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The role of interfacial interactions in the dynamic mechanical response of functionalized SWNT–PS nanocomposites

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Abstract

The dynamic mechanical properties of nanocomposites of functionalized single-walled carbon nanotubes dispersed in polystyrene are reported as a function of temperature. For nanocomposites containing less than 0.1 wt% nanotubes, the enhancement of the magnitude of the complex modulus $|E^*| = \sqrt{E'^2 + E''^2}$, where E' and E'' are the elastic and loss moduli, respectively, exceeded the predictions of the Halpin–Tsai model (this model is often used to predict the properties of macroscopic composites). In this concentration range, however, the loss tangent, $\tan\delta = E''/E'$, of the nanocomposite remained comparable to that of pure PS, i.e., comparable elasticity. At larger concentrations the mechanical response became more elastic than PS, but the magnitude of the complex modulus fell appreciably below predictions based on the Halpin–Tsai model. An alternate hypothesis that relies on the role of attractive interactions between the nanotubes and polystyrene chains, and consistent with previous Raman scattering and glass transition temperature data, is proposed to describe the observed dynamic response.

Keywords: Nanocomposite; Dynamic mechanical analysis; Nanotube

1. Introduction

The development of advanced polymer hybrids based on carbon nanotubes has been stymied by nanotube aggregation in the polymer matrix. Aggregation into bundles or ropes limits the overall effectiveness of nanotubes at improving the (mechanical) properties of the nanocomposite. Dispersion of the nanotubes in the polymer host is enhanced significantly by functionalizing the nanotubes, thereby increasing the compatibility with the polymer [1–5]. In studies of the electrical conductivity of polymer nanocomposites it has been demonstrated that the functionalized SWNTs form percolating networks at volume fractions an order of magnitude lower than those formed with pristine SWNTs [2,6].

The interactions at the polymer–nanotube interfaces have the effect of creating what is identified in the literature as an "interphase" [7,8] in the vicinity of the nanotube. A recent paper demonstrates that changes in the glass transition temperature are tunable by changing the matrix–nanoparticle interaction [9]. This follows directly from the observation that property changes in polymer nanocomposites and polymer thin films can be directly correlated [10]. While these studies primarily examined the glass transition, the mechanical properties of nanocomposites are affected by the transfer of stress between the polymer host and the nanotubes which is facilitated by functionalization [11]. Previous studies have shown significant increases in mechanical properties in systems with functionalized nanotubes [12,13]. Raman spectroscopy has demonstrated the importance of a strong mechanical interface even with pristine nanotubes as in the case of poly(methylmethacrylate) [14–17]. Our previous study demonstrates that the elastic modulus of similar PMMA based carbon nanotube

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nanocomposites can be changed appreciably with very low (0.01 wt%) concentrations of nanotubes; this is presumably a result of the excellent dispersion and the enhanced interface in such nanocomposites [18].

Polystyrene is a commonly used engineering polymer that does not show strongly favorable interactions with SWNTs. Functionalization of SWNTs has been shown to provide enhanced mechanical and interfacial properties compared to pristine SWNTs. Mitchell et al. showed that as low as 1.5 wt% functionalized SWNTs can form a percolating network in PS hosts which has a significant effect on the viscoelastic behavior of the material. These nanocomposites were shown to form a percolating mechanical network at 1.5 wt%, inducing pseudo-elastic behavior at temperatures above the T_g of the PS [4]. Enhancements of the glass transition temperature of thin PS films have also been documented in these PS–nanotube materials by Pham et al. [19]. In fact, the nanotubes have the effect of eliminating the confinement induced thickness dependence of the T_g of films in the nanometer-thickness range. More recently, Hadjiev et al. have used Raman spectroscopy to elucidate the enhancement of the interfacial stress transfer of the functionalized nanotubes when compared to the pristine nanotubes in polystyrene [20].

While low concentrations of SWNTs (<1 wt%) are somewhat common in studies of electrical conductivity, the mechanical properties of these nanocomposites are more rare than those with greater concentrations of SWNTs [6,21,22]. However, there have been some promising results in this concentration range [18]. In this paper, dynamic mechanical analysis (DMA) is used to examine the effect of a range of concentrations (0.01–1.5 wt%) of functionalized 4-(10-hydroxydecyl) benzoate SWNTs on the mechanical properties of polystyrene.

