg/mL for GO) was mixed with *N,N*-dimethylformamide (DMF, 10 mL), hydrazine hydrate (2 μ L) and then ammonia solution was added into the mixture to adjust pH to 9–10. After uniformly mixing, the reduction was conducted at 95 °C for 1 h. The obtained CRGO was washed by tetrahydrofuran (THF) and methyl ethyl ketone (MEK) for three times separately, and vacuum-filtered by PTFE membranes of 0.22 μ m.

The washed CRGO was dispersed into MEK and the suspension was sonicated for 15 min before adding PMMA/SAN with different compositions at 15 wt% to the suspension. The mixture was then sonicated for another 15 min to achieve the uniform dispersion of CRGO in the PMMA/SAN blend solution. Subsequently, the suspension was cast onto the plate glasses at 30 °C. After the solvent evaporated at an ambient environment for 24 h, the samples were dried at 50 °C, 70 °C, 90 °C, 110 °C and 130 °C for another 5 days in vacuum oven to remove the residual MEK. The dried films were compressed under 10 MPa and 120 °C into a disc with a diameter of 25 mm and the thickness of 1.2 mm. Here, the PMMA/SAN blends denoted by *A/B* and PMMA/SAN/nanoparticle samples denoted by *A/B/x* were prepared by solution casting, where *A* and *B* are the volume fraction of PMMA and SAN in the binary blend, respectively. *x* is the volume fraction of nanoparticles compared to the total amount of polymers.

Characterization Techniques

Contact angle measurements

The contact angle measurement was conducted with a Harke-SPCA instrument (Perking Harke Experimental Instrument Factory, Beijing, China). The surface tension γ can be determined by contact angle of water and ethylene glycol. The sample preparation of CRGO for contact angle measurements was reported by Cabrales^[47]. After the reduction, the product was washed and centrifuged by ultrapure water for 3 times to remove the residual reactant and solvent. Then the supernatant was used to obtain a thin film by spin-coated onto the glass slide.

Transmission electron microscopy (TEM)

The dispersion of CRGO and morphological evolution of nanocomposites were observed by a transmission electron microscope (TEM, JEM 1200EX, Japan). The samples subjected to different annealing processes were quenched to freeze their morphology. Their TEM specimens were prepared by ultramicro-toming with a diamond knife.

Simultaneous measurements of rheological and electrical behaviors

The setup for simultaneous measurement of rheological and electrical behaviors was mentioned elsewhere^[5, 48, 49]. The samples were annealed at 60 °C for 24 h to relieve the internal stress before simultaneous measurements. Rheological measurements were conducted on the advanced rheometric expansion system (ARES-G2 rheometer, TA Instruments Corporation, USA) and volume resistance was simultaneously measured with a digital picoammeter (Keithely 6487 picoammeters, Keithley Instruments Inc., USA). Dynamic time sweep was performed with a frequency (ω) of 0.3 rad·s^{−1} under 1% strain at different temperatures, and the applied direct voltage was less than 1 V. Experiments with various strain amplitudes showed that the influence of 1% strain amplitude on electrical resistance was negligible^[50].

Dynamic rheological measurements

Dynamic rheological measurements were also conducted using ARES-G2 with parallel plate geometry of 25 mm in diameter. Two kinds of measurements were performed under conditions as following: (i) isochronal temperature sweeps from 145 °C to 220 °C at 0.3 rad·s⁻¹ and the heating rates of 1.0 K·min⁻¹; (ii) isothermal frequency sweeps ranging from 100 rad·s⁻¹ to 0.01 rad·s⁻¹ at various temperatures. The strains in these two measurements were both maintained as 1% ensuring that all the measurements were in the linear viscoelastic region.

RESULTS AND DISCUSSION

Phase Diagram of PMMA/SAN Polymer Blends and Ternary Nanocomposites

In general, phase separation temperature of polymeric blends can be determined by optical microscopy^[51], light scattering^[52] and rheological measurements^[53]. However, the sample turbidity of polymer blends with nanoparticles, especially those with high loadings, makes it rather difficult to obtain the cloud point by optical methods^[54]. Rheological measurements is widely used to infer the phase separation temperature in complex systems through the changes in linear viscoelastic response as the system evolves from homogeneous through metastable to the phase-separated regime. Hence, the binodal temperature (T_b) can be obtained by the failure of time-temperature superposition (TTS) principle^[55], tail in the Cole-Cole plot^[56], and so on. Here, T_b s for the PMMA/SAN blends and PMMA/SAN/CRGO nanocomposites are acquired by the Cole-Cole plot. As an example, Fig. 1 shows the Cole-Cole plots of loss viscosity η'' against dynamic viscosity η' at different temperatures for PMMA/SAN (57/43) blend and PMMA/SAN/CRGO (57/43/0.2) nanocomposite. It can be found that the cole-cole plot is arc-shaped at low temperatures, but a tail or an upwarp of the plot emerges at high temperatures, *i.e.* $T > 165$ °C for the blend and $T > 160$ °C for the nanocomposite. Such tail may grow into another circular arc at sufficiently high T , representing the interfacial relaxation of the domain. T_b can be determined by series dynamic frequency sweep measurements at demixing temperatures, and T_b s of PMMA/SAN (57/43) blend and PMMA/SAN/CRGO (57/43/0.2) nanocomposite are deduced from the emergence of tail in the Cole-Cole plots at ~165 °C and 163 °C, respectively. As it is considered to be more sensitive way to detect the onset of phase separation than the failure of TTS^[57], T_b s obtained from the other methods aren't given here.

