

EFFECT OF SHEARING ON THE CRYSTALLIZATION BEHAVIOR OF POLY (BUTYLENE TEREPHTHALATE) AND PBT NANOCOMPOSITES

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ABSTRACT

Poly (butylene terephthalate) (PBT) is an engineering thermoplastic polyester with excellent mechanical properties and a fast crystallization rate widely processed via extrusion and injection molding. Such processes require very complex deformation histories, which can influence the ultimate properties of the processed material and parts. For such systems, flow-induced structural changes in the material as a function of processing are of increasing interest in the field of polymer processing. Linear viscoelastic material functions, including the storage and loss moduli and magnitude of complex viscosity, are very sensitive to the structural changes occurring in the polymer melt.

This initial study focuses on the shear-induced crystallization of PBT and PBT nanocomposites with multi-walled carbon nanotubes (MWNTs). (Shear-induced crystallization is a subset of the more general flow-induced crystallization behavior which is the long-term goal of this research.) The effects of shear history on the isothermal crystallization behavior of these materials were investigated. Time sweep experiments at constant frequency, temperature and strain amplitude were carried out employing small-amplitude oscillatory shear within a parallel-plate geometry. Samples obtained upon quiescent crystallization suggested that the rate of crystallization and crystallization temperatures were modestly affected by the presence and concentration of the nanotubes, consistent with the findings of the earlier reports. However, the characterized shear-induced crystallization behavior of the

nanocomposites presented here indicate more significant changes in the crystallization temperature and the rate of crystallization occur as a result of the incorporation of the carbon nanotubes. The shear-induced crystallization behavior was affected by the deformation rate, temperature, and the concentration of the carbon nanotubes. These findings indicate that shear-induced crystallization of polymer nanocomposites (and in general flow-induced crystallization effects due to arbitrary flow fields in the melt state during processing) should be an integral part of attempts to generate a comprehensive understanding of the development of the microstructural distributions and the coupled ultimate properties of polymer nanocomposites.

Keywords: MWNTs, Poly (butylene terephthalate), flow-induced crystallization, nanocomposite rheology

INTRODUCTION

Poly (butylene terephthalate) (PBT) is a semicrystalline thermoplastic with a wide range of applications, including those in electronics and telecommunication equipment, computers, electrical connectors and automotive parts in both 'under the hood' and exterior applications. PBT has a low glass transition temperature, a fast crystallization rate and good moldability. Meanwhile, the use of nanofiller within a polymer matrix has drawn considerable interest in the polymer industry as a means to modify/enhance the properties of various polymers. In particular, multiwalled carbon nanotubes (MWNTs) have stimulated great interest in the field of nanocomposite materials because of their high aspect ratio, low density, high tensile modulus, and high electrical conductivity.

While a number of advances have recently been made in solvent-based or solution-based processing of polymer nanocomposites, such techniques are not particularly industry-friendly as they often require the use of expensive and toxic solvents with environmental restrictions. More compatible with industrial processes are melt-mixing techniques, where adequate shear forces are necessary to disperse the nanofiller within the polymer. Several studies have been reported in the literature which aim to quantify the crystallization kinetics in molten semi-crystalline polymers, including PP,^{1,2} PBT,³⁻⁹ PET,^{10,11} Nylon 6,¹² *i*-PP,¹³ and PTT.¹⁴ The structure and properties of the nanocomposite can be further influenced by the large surface area of the MWNTs, which can act as nucleating agents influencing the crystallization process. For example, it is known that the incorporation of nanoparticles into a polymeric matrix followed by quiescent crystallization can alter the crystallinity of the polymer matrix¹⁵ and the resulting nanocomposite morphology.¹⁶ However, realistic nanocomposite samples are never manufactured under quiescent conditions but rather are derived from a complex thermo-mechanical history during which the macromolecules undergo rapid shear and extension followed by rapid quenching. Clearly the crystallinity that is achieved and the morphological zones which are established are affected by the shearing/extensional deformation of the macromolecules during the nanocomposite processing in the melt state.