2. Experimental

Single-walled carbon nanotubes from Tubes@Rice prepared by the HiPco process were used in this study. The nanotubes were purified using the standard nitric acid/hydrochloric acid based wash method followed by soft baking. The metal content, estimated by EDX, was less than 5 wt% and the non-fullerene type carbon impurities less than 1%. The average length of the nanotubes based on AFM measurements of depositions of tubes from dilute solution indicated a number average length of ~900 nm. On the basis of the chiral distributions of the nanotubes obtained from spectroscopic methods, we conclude that the average diameter of the nanotubes is ~0.9 nm.

The nanotubes were functionalized and nanocomposite materials were prepared as described by Mitchell et al. [4]. DMA samples were prepared in the following manner: polystyrene and functionalized carbon nanotubes were dissolved in toluene in a glass Petri dish. Toluene was then evaporated at 55 °C, which took several hours. The resulting sample was dried in a vacuum oven at 150 °C for 2 days and subsequently pressed between two aluminum foil sheets at 210 °C for 1 min to the desired thickness using ~1 ton of force, which resulted in an ~160 lbs/in.^{2}. The samples were cut to size and loaded into the testing geometry.

Dynamical mechanical measurements of the temperature dependencies of the elastic moduli, $E'(T)$ and loss moduli, $E''(T)$ (and hence the damping factor $\tan\delta = E''/E'$) were performed on rectangular bar samples with dimensions of $\sim 12 \times 8 \times 1\ \text{mm}^3$ using a dynamic mechanical analyzer in the rectangular tension mode. The samples were clamped with a consistent 40 cNm torque in all tests to achieve consistent and reproducible results. An initial strain sweep was performed at a temperature of −150 °C to determine an appropriate strain for testing in the temperature ramp mode. The strain applied for the temperature ramp experiments was 0.01% for all samples. This strain provided the largest linear response that was within the force range of the instrument.

The temperature ramp tests were performed between −150 °C and 100 °C. This temperature range was selected to avoid large-scale deformation of the sample due to the glass (α) transition. The samples were cooled with liquid nitrogen to −150 °C and given 10 min to equilibrate at that temperature. Data were obtained from frequency sweeps at a constant temperature with 5 °C temperature increments. An equilibration time of 5 min was allowed at each new temperature.

The macroscopic dispersion of the nanotubes in the samples was analyzed using a Zeiss Axiovert 405M optical microscope at a magnification of 500×. This measurement provided a large area assessment of the gross morphological features of the samples. For the purposes of this study, this level of morphological information provided by optical microscopy was sufficient and will subsequently become clear.

3. Results and discussion

The temperature dependencies of the complex moduli ($|E^*| = \sqrt{E'^2 + E''^2}$) and loss tangent ($\tan\delta$) for the PS–fSWNT nanocomposites with low concentrations of functionalized nanotubes are plotted in Fig. 1a and b, respectively. The magnitudes of moduli of the nanocomposites containing less than 0.1 wt% functionalized SWNTs were ~15–30% higher than those of pure PS. The damping factors of the nanocomposites, $\tan(\delta) = E''E'$, the ratio of energy dissipated to energy stored per cycle, are comparable in magnitude to those of pure PS. With regard to these $\tan\delta$ data, no peaks corresponding to sub-T_g relaxations were apparent in the damping factor data, similar to the behavior of pure PS below 50 °C.

Models used to predict the properties of macroscopic composites generally rely on continuum approximations and volume additivity. One commonly used model is the Halpin–Tsai model [23,24]. This model would predict that the modulus of a PS–fSWNT nanocomposite with randomly oriented nanotubes would be represented by

$$\frac{E^*_{\text{Comp}}}{E^*_{\text{PS}}} = \frac{1 + \zeta\eta\phi_{\text{SWNT}}}{1 - \eta\phi_{\text{SWNT}}} \tag{1}$$