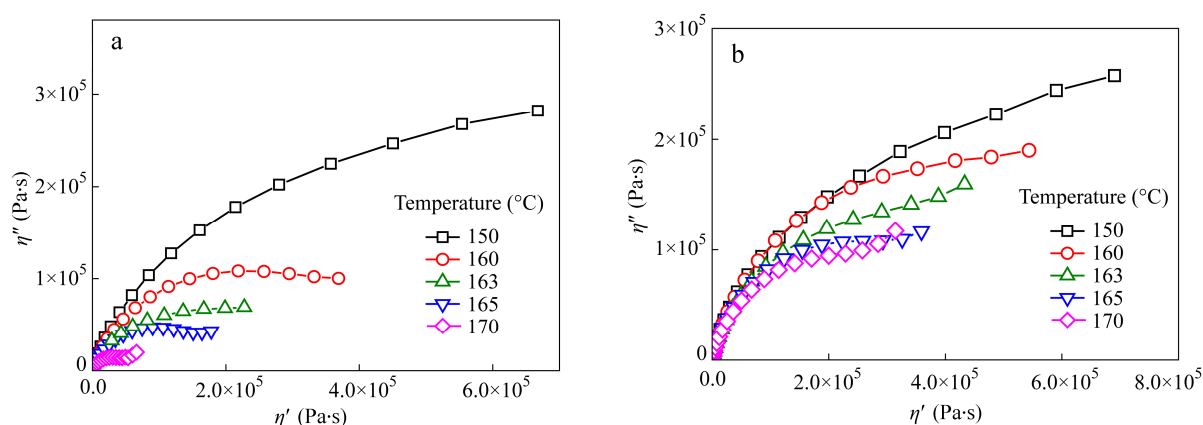


Fig. 1 Cole-cole plots of (a) PMMA/SAN (57/43) blends and (b) PMMA/SAN/CRGO (57/43/0.2) nanocomposites at different temperatures

Another phase separation temperature, spinodal temperature (T_s) is the boundary temperature between the metastable and unstable regimes. Such temperature is usually obtained by dynamic temperature measurements based on the theoretical approach of Fredrickson and Larson^[58]. However, T_s s obtained by this method are obviously dependent on the heating rate and our abovementioned T_b s are obtained from the isothermal

measurements. Hence, T_s can be also obtained by isothermal dynamic frequency sweep tests and independent on the heating rate. The gel-like behavior or long-range continuity has been observed in the unfilled or nanofillers-filled polymer blends with the co-continuous morphology formed at the early stage of spinodal decomposition (SD) phase separation^[53, 57, 59, 60]. The critical gel-like behavior refers to the phenomenon at low frequencies(ω s) which is shown mathematically by Eq. (1).

$$G', G'' \propto \omega^a, 0 < a < 1; \tan \delta = G''/G' = \tan \frac{n\pi}{2} \quad (1)$$

It implies that storage modulus G' and loss modulus G'' have the same dependence of frequency at different ω s. In other words, the loss angel tangent ($\tan \delta$) value is constant at terminal regime. Figure 2 shows the temperature dependence of $\tan \delta$ under various frequencies for PMMA/SAN (57/43) blends and (b) PMMA/SAN/CRGO (57/43/0.2) nanocomposites. At higher ω s, $\tan \delta$ values for unfilled and filled systmes are dependent on the frequency and temperature, while at lower ω s, their $\tan \delta$ values of different frequencies all converge in a small temperature region, implying that $\tan \delta$ becomes independent of frequency at a certain temperature. Actually, the measurements include some experimental errors, and hence the arithmetic mean of the intersections for these plots can be considered as gel point, or T_s in our research.

