

Effect of Functionalization on the Crystallization Behavior of MWNT-PBT Nanocomposites

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ABSTRACT

There is tremendous interest in using low loadings of multiwalled carbon nanotubes (MWNTs) to enhance the multifunctional properties of polymers, with functionalization often pursued to increase the dispersion and effective reinforcement of MWNTs within the polymer. In our interest to understand the effect of MWNT functionalization on Poly (butylene terephthalate) (PBT) crystallization kinetics, morphology and mechanical properties, nanocomposites were fabricated with both as-received and carboxyl group (-COOH) functionalized MWNTs. Initial results indicate as-received and functionalized nanotubes alter the crystallization temperature and crystal size for quiescent samples. In addition, isothermal crystallization studies using an Advanced Rheometric Expansion System (ARES) show that the addition of MWNTs increases the rate of PBT crystallization. However, functionalization was found to decrease the rate of nanocomposite crystallization as compared to nanocomposites samples prepared using pristine MWNTs, suggesting that nanotube functionalization weakens the nucleation effect observed in the nanocomposite samples. These results suggest that semicrystalline polymer nanocomposite crystallization kinetics and morphology can be significantly influenced by nanoparticle functionalization and chemistry. Further study of how these changes impact the rheological and multifunctional properties of semicrystalline nanocomposite systems are ongoing.

INTRODUCTION

Poly (butylene terephthalate) (PBT) is a semicrystalline thermoplastic with a wide range of applications due to its fast crystallization rate, good moldability and mechanical properties. Meanwhile, the use of carbon nanotubes (CNTs) within polymeric materials has drawn considerable interest in the polymer industry as a means to impart multifunctional properties to various polymers. In particular, multiwalled carbon nanotubes (MWNTs) have stimulated great interest in the field due to their high aspect ratio, low density, high tensile modulus and strength, and high electrical conductivity. Effective properties of polymer-CNT nanocomposites are greatly affected by the dispersion of CNTs in polymer matrix, and the interface adhesion between the CNTs and the matrix [1-4]. In addition, the physical, chemical, and mechanical properties of semicrystalline polymers depend on the crystalline structure and the degree of crystallinity within the polymer. Further, it is well known that under quiescent crystallization, nanoparticles within a semicrystalline polymer can alter the crystallinity of the polymer matrix

and the resulting nanocomposite morphology due to the large surface area of the MWNTs, which can act as nucleating agents influencing the crystallization process [5].

Functionalization can often increase the effectiveness of nanotube reinforcement, often attributed to better dispersion of the MWNTs within the polymer and enhanced chemical interaction at the molecular level [6]. However, it is important to understand the effect of functionalization on the crystallization kinetics and morphology of semi-crystalline polymer nanocomposites. In this study the effect of CNT functionalization on the crystallization behavior of PBT nanocomposites prepared with pristine MWNTs and carboxyl-functionalized MWNTs (COOH-MWNTs) via a melt blending technique is pursued. Isothermal and non-isothermal crystallization behaviors were investigated using an Advanced Rheometric Expansion System (ARES) and differential scanning calorimetry (DSC), respectively.

EXPERIMENTAL DETAILS

PBT pellets obtained from Ticona Polymers (NC) were dried in a vacuum oven at 125°C for 4h before use. MWNTs were purchased from Sunnano (China) and have a diameter of 10-30 nm and an average bulk density of 1.50 g/cm³ as reported by manufacturer. Concentrated H₂SO₄ (98% purity) and HNO₃ (70% purity) were purchased from Sigma Aldrich. For MWNT functionalization, 2.5 g of MWNTs were oxidized in 26 ml of 3:1 molar ratio acid solution (H₂SO₄:HNO₃) for 3h at 80°C with magnetic stirring using a reflux system. The MWNTs were then washed with deionized water using a porous glass filter until a pH of 7 was obtained, after which the samples were dried in an oven for 24h at 100°C. Transmission Electron Microscopy (TEM) images were obtained on a JEOL 100CX machine. IR characterization was conducted using a Vector 33 Bruker spectrophotometer at 100 scans at a resolution of 3 cm⁻¹ in KBr tablets.

All samples were melt-compounded in a Haake torque rheometer with a 300 ml intensive mixing head. The rheometer is an intensive mixer (a mini-Banbury mixer) with the capability of measuring torque and specific energy input during the mixing process under isothermal conditions. Mixing of MWNTs with PBT was carried out at 245°C for 8 minutes at 32 rpm. The loading levels of the nanocomposites were 0.5% (by volume) of MWNTs. After mixing the nanocomposite was removed and sealed within two polyethylene bags. These specimens were compression molded using a Carver hot press at 245°C for 5 minutes prior to rheological characterization. Pure PBT was processed under identical conditions as a control.