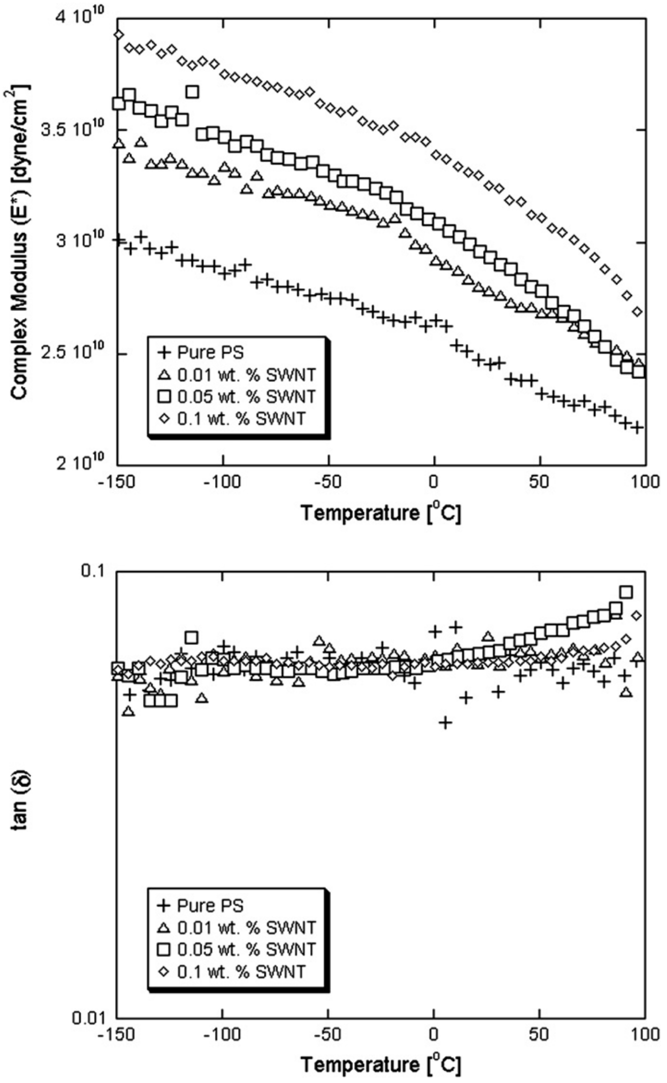

Fig. 1. The temperature dependence of the magnitude of the complex modulus, $|E^*|$, and damping factor, tan (δ), for pure polystyrene and three nanocomposites containing low concentrations (0.01–0.1 wt%) of functionalized SWNTs at a frequency of 100 rad/s.

where E^*_{PS} and E^*_{Comp} are the magnitude of the complex moduli for pure PS and the composite, respectively; ϕ_{SWNT} is the volume fraction of the single-walled carbon nanotube; ζ is a shape parameter (defined as the aspect ratio of the nanotube, $\zeta = 1000$ measured for our nanotubes) and η is defined by

$$\eta = \frac{E^*_{\mathrm{SWNT}}/E^*_{\mathrm{PS}} - 1}{E^*_{\mathrm{SWNT}}/E^*_{\mathrm{PS}} + \zeta} \tag{2}$$

Using the information describing our nanotubes and assuming a value of 1.0×10^{13} dyne/cm^2 for the complex modulus of the single-walled nanotubes, η is calculated to be 0.29 at room temperature. Eq. (1) predicts values of the moduli for the SWNT-based nanocomposites that are lower than the experimentally determined values (Fig. 1a). Moreover, predictions based on volume additivity, which would be appropriate for infinitely long nanotubes oriented in one direction

$$E^*_{\mathrm{Comp}} = \phi_{\mathrm{SWNT}} E^*_{\mathrm{SWNT}} + (1 - \phi_{\mathrm{SWNT}}) E^*_{\mathrm{PS}} \tag{3}$$

also underpredict the experimentally determined complex moduli.

It would be reasonable to assume, based on continuum models, that the addition of the purely elastic SWNTs would lead to a mechanical response that is more elastic. However, our data reveal that low concentrations, less than 0.1 wt%, of functionalized SWNTs did not modify the damping factor of the nanocomposites (Fig. 1b); only at high concentrations of functionalized SWNTs made the nanocomposite more elastic (Fig. 2), i.e., smaller tan (δ). Hence for concentrations less than 0.1 wt%, based on continuum theory, the damping factor data appear to be at odds with the $|E^*|$ dependence on ϕ_{SWNT}, as the addition of a purely elastic phase should both increase