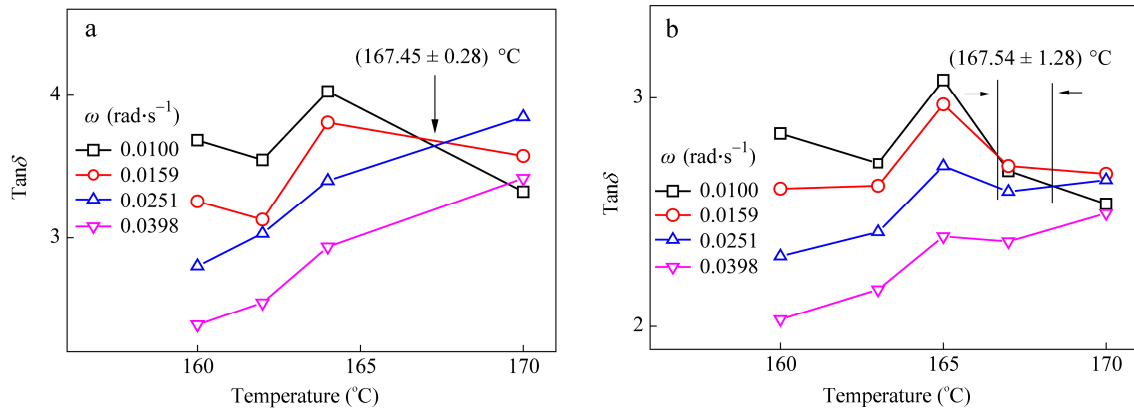


Fig. 2 Temperature dependence of $\tan \delta$ under different frequencies (0.01–0.0398 $\text{rad}\cdot\text{s}^{-1}$) for PMMA/SAN (57/43) blends and (b) PMMA/SAN/CRGO (57/43/0.2) nanocomposites

Based on the above obtained T_b and T_s , the phase diagrams of PMMA/SAN blends and PMMA/SAN/CRGO nanocomposites are given in Fig. 3. It should be noted that the concentration (0.2 vol%) of CRGO chosen here is too low to form the effective agglomeration at the early stage of phase separation which was determined by simultaneous measurement of rheological and electrical behaviors (discussed later in the text). Hence, the effect of 0.2 vol% CRGO aggregation on the modulus of the nanocomposites at the early stage of phase separation may be neglected and the contribution of morphology evolution to their modulus for such nanocomposite can be used to obtain their phase separation temperature. The incorporation of 0.2 vol% CRGO obviously decreases their T_b , but increases T_s of PMMA/SAN blend matrix with the compositions of 37/63 and 47/53 and just little increases that of PMMA/SAN (57/43) matrix. It is well known that T_b is the boundary temperature between the homogeneous and metastable regime and at such temperature the phase separation occurs according to the nucleation and growth (NG) mechanism. Hence, the obvious decrease of T_b for the nanocomposites suggests that the incorporated CRGO may act as a nucleating agent inducing the NG phase separation. Thermally reduced graphene sheet was also observed to induce the NG phase separation in PMMA/poly(α -methyl styrene-*co*-acrylonitrile) (PMMA/P α MSAN) blends^[32]. Furthermore, the different increases of T_s for the nanocomposite indicate that CRGO may retard the concentration fluctuation at the early stage of spinodal decomposition for PMMA/SAN blend matrix, especially the diffusion of SAN segments. Here,

the decline of T_b and the increment of T_s indicate that the presence of CRGO may lead to the expansion of their metastable region and the nucleating agent role of CRGO may induce the phase separation of PMMA/SAN blend matrix according to the NG mechanism in the wider annealing temperature region. However, the shape of phase diagram may be hardly influenced by the existence of 0.2 vol% CRGO. In other words, the effect of CRGO on the phase separation temperature of PMMA/SAN matrix is almost independent on the composition of their blend matrix. Such phenomenon is different from those found in PMMA/SAN/SiO₂ systems, for which the effect of nanofiller on their phase separation temperature remarkably depends on their blend matrix composition due to the composition difference of the surface layer from that of the matrix^[52]. The presence of nanofiller was reported to induce or delay the phase separation process of polymer blend matrix^[61, 62]. Hence, the surface chemistry, characteristic, concentration and dispersion of the nano-fillers should play an important role in affecting the thermodynamics of phase separation in blend matrix.

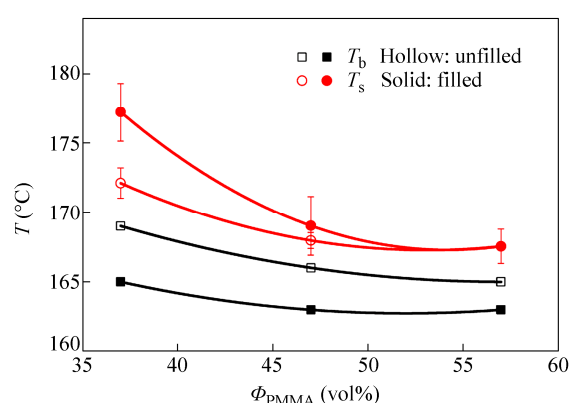


Fig. 3 Phase diagrams of PMMA/SAN blends and 0.2 vol% CRGO filled PMMA/SAN nanocomposites