To analyze the non-isothermal crystallization behavior of PBT and PBT nanocomposites, Differential Scanning Calorimetry (DSC) studies were conducted using a TA Instruments (New Castle, DE) DSC model Q1000. The DSC samples were ramped between 25 to 250°C at heating and cooling rates of 10°C/min and maintained at isothermal conditions for 5 minutes at 25 and 250°C at each end temperature. The melting point was measured as the samples were heated while crystallization temperatures were determined as the samples were cooled from 250°C to 25°C. The relative degree of crystallinity was determined as the ratio of the integrated heat of fusion of the sample over the heat of fusion of purely crystalline PBT, with a heat of fusion for 100% crystal PBT (140 J/g) obtained from the literature [7].

For the isothermal crystallization study, the linear viscoelastic material functions of PBT, MWNT-PBT and COOH-MWNT-PBT (referred to hereafter as fMWNT-PBT) nanocomposites were characterized by employing small-amplitude oscillatory shear using an ARES Advanced Rheometric Expansion System, also from TA Instruments. Oven temperature is controlled within ± 0.1°C. The test fixtures consisted of 25 mm diameter stainless steel parallel plates. During the

experiments, after the samples were melted at 245°C and the final gap set to 0.7mm excess specimen protruding out of the gap was carefully trimmed using a razor blade. After temperature equilibration at 215°C, samples were allowed to relax for 5 minutes after which they were cooled to the targeted test temperature for characterization.

DISCUSSION

Figures 1 and 2 show TEM images of pristine and COOH-functionalized MWNTs, respectively. In figure 1 long nanotubes with relatively well graphitized walls are observed. By comparison, figure 2(a) shows a very long functionalized MWNTs which maintains its length after oxidation; however, some damage is observed along its walls (indicated by arrows). Figure 2(b) shows similar damage caused by oxidation, with what appears to be short nanotubes produced by the breaking of some large nanotubes (indicated by circles).

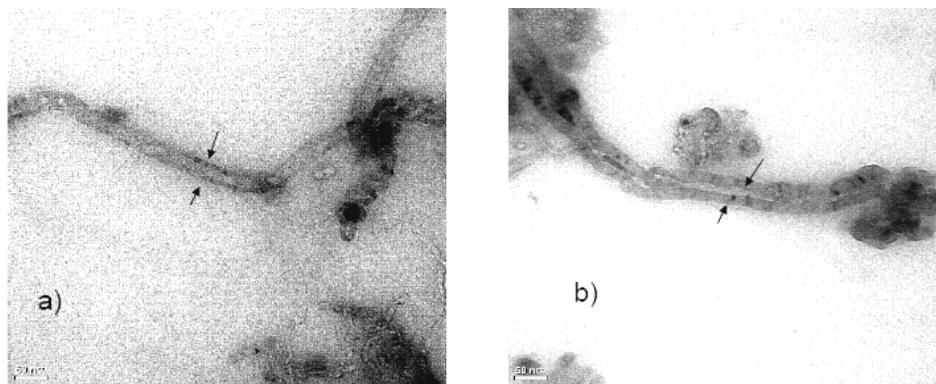


Figure 1. TEM images of pristine carbon nanotubes (MWNTs). (Scale bar = 50 nm.)



Figure 2. TEM images of functionalized carbon nanotubes. Arrows indicate where nanotubes appear damaged by the functionalization process. (Scale bars: left = 50 nm, right = 100 nm.)

Figure 3 shows the IR spectra of pristine MWNTs and functionalized MWNTs from 850 cm^{-1} to 2000 cm^{-1} . Here one can observe three typical bands that correspond to carboxyl groups (-COOH) produced on the functionalized MWNT surface. These bands correspond to the

$\nu(\text{C}=\text{O})$ at 1725 cm^{-1} , the O–H band vibration shift to high wavenumber at 1384 cm^{-1} [8], and the C=O bond at 1210 cm^{-1} , respectively. These typical bands with slight variations in wavelength have been found in other carbon nanotube oxidation processes developed by our group using different oxidation reagents [9]. In addition, at wavenumbers where the E_{1u} IR phonon mode is found normally (approximately 1580 cm^{-1}), one observes a clear enhancement in the spectrum of functionalized MWNTs compared to that of the as-received MWNTs. This is attributed to the influence of the C=O vibration of carboxylate groups produced in oxidation process and generated in the region of 1550 and 1615 cm^{-1} [10,11].