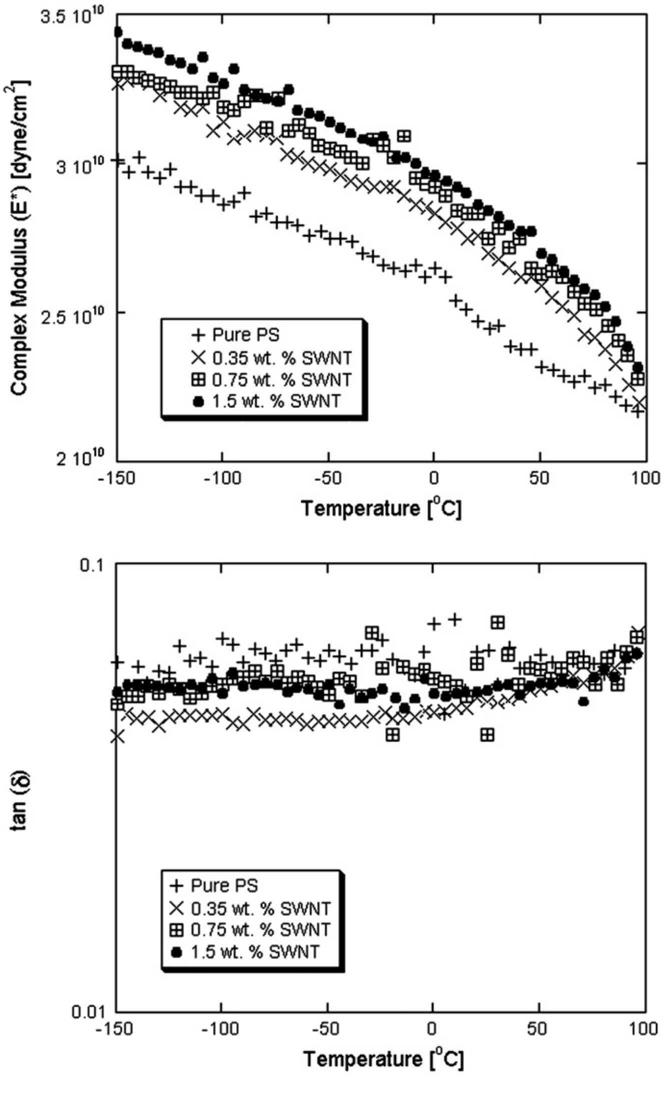

Fig. 2. The temperature dependence of the magnitude of the complex modulus, $|E^*|$, and damping factor for pure polystyrene and three nanocomposites containing higher concentrations (0.35–1.5 wt%) of functionalized SWNTs at a frequency of 100 rad/s.

the magnitude of the complex modulus and the elasticity of the composite.

From the foregoing, it is evident that any mechanism based solely on mechanical reinforcement cannot explain the increase in complex modulus. An alternate mechanism of property enhancements is evident in these nanocomposites. The influence of interfacial interactions of the SWNT phase is crucial to understand the enhancement of $|E^*|$ of this system. The interfacial interactions between the SWNT surfaces and the polymer matrix chains are known to modify the properties of the polymer in the vicinity of the SWNT. The length-scales over which the properties of polymers are affected are believed to be as much as several radii of gyration away from the interface, thereby creating the so-called "interphase" zone [8,13,25–28]. Because of the large surface area of the SWNTs, such interfacial interactions can influence the bulk properties of the nanocomposite, even at low concentrations of nanoparticles. Therefore, the fact that $|E^*|$ of the nanocomposite exceeded predictions based on continuum-based volume additivity models is not unexpected; these models do not account for the influence of such interactions.

Raman spectroscopy has been used to examine the interactions between polymer chains and carbon nanotubes and provide evidence of strong PS–fSWNT interactions [14–16,29,30]. Specifically, Raman spectroscopic measurements of this PS-based nanocomposite system reveal that polystyrene did not significantly modify the tangential modes of the pristine SWNTs, whereas the tangential modes of functionalized samples exhibited an upshift, reflecting the presence of attractive interactions. Recently we showed that 0.01 wt% of nanocomposites of pristine SWNT in PMMA, a system in which shifts of Raman spectroscopy peaks reveal the presence of strong PMMA–SWNT interactions, exhibited a modulus that was 10% greater than that of pure PMMA [18].

Having established the existence of specific PS–nanotube interactions, the compositional dependence of the complex moduli is now further discussed. The increase of $|E^*|$ with increasing ϕ_{SWNT}, for $\phi_{\mathrm{SWNT}} < 0.1$ wt%, is to be expected based on the large interfacial area of the nanotubes and the existence of the specific polymer–nanotube interactions. The effect on the bulk properties is to be expected. The $|E^*|$s of the nanocomposites containing greater amounts of functionalized SWNTs, $\phi_{\mathrm{SWNT}} > 0.35$ wt%, shown in Fig. 2a, are larger than those of pure PS at all temperatures by greater than 10%. Fig. 2b contains the tan (δ) data of these nanocomposites. While no relaxation peaks are apparent in the tan (δ) data, the data for all three nanocomposites were systematically lower than that of the pure PS, revealing an increase in the elasticity of the system.