Dispersion State of CRGO and Morphology of Nanocomposites

The role of CRGO in affecting the phase separation of PMMA/SAN blend matrix may be elucidated by a detailed morphology analysis. Here, the dispersion state of 0.5 vol% CRGO in PMMA, SAN and PMMA/SAN (57/43) nanocomposites without annealing was observed by TEM, as shown in Fig. 4. It can be found that the CRGOs are relatively well dispersed in the three homogeneous nanocomposites, indicating that the presence of CRGO hardly destroys the homogeneity of PMMA/SAN blend. But the dispersion states of CRGO in the three matrices are different. There are most exfoliated (hair-like) CRGOs and just a few small aggregates of CRGOs in SAN and PMMA/SAN two homogeneous matrices (Figs. 4a and 4c), while most CRGOs are aggregated in PMMA matrix (Fig. 4b). The different dispersion states of CRGOs in the three homogeneous matrices may indicate that CRGO has more affinity for SAN than for PMMA. The blend morphology and the corresponding dispersion of CRGOs for PMMA/SAN/CRGO (57/43/0.5) nanocomposites at different stages of phase separation were also studied by TEM, as shown in Fig. 5. Although the samples were not stained, the two components had sufficient contrast. Here, the SAN-rich phase appears dark while the PMMA-rich phase appears bright in the bright-field TEM micrographs. The PMMA/SAN (57/43) blends in presence of CRGOs (0.5 vol%) show the co-continuous morphology after being annealed for 500 s and 10 h, indicating the emergence of phase separation according to the SD mechanism. Furthermore, the CRGOs are dispersed in the SAN-rich domain (dark region) at the early stage of phase separation (Fig. 5a). With the evolution of phase separation, the CRGOs are still located in the coarsening SAN-rich domain and form some small clusters at the late stage of SD (Fig. 5b). The localization of CRGO in the SAN-rich phase for the phase-separated PMMA/SAN system is similar with those of RGO and MWCNTs in the P α MSAN phase for PMMA/P α MSAN blend^[32, 63]. In an immiscible or partial miscible blend, the minimization of the interfacial energy is the thermodynamic driving force for the filler to localize in a specific phase or at the interface^[64]. A quantitative estimation of wetting

coefficient may give the idea about the selective localization of CRGOs in the blend matrix driven by the thermodynamic forces, providing the surface free energy of the components. It is well-known that according to the Young's equation, the location of filler in a polymer blend matrix can be also predicted by evaluating the wetting coefficient ω_a ^[65].

$$\omega_a = \frac{\gamma_{\text{filler-A}} - \gamma_{\text{filler-B}}}{\gamma_{\text{A-B}}} \quad (2)$$

where γ_{i-j} is the interfacial tension between the components pair i and j . The fillers are predicted to locate in the A-rich phase when $\omega_a < -1$, at the interface between two phases when $-1 \leq \omega_a \leq 1$ and within the B-rich phase when $\omega_a > 1$. Here, the interfacial tension between two components can be calculated from the surface tensions of components using the harmonic mean:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left[\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right] \quad (3)$$

where γ_i is the surface tension of components i ; γ_i^d and γ_i^p are the dispersive part and polar part of the surface tensions of components i , respectively. In this work, the surface tensions of PMMA and SAN are extrapolated to the investigated temperatures using the temperature coefficients ($-d\gamma/dT$) extracted from the literatures^[66]. Then the interfacial tensions between pairs of components and the wetting coefficients are calculated using Eqs. (2) and (3) and summarized in Table 1. Here, it should be noted that the surface tension of CRGO was obtained as $52.30 \text{ mJ}\cdot\text{m}^{-2}$ by contact angle measurements, which is approximate to the values $46.7 \text{ mJ}\cdot\text{m}^{-2}$ reported by Cabrales^[47]. It is obvious that all the ω_a values in the investigated temperature region are higher than 1. Thus,

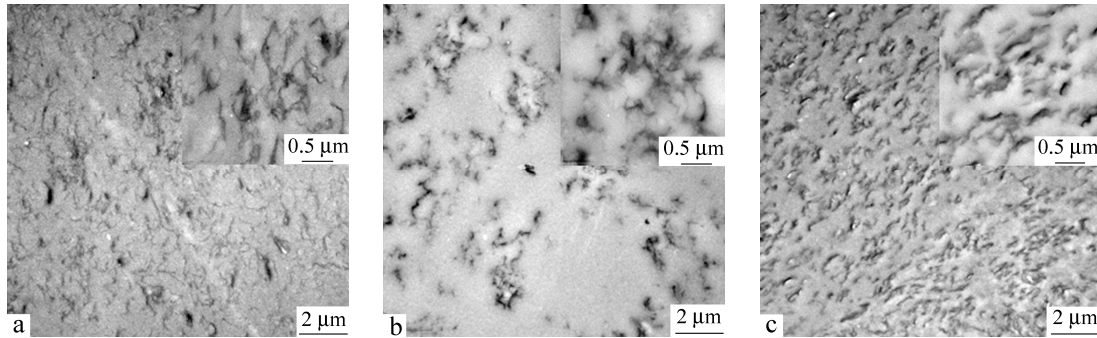


Fig. 4 TEM micrographs of (a) SAN/CRGO (100/0.50), (b) PMMA/CRGO (100/0.50) and (c) PMMA/SAN/CRGO (57/43/0.50) nanocomposites without annealing