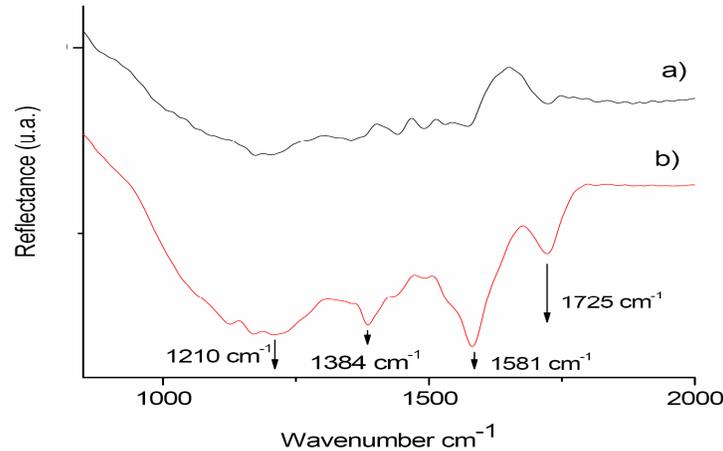


Figure 3. IR spectra of carbon nanotubes. a) Pristine carbon nanotubes (MWNTs), b) Functionalized carbon nanotubes (COOH-MWNTs).

The impact of MWNT functionalization on the non-isothermal crystallization behavior of PBT nanocomposites under quiescent conditions was analyzed with DSC. The melting onset temperature ($T_{m,o}$), peak melting temperature ($T_{m,p}$), crystallization onset temperature ($T_{c,o}$), crystallization peak temperature ($T_{c,p}$), and degree of crystallinity (X_c) of the pure PBT and PBT nanocomposites are reported in table 1. The actual melting temperature (T_m) can be defined as the temperature at which the last trace of crystal disappears in the sample during heating from 25°C to 250°C . Table 1 shows a slight decrease in T_m and a slightly higher crystallinity in the nanocomposite samples attributed to the high surface area and the nucleation effect of the nanotubes. Table 1 indicates that both pristine and functionalized nanotubes act as heterogeneous nucleating agents, which can be seen from the increase in crystallization peak temperature ($T_{c,p}$) of 0.5% MWNT-PBT and 0.5% fMWNT-PBT nanocomposites samples compared to pure PBT processed under similar conditions. It should also be noted that the PBT nanocomposites prepared from functionalized MWNTs have a lower crystallization temperature as compare to 0.5% MWNT-PBT nanocomposites. This indicates that the functionalization of MWNTs weakens the heterogeneous nucleation effect of the nanotubes and hence decreases the rate of PBT crystallization (discussed in next section). A similar effect has been reported behavior in the literature for Nylon-6 [12] and Poly (ethylene oxide) (PEO) MWNT nanocomposites [13].

The effect of MWNT functionalization on isothermal crystallization behavior was next studied using ARES. As the linear viscoelastic material functions (storage moduli (G'), loss moduli (G''), magnitude of complex viscosity $|\eta^*|$) are very sensitive to structural changes in the polymer melt, they can provide information on the change in the physicochemical properties of the polymer during deformation. Figure 4 shows the results obtained for the G' , G'' , $|\eta^*|$ and

the loss tangent ($\tan \delta = G''/G'$) as a function of time for PBT and PBT nanocomposites at a constant frequency of 5 rps with 1% strain amplitude at 215°C (note this is above the crystallization temperatures recorded in table 1). As shown in Figure 4(a), an increase in G' was observed for 0.5% MWNT-PBT and 0.5% fMWNT-PBT nanocomposites that was not observed for pure PBT under similar conditions. This indicates a sharp increase in the crystallization rate due to the incorporation of the MWNTs. One possible mechanism for the crystallization of the nanocomposite at a temperature which is above the crystallization temperature of PBT is that the nanotubes are acting as heterogeneous nucleating agents and increase the overall rate of PBT crystallization by providing more nucleating sites. Further, it can also be seen that the PBT nanocomposites samples prepared using pristine MWNTs have a higher rate of crystallization than the 0.5% fMWNT-PBT nanocomposites, which can be clearly seen by comparing the induction time (time at which a steep rise in G' is observed) for crystallization for these samples. This decrease in crystallization rate (or increase in induction time for crystallization) for the functionalized MWNT samples could be due to a weakening of the nucleating effect of functionalized MWNTs, which is consistent with the DSC results shown in Table 1. Similar behavior is also observed in the other viscoelastic functions shown in figure 4(b-d); for example, enhanced crystallization increases the magnitude of complex viscosity with time.