The dependence of $|E^*|$ on the fSWNT concentration is summarized in Fig. 3 for all the concentrations examined. Data for $|E^*|$ at 25 °C for all of the samples, along with the prediction of the Halpin–Tsai equation and for volume additivity, are shown. The magnitude of the complex modulus was greatest in samples containing less than 0.35 wt% functionalized SWNTs. While $|E^*|$ of the functionalized SWNTs nanocomposites with low concentrations was greater than predicted by the Halpin–Tsai equation or volume additivity, the $|E^*|$s of the composites with more than 0.35 wt% were significantly lower than predicted. The trends exhibited by the nanocomposite at this temperature, 25 °C, are representative of trends observed at the lowest temperatures, up to approximately 60 °C.

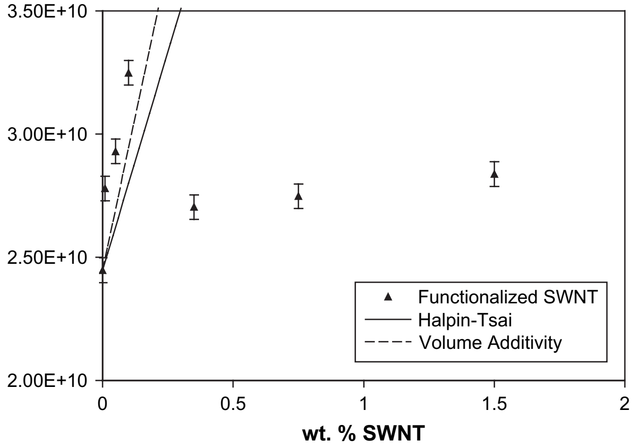

Fig. 3. The magnitude of the complex modulus, $|E^*|$, of all samples, with both functionalized and pristine SWNTs, at 25 °C. The line represents the calculated values from the Halpin–Tsai equation.

The distribution of functionalized SWNTs in the PS host is largely responsible for the dynamic mechanical behavior of the nanocomposites. At sufficiently low concentrations, the nanotubes would be expected to be individually dispersed, with PS–nanotube interactions maximized. Under these conditions, $|E^*|$ would increase rapidly with ϕ_{SWNT}. Eventually, the concentration of nanotubes becomes sufficiently large that the tubes are in proximity and are able to interact and form aggregates or nematically ordered bundles with virtually no individual dispersed nanotubes, reflecting stronger nanotube–nanotube interactions than PS–nanotube interactions, despite the functionalization. Optical micrographs of the samples reveal qualitative and quantitative differences between samples containing more than 0.35 wt% fSWNT and those containing less. The higher concentration samples reveal evidence of large aggregates or bundles. Under these conditions the effective area of contact between the nanotubes and polymer chains is decreased. In fact, the samples containing $\phi_{\mathrm{SWNT}} > 0.35$ wt% nanotubes are distinctly more heterogeneous than the lower concentration samples (see Fig. 4). The heterogeneity is reflected not only in the local concentration of nanotubes (with dimensions on the order of many microns), but is necessarily expected to be so for the glass transition and the modulus. Hence, the mechanical response of the nanocomposite would be similar to a macroscopic composite containing an elastic filler material; $|E^*|$ increases, while tan (δ) decreases, with increasing ϕ_{SWNT}. In other words, the "nano effect" is largely lost as the dimensions of the aggregates become on the order of microns.