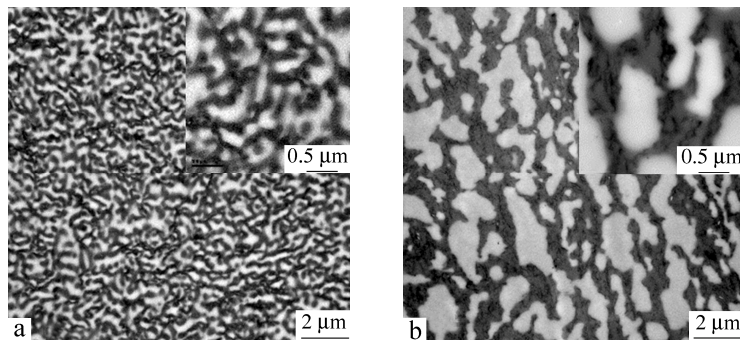


Fig. 5 TEM micrographs of PMMA/SAN/CRGO (57/43/0.50) nanocomposites annealed at 180 °C for (a) 500 s and (b) 10 h

it can be concluded that CRGO will tend to be located in the SAN-rich phase, which is consistent with our TEM results. Furthermore, it is known that all the π - π conjugation takes place when two aromatic rings get close. The π - π conjugation occurs between CRGO honeycomb and SAN benzene ring, which might lead to the preferential localization of CRGO in the SAN-rich phase after the phase separation of blend matrix^[32]. The affinity of CRGO to SAN may result in the redistribution of the blend components in the surface layer of CRGO and the bulk. In other words, SAN is the majority in the surface layer of CRGO. For such blend, the critical composition of PMMA/SAN in weight is reported in some previous researches to be close to 70/30^[22, 53, 59, 67]. However, the CRGO loading for the samples used in the above section is just 0.2 vol% and it can hardly change the blend compositions of bulk. Hence, just the blend composition for the surface layer of CRGO becomes the *off*-critical composition and the SD phase-separation should occur at a higher temperature to jump from the metastable regime to the unstable regime during heating.

Table 1. Interfacial tension and wetting coefficient according to the harmonic mean equation

Temperature (°C)	Interfacial tension (mN/m)			Wetting coefficient ω_a	Location prediction
	$\gamma_{\text{PMMA-CRGO}}$	$\gamma_{\text{SAN-CRGO}}$	$\gamma_{\text{PMMA-SAN}}$		
20	6.33	2.42	2.04	1.92	SAN
170	4.44	0.95	1.56	2.24	SAN
180	4.32	0.86	1.55	2.23	SAN
190	4.20	0.79	1.53	2.23	SAN
200	4.06	0.72	1.50	2.23	SAN

Dynamic Percolation of PMMA/SAN/CRGO Nanocomposites during Isothermal Phase Separation

In general, the dispersion of CRGOs in polymer matrix at high temperatures is always in a non-equilibrium state and they tend to aggregate together in order to reduce the excess interfacial energy^[1, 48, 49]. The driving force for the aggregation might be the strong dispersive interaction between the filler and polymer matrix as well as the depletion interaction between the adjacent filler particles^[48, 49]. Here, simultaneous measurements of conductive and rheological properties were performed to trace the variation of volume resistivity ρ and dynamic modulus. Figure 6 shows the time evolution of ρ for neat PMMA, SAN, PMMA/SAN (57/43) polymer systems and 0.2 vol% CRGO filled nanocomposites isothermally annealed at 180 °C. It is obvious that the ρ values for the three neat polymer systems vary slightly during annealing and the ρ value of SAN is similar with that of PMMA/SAN blend and two magnitudes lower than that of PMMA. The initial ρ values of SAN/CRGO (100/0.2) and PMMA/SAN/CRGO (57/43/0.2) nanocomposites change slightly and have the same magnitude with those of neat polymer systems at the early stage of annealing before a critical time. Then their volume resistivities drop rapidly and finally tend to appear constant at infinite time. Such critical time is called dynamic percolation time (t_{PR}), when the first conductive pathway generates. The remarkable decay of ρ is referred to dynamic conduction (DC) percolation^[68]. For PMMA/CRGO (100/0.2) nanocomposite, there is no initial plateau at the beginning of isothermal treatment, implying the conductive network of CRGO may form even in the sample preparation. As shown in Fig. 4(c), some remarkable aggregates of CRGO may agglomerate to build continuous network locally in PMMA/CRGO nanocomposite without any annealing. For ternary nanocomposite, the DC percolation is also influenced by the morphology evolution of blend matrix and the distribution of CRGO upon annealing. Compared to SAN/CRGO (100/0.2), the dynamic percolation time of PMMA/SAN (57/43/0.2) nanocomposite is in advance, and its ρ decreases more greatly than that of SAN/CRGO (100/0.2), indicating that at t_{PR} , the phase separation of PMMA/SAN (57/43) blend matrix has taken place and most CRGOs may migrate to SAN-rich phase with the evolution of phase separation. The affinity of CRGO to SAN phase has been proven in the TEM micrographs and the estimation of wetting coefficients. The effective volume fraction of CRGO in SAN-rich phase increases owing to the CRGO migration during phase separation, which may accelerate the evolution of volume resistivity.