Table 1. Melting and crystallization temperature and crystallinity of PBT nanocomposites

Sample	$T_{m,o}$ (°C)	$T_{m,p}$ (°C)	T_m (°C)	X_c (%)	$T_{c,o}$ (°C)	$T_{c,p}$ (°C)
Pure PBT	208.6	227.2	238.4	20.7	191.3	173.3
0.5 MWNT – PBT	205.8	225.6	236	22.1	213.2	202.7
0.5% COOH-MWNT-PBT	203.5	225.4	235.4	23.4	210.5	199.6

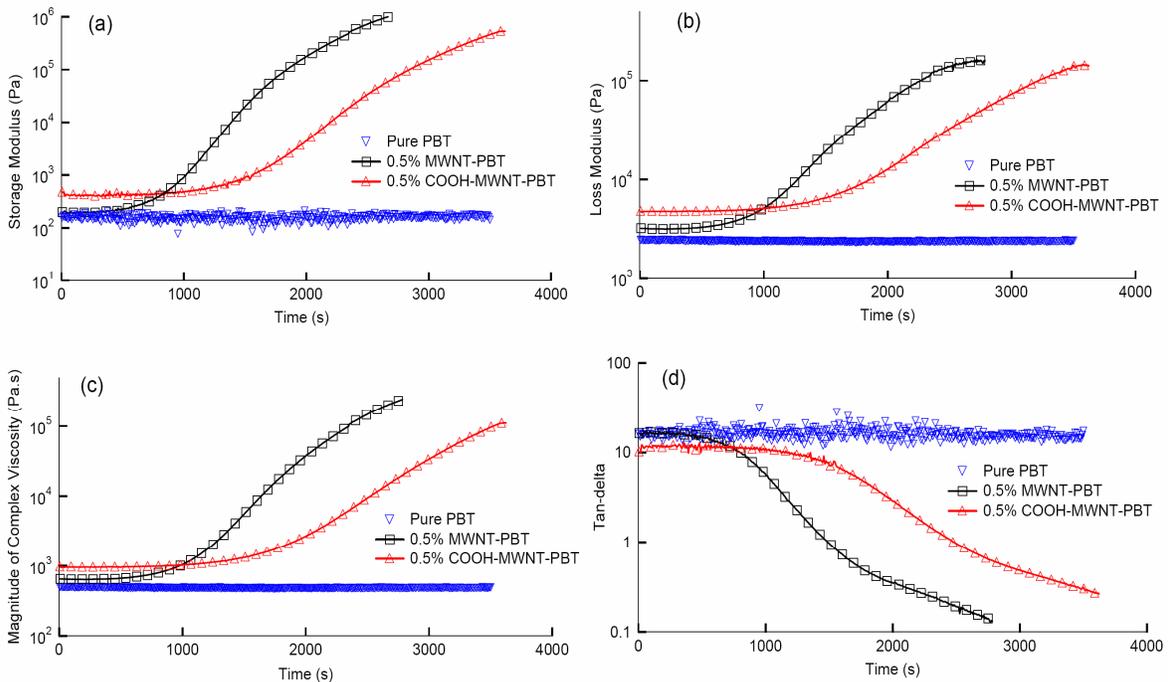


Figure 4. Variation of G' , G'' , $|\eta^*|$ and $\tan \delta$ with time at 1% strain, 5 rps, 215°C.

CONCLUSIONS

The addition of pristine and functionalized (-COOH) MWNTs increased the rate of PBT crystallization due to heterogeneous nucleation. While the addition of nanotubes increases the rate of PBT crystallization, functionalization was found to decrease the relative rate of PBT crystallization as compared to nanocomposites samples prepared using pristine MWNTs. This suggests that functionalization weakens the observed nucleation effect. No crystallization was observed for pure PBT under identical conditions. These results suggest that semicrystalline polymer nanocomposite crystallization kinetics and morphology can be altered via nanoparticle functionalization and chemistry. Further study of how these changes impact the rheological and multifunctional properties of semicrystalline nanocomposite systems are ongoing.

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