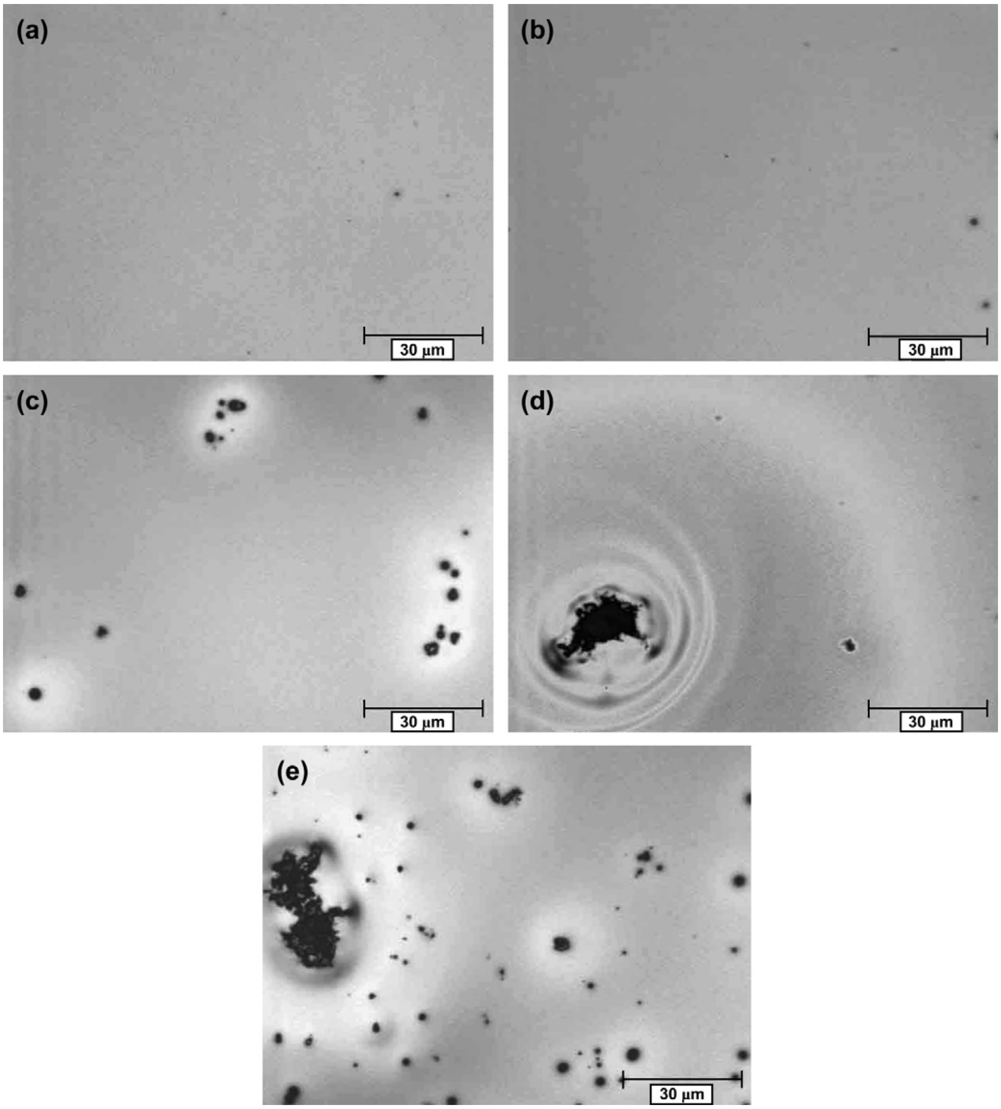

Fig. 4. Optical micrographs of spun coat PS films with five different concentrations of functionalized SWNTs [(a) 0 wt%, (b) 0.01 wt%, (c) 0.1 wt%, (d) 0.35 wt%, and (e) 0.75 wt%].

4. Conclusion

We have shown that the dynamic mechanical properties of functionalized SWNT–PS nanocomposites are very sensitive to PS–nanotube interfacial interactions and to the dispersion of nanotubes and to size of SWNT aggregates throughout the PS host, i.e., morphology. For samples containing $\phi_{\mathrm{SWNT}} < 0.35$ wt% nanotubes, the complex modulus increased rapidly with nanotube concentration, in excess of the predictions of conventional macroscopic composite theory. However, the dissipation factor remained comparable to that of pure PS. For samples containing concentrations of nanotubes $\phi_{\mathrm{SWNT}} > 0.35$ wt%, there was a rapid drop in $|E^*|$, reflecting aggregation of the nanotubes into large micron-scale aggregates. In this larger concentration regime, the morphology is distinctly more heterogeneous, and the system exhibited behavior that was more akin to that of a macroscopic composite, with an increasing $|E^*|$ with ϕ_{SWNT} and enhanced elasticity. In the low ($\leq$0.1 wt%) concentration regime, where a stronger dependence of $|E^*|$ on ϕ_{SWNT} was observed, the elasticity remained comparable to that of pure PS. This latter observation is not well understood, but it suffices to mention that it was also observed in the PMMA–SWNT system.