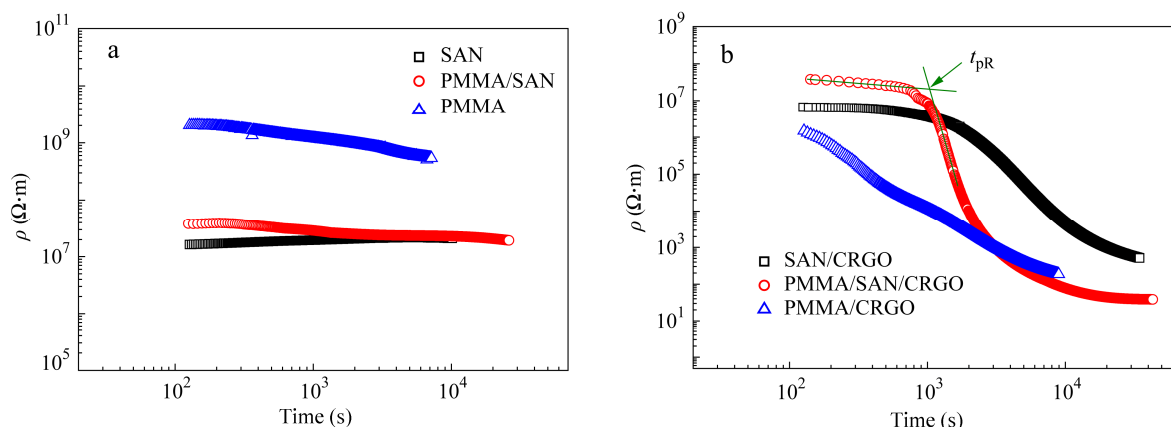


Fig. 6 Time evolution of volume resistivity ρ for (a) neat PMMA, SAN, PMMA/SAN (57/43) systems and (b) SAN/CRGO (100/0.2), PMMA/CRGO (100/0.2) and PMMA/SAN/CRGO (57/43/0.2) nanocomposites at 180 °C

Figure 7(a) shows the corresponding variations of G' for PMMA/SAN (57/43) binary blend, 0.2 vol% CRGO filled PMMA, SAN and PMMA/SAN (57/43) nanocomposites to clarify the contributions of phase separation and filler agglomeration, respectively, to the evolution of modulus. For the unfilled polymer blend, it is clear that at the beginning of phase-separation G' increases with time and then G' decreases a little with the extending of annealing time. Such variation in G' is just attributed to the morphology development of this blend^[69]. The initial increase of G' arises from the formation of new co-continuous phase interface at the early stage of SD and the following decrease of G' may be attributed to the decrease of interfacial area induced by the domain coalescence and the morphology transition from percolation to droplet of SAN-rich domain in the late stage of phase separation due to the excess of interfacial energy^[63, 70]. Figure 7(b) shows the blend morphology after being annealed for 10 h at 180 °C and affirms the breakup of SAN-rich (dark region) phase network. The PMMA/CRGO (100/0.2) and SAN/CRGO (100/0.2) binary nanocomposites also show the marked increases in G' after a critical annealing time (t_{pG}), appearing as dynamic modulus (DM) percolation due to CRGO agglomeration in the melt^[71]. The poor dispersion of CRGO in PMMA leads to the obvious agglomeration and the reduction of the mobility of macromolecular chains between the CRGO aggregates and then the dramatic increase of G' at $t > 400$ s during annealing, while the interaction between CRGO and SAN restricts the aggregation of CRGO in the SAN matrix and results in the gentle increase of G' , which is consistent with the above-mentioned conductivity results. The modulus variation of the ternary nanocomposite can be regarded as the superimposition contribution of phase separation and CRGO agglomeration. It can be found that a small increase of G' for ternary nanocomposite appears at $t > 200$ s, while the increases of G' for binary nanocomposites emerge at $t > 450$ s, indicating that the co-continuous morphology formed in PMMA/SAN blend matrix plays a dominant role at the early stage of annealing. CRGO agglomeration may be predominant at the middle and late stages of annealing, because the little decrease of modulus induced by phase coalescence and morphology transition from co-continuous to insular structure is covered up by the obvious modulus increase due to the CRGO agglomeration^[20]. Figure 7(c) shows the TEM micrograph for ternary nanocomposite after being annealed for 500 s at 180 °C. It can be found that PMMA/SAN (57/43) blend matrix shows co-continuous morphology and most CRGOs move to the SAN-rich phase (dark region). t_{pR} for this ternary nanocomposite is about 1000 s in Fig. 6(b), implying that the phase separation of matrix occurs prior to the dynamic resistivity percolation.