Earlier studies have focused on the preparation, structure and physical properties of nanocomposites, however, limited work has been carried out on their rheological behavior.¹⁷⁻²⁰ Furthermore, detailed studies which link the crystallization kinetics of such nanocomposites to their rheological behavior on one hand and to their processability on the other hand are clearly missing. Industrial polymer processing methods involve very complex deformation histories, which may affect the nucleation and crystallization behavior of polymers and their nanocomposites. For example, it is known that the application of a shear stress to a polymer melt at temperatures which are in the vicinity of the crystallization temperature of the polymer leads to the shear-induced orientation of the macromolecules, thus reducing the entropy of the melt and leading to an increase of the crystallization temperature and thus to flow-induced crystallization.²¹⁻²³ It is anticipated that the incorporation of the nanoparticles will further alter the shear-induced crystallization behavior. Thus, a detailed understanding of the roles played by the nucleation and crystallization processes under shear is necessary to optimize the processing of the nanocomposite and to tailor their various ultimate properties. This study is part of a larger study which aims to: (1) to study the linear viscoelastic material functions and coupled isothermal crystallization behavior of MWNT-PBT nanocomposites and (2) to study the effect of the presence and concentration of the MWNTs on flow-induced crystallization behavior of MWNT-PBT nanocomposites and on the development of the microstructural distributions in articles processed from MWNT-PBT nanocomposites. In the current work the focus is limited to the shear-induced crystallization of the

PBT nanocomposites; efforts studying enhanced crystallization due to arbitrary flow fields in the melt (flow-induced crystallization) are ongoing.

EXPERIMENTAL

Materials

PBT pellets were obtained from Ticona Polymers (NC). PBT pellets were dried in a vacuum oven at 125°C for 4h to remove moisture prior to their use. MWNTs were purchased from Sunnano (China). As reported by the manufacturer, the diameter of the MWNTs was 10-30 nm, and the average bulk density was 1.5 g/cm³.

Melt blending of MWNT-PBT nanocomposites

There are several ways of dispersing nanofillers in polymers such as solution mixing, in-situ polymerization and melt compounding. Melt compounding is preferred due to low cost, high productivity, and compatibility with conventional polymer processing techniques. MWNT-PBT nanocomposites were melt compounded in a Haake torque rheometer with a 300 ml intensive mixing head. The torque rheometer is an intensive mixer (a mini-Banbury mixer) with the capability of measuring torque and hence specific energy input during the mixing process under isothermal conditions. Mixing of MWNTs with PBT was carried at 245°C for 5 minutes at 32 rpm. The loading levels of the nanocomposites were 0.5 and 1.0% (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, followed by rheological characterization. Pure PBT was processed under identical conditions as a control.

Rheological characterization

The linear viscoelastic material functions of PBT and MWNT-PBT nanocomposites were characterized by employing small-amplitude oscillatory shear using an ARES (Advanced Rheometric Expansion System) with a force rebalance transducer (2K-FRTN1) available from TA Instruments. The actuator of the ARES is a *dc* servomotor with a shaft supported by an air bearing with an angular displacement range of 0.05-500 mrad. Oven temperature is controlled within $\pm 0.1^\circ\text{C}$. The test fixtures consisted of 25mm 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. Upon loading and temperature equilibration, the specimen was allowed to relax for 5 minutes, after which it was cooled to the targeted test temperature for the characterization of the dynamic properties as a function of the strain amplitude, frequency and time.

Thermal Analysis

Differential Scanning Calorimetry (DSC) studies were conducted using a TA Instruments (New Castle, DE) DSC model Q1000 on pure PBT and PBT nanocomposites. The DSC samples were ramped from 25 to 255°C, and maintained at isothermal

conditions for 10 minutes at 25 and 255⁰C. The heating and cooling rates were 15⁰C/min and 10⁰C/min, respectively. The melting point was measured as the samples were heated to a temperature of 255⁰C, while crystallization temperatures were determined as the samples were cooled to 25⁰C. 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.