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References

[1] Eitan A, Jiang K, Dukes D, Andrews R, Schadler LS. Chemistry of Materials 2003;15(16):3198–201.

[2] Ramasubramaniam R, Chen J, Liu H. Applied Physics Letters 2003; 83(14):2928–30.

[3] Viswanathan G, Chakrapani N, Yang H, Wei B, Chung H, Cho K, et al. Journal of the American Chemical Society 2003;125(31):9258–9.

[4] Mitchell CA, Bahr JL, Arepalli S, Tour JM, Krishnamoorti R. Macromolecules 2002;35(23):8825–30.

[5] Zhu J, Kim J, Peng H, Margrave JL, Khabashesku VN, Barrera EV. Nano Letters 2003;3(8):1107–13.

[6] Benoit JM, Corraze B, Lefrant S, Blau WJ, Bernier P, Chauvet O. Synthetic Metals 2001;121(1–3):1215–6.

[7] Bower C, Rosen R, Jin L, Han J, Zhou O. Applied Physics Letters 1999;74(22):3317–9.

[8] Ding W, Eitan A, Fisher FT, Chen X, Dikin DA, Andrews R, et al. Nano Letters 2003;3(11):1593–7.

[9] Bansal A, Yang H, Li C, Benicewicz BC, Kumar SK, Schadler LS. Journal of Polymer Science, Part B: Polymer Physics 2006;44(20): 2944–50.

[10] Bansal A, Yang H, Li C, Cho K, Benicewicz BC, Kumar SK, et al. Nature Materials 2005;4(9):693–8.

[11] Gojny FH, Nastalczyk J, Roslaniec Z, Schulte K. Chemical Physics Letters 2003;370(5–6):820–4.

[12] Geng H, Rosen R, Zheng B, Shimoda H, Fleming L, Liu J, et al. Advanced Materials 2002;14(19):1387–90.

[13] Ramanathan T, Liu H, Brinson LC. Journal of Polymer Science, Part B: Polymer Physics 2005;43(17):2269–79.

[14] Wood JR, Wagner HD. Applied Physics Letters 2000;76(20):2883–5.

[15] Wood JR, Zhao Q, Wagner HD. Composites, Part A: Applied Science and Manufacturing 2001;32A(3–4):391–9.

[16] Zhao Q, Wood JR, Wagner HD. Applied Physics Letters 2001;78(12): 1748–50.

[17] Eitan A, Fisher FT, Andrews R, Brinson LC, Schadler LS. Composites Science and Technology 2006;66(9):1162–73.

[18] Putz K, Mitchell CA, Krishnamoorti R, Green PF. Journal of Polymer Science, Part B: Polymer Physics 2004;42(12):2286–93.

[19] Pham JQ, Mitchell CA, Bahr JL, Tour JM, Krishanamoorti R, Green PF. Journal of Polymer Science, Part B: Polymer Physics 2003;41(24): 3339–45.

[20] Hadjiev V, Mitchell C, Arepalli S, Bahr J, Tour J, Krishnamoorti R. Journal of Chemical Physics 2005;122(12).

[21] Cooper CA, Ravich D, Lips D, Mayer J, Wagner HD. Composites Science and Technology 2002;62(7–8):1105–12.

[22] Stephan C, Nguyen TP, Lahr B, Blau W, Lefrant S, Chauvet O. Journal of Materials Research 2002;17(2):396–400.

[23] Halpin JC. Journal of Composite Materials 1969;3:732–4.

[24] Halpin JC, Kardos JL. Polymer Engineering Science 1976;16(5):344–52.

[25] Bitsanis I, Hadziioannou G. Journal of Chemical Physics 1990;92(6): 3827–47.

[26] Wu W, Majkrzak CF, Satija SK, Ankner JF, Orts WJ, Satkowski M, et al. Polymer 1992;33(23):5081–4.

[27] Torres JA, Nealey PF, de Pablo JJ. Physical Review Letters 2000;85(15): 3221–4.

[28] Diakoumakos CD, Raptis I. Polymer 2002;44(1):251–60.

[29] McCarthy B, Coleman JN, Czerw R, Dalton AB, Byrne HJ, Tekleab D, et al. Nanotechnology 2001;12(3):187–90.

[30] Czerw R, Guo Z, Ajayan PM, Sun Y-P, Carroll DL. Nano Letters 2001; 1(8):423–7.