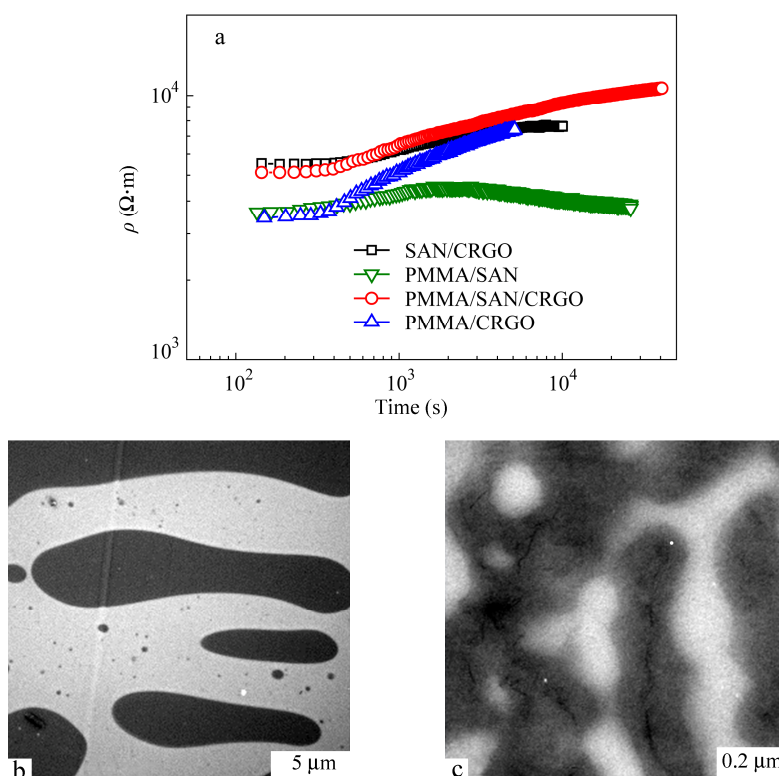


Fig. 7 (a) Time evolution of G' for PMMA/SAN (57/43) blends, SAN/CRGO (100/0.2), PMMA/CRGO (100/0.2) and PMMA/SAN/CRGO (57/43/0.2) nanocomposites at 180 °C, (b) TEM micrograph of PMMA/SAN (57/43) after being annealed for 10 h at 180 °C and (c) TEM micrograph of PMMA/SAN/CRGO (57/43/0.20) after being annealed for 500 s at 180 °C

The influence of CRGO volume fraction (ϕ) on the dynamic percolation for PMMA/SAN/CRGO nanocomposites was also investigated further at 180 °C, as shown in Fig. 8. t_{pR} decreases sharply with increasing ϕ . The initial plateau of ρ for the nanocomposites with the ϕ (CRGO) of 0.28 and 0.5 can hardly be found in Fig. 7(b) and t_{pR} for such two systems may be shorter than 100 s, implying that the conductive pathway of CRGO in the polymer melt may form at the early stage of annealing. Furthermore, the DM percolation also becomes significant and t_{pG} reduces with increasing ϕ . At a given time, the increment of G' with increasing ϕ may be mainly ascribed to the hydrostatic reinforcement effect. It is well known that the incorporation of nano-filler may stabilize the phase structure of polymer blend matrix through the retardation of macromolecular diffusion^[67]. Hence, the effect of CRGO content on the contribution of modulus increment arising from the phase separation can be neglected. Here, the reduction of t_{pR} and t_{pG} with the increase of ϕ indicates that the increment of CRGO content may accelerate the dynamic percolation^[72].

Annealing temperature is another factor influencing the morphology evolution of blend matrix and CRGO agglomeration. When the nanocomposites are heated to a given temperature above T_g of the blend matrix, the CRGO distribution are broken to redistribute, and the preexisting continuous network would be destroyed partially due to the expansion of polymer blends, and reestablished during annealing^[49]. Figure 9 shows the time dependence of G' and ρ for PMMA/SAN/CRGO (57/43/0.2) ternary nanocomposites during annealing at 170–200 °C. With the increase of annealing temperature, the decay of ρ accelerates and t_{pR} rapidly decreases, indicating that the temperature increment can accelerate the DR percolation. However, the time evolution plots of G' at various annealing temperatures have self-similarity and the decrease of t_{pG} with the temperature increasing is less obvious than that of t_{pR} , suggesting that the temperature increment may just accelerate the DM percolation little.

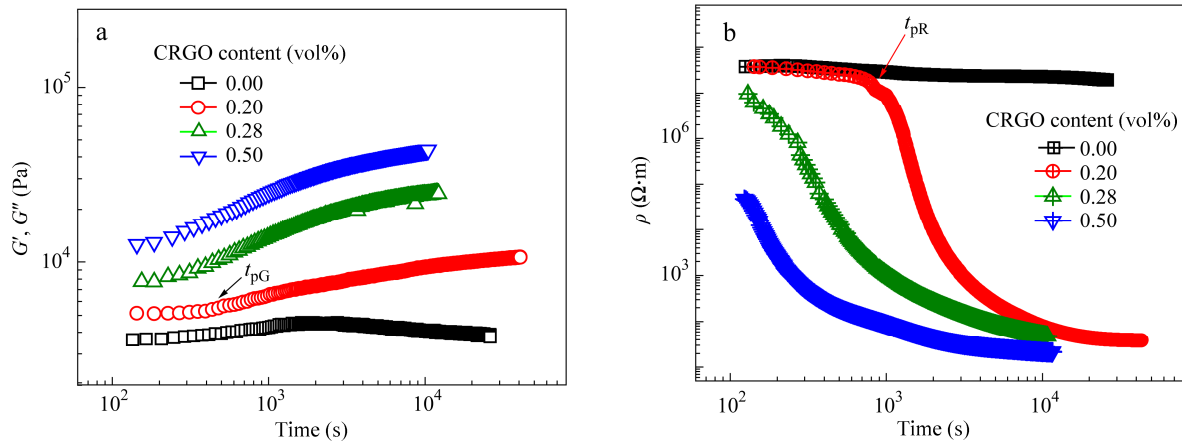


Fig. 8 Time evolution of (a) G' and (b) ρ for PMMA/SAN/CRGO (57/43/ x) nanocomposites with different CRGO volume fractions ϕ at 180 °C

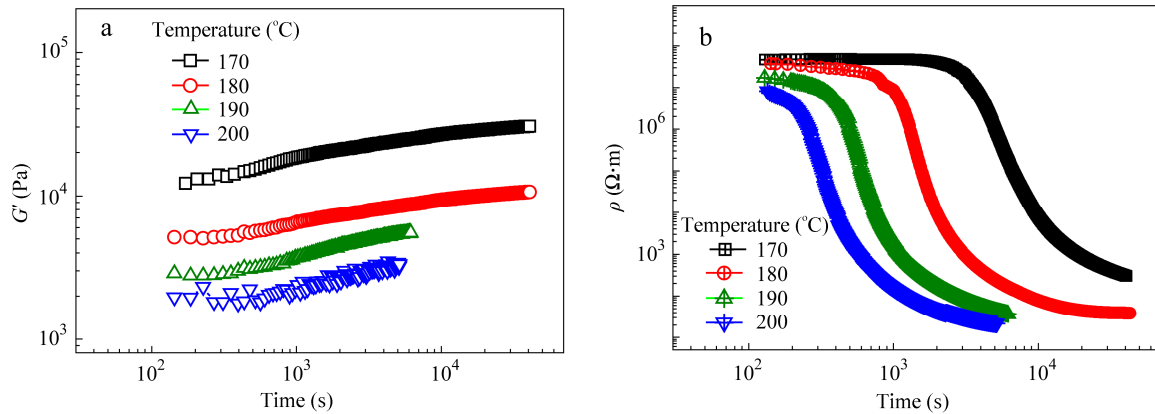


Fig. 9 Time evolution of (a) G' and (b) ρ of PMMA/SAN/CRGO (57/43/0.20) nanocomposites at different annealing temperatures

It is known that the incorporation of nanofillers into polymers leads to dramatic changes in viscoelasticity of the melt. The modulus increment due to filling can be mainly ascribed to the direct bridging of single chains adsorbed on different aggregates, the entanglement between chains adsorbed on separate aggregates and the entanglement of non-adsorbed bulk chains^[71, 73]. If the polymer matrix is a blend not of homopolymers, their modulus variation is more complex. Song *et al.* reported that in the CB filled immiscible PP/polystyrene (PP/PS) nanocomposites, the modulus increment arises from two parts of contributions: the CB agglomeration and the phase coalescence of PP/PS blend matrix^[74]. However, the investigated blend matrix PMMA/SAN (57/43) is partially miscible and their morphology evolution is even more complex than that of immiscible blend matrix. During the isothermal annealing, the blend matrix may experience the transition from miscible to percolation structure and from percolation to droplet structure. Hence, their modulus contribution from the morphology evolution first increases and then decreases, as shown in Fig. 7(a). With the increase of annealing temperature, the morphology develops rapidly and the modulus increment stage is rapidly replaced by the modulus reduction stage. In other words, some modulus increment induced by the CRGO agglomeration at high annealing temperature may be offset by the modulus reduction caused by the morphology transition from percolation to droplet. Thus the influence of annealing temperature on the DM percolation is not obvious.

The different evolutions of ρ and G' result from different mechanisms. The DC percolation reflects the formation of CRGO conductive network in PMMA/SAN blend, while the DM percolation reflects the total

contributions from the morphology evolution of blend matrix, the CRGO migration and agglomeration in the SAN-rich phase, where the interfacial tension between CRGO and SAN plays a crucial role in driving the CRGO migration and agglomeration.

CONCLUSIONS

Thermally induced phase separation in PMMA/SAN blends has been investigated in the presence of CRGO by melt rheology, simultaneous measurements of rheological and conductive properties and microscopic techniques. The incorporation of CRGO results in the slight decrease of T_b and the increase of T_s , indicating the expansion of their metastable regime. Thermal treatment of PMMA/SAN/CRGO nanocomposites at given temperatures well above the phase-separation temperature induces the phase-separation of blend matrix and then the CRGOs well dispersed in homogeneous blend matrix migrate into the SAN-rich domains gradually to form the CRGO conductive network, due to the macromolecules' Brownian movement, owing to the affinity of CRGO to SAN. The nanocomposites show the more pronounced DC and DM percolation. The DC percolation reflects the formation of CRGO conductive network in the matrix, while the DM percolation reflects the total contributions from the morphology evolution of blend matrix, the CRGO migration and agglomeration in the SAN-rich phase. The phase separation induced selective localization of CRGOs in the PMMA/SAN blends also results in a dramatic transition from an insulating homogeneous material at room temperature to a highly conductive material in the melt. The thermal-induced phase separation of blend matrixes can be a useful tool for controlling the dispersion of conductive fillers in the blend matrixes and further improving their electrical properties.

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