RESULTS AND DISCUSSION

Linear viscoelastic material functions (storage moduli, loss moduli, magnitude of complex viscosity) are very sensitive to structural changes in the molten polymer and can provide information on the change in the physicochemical properties of the polymer during deformation. For example, for thermally sensitive polymer melts, an irreversible decrease in viscosity with time at a constant shear rate suggests the possibility of thermal degradation of polymer molecules, whereas an irreversible increase in viscosity with time suggests the possibility of chemical cross-linking between polymer molecules. Both thermal degradation and chemical cross-linking are irreversible in the rheological response. On the other hand, a reversible change in the linear viscoelastic properties with time during shearing under constant frequency, temperature and strain amplitude indicates a change in physical state generally associated with the flow-induced crystallization of the polymer melt at a temperature which is greater than the crystallization temperature of the pure melt. During the time sweep experiment unbounded monotonic increases in the storage moduli (G'), magnitude of complex viscosity $|\eta^*|$, and loss moduli (G'') with time suggest the onset of crystallization induced by the applied shear. Pennings and co-workers have documented that the morphology of such crystals is typically of the “shish kebab” type and is thus very different than the spherulitic morphologies that are generally observed under quiescent crystallization conditions.^{24,25}

Effect of MWNTs on nanocomposite rheology

Figure 1 shows the results obtained for the G' , η^* , G'' and the loss tangent ($\tan \delta = G''/G'$) versus time for PBT and PBT nanocomposites for a constant frequency of 4 rps with 5% strain amplitude at 210⁰C. As shown in Figure 1(a), an abrupt increase in G' was observed for 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 MWNTs into PBT. Furthermore, an increase in the concentration of MWNTs shows a decrease in the induction time for crystallization. One possible mechanism for the crystallization of the nanocomposite at a temperature which is above the crystallization temperature of PBT is the acting of the nanoparticles as heterogeneous nucleating sites.¹² During heterogeneous nucleation the rate of nucleation can be associated with the concentration of the heterogeneous nuclei. The decrease of the induction time for crystallization with increased concentration of

nanotubes may be associated with an increase of the nucleation rate with increasing concentration. A decrease in induction time for crystallization under quiescent conditions has also been reported and associated with the presence of nanoparticles.^{18,26} However, to our knowledge this is the first time that the flow-induced crystallization behavior has been linked to the incorporation of nanoparticles.

Figure 1(b) shows a sharp increase in viscosity due to an increase in volume fraction of crystallites with time. The formation of the crystals should lead to increases in affine junction points in the entangled melt to render relaxation more difficult, thus increasing both the elasticity and the viscosity of the melt. The magnitude of complex viscosity values of PBT nanocomposites are orders of magnitude higher than those of the pure PBT, indicating the introduction of a significant degree of crystallinity as induced by the presence of the MWNTs. Figure 1(c) shows an increase in loss moduli with time, up to a maximum value as has also been observed in another study.¹⁷ (In the current study the decrease in G'' after this point is attributed to the effects of the machine compliance and should be discarded, as at greater crystallinity and thus higher shear stress values the compliance limit of the instrument is reached and the strain can no longer be controlled.) Figure 1(d) shows a decrease of $\tan \delta$ with time, with the addition of MWNTs greatly reducing the loss tangent as affected by the more significant increases in the elasticity (as represented by the storage modulus, G') in comparison to the increase of the viscous energy dissipation as represented by the loss modulus G'' .

Effect of applied shear on nanocomposite rheology

Figure 2-5 show the variation of G' , η^* , G'' and $\tan \delta$ for PBT and PBT nanocomposite melts with time at 210⁰C and 5% strain amplitudes at frequencies ranging from 0.5 to 4 rps. An increase in frequency did not change the crystallization rate for pure PBT (see Figure 2(a) and Figure 3(a)). However, an increase in crystallization rate and decrease in induction time for crystallization was observed with increasing frequency for PBT nanocomposites as shown in Figure 2(b, c) and Figure 3(b, c).

The work of de Gennes in dilute solutions of polymers has revealed that during flow the polymer chains undergo a step change from a random coil to a fully extended chain conformation at a critical strain rate, without any intermediate stable chain conformations.²⁷ The subsequent studies of Keller et al have provided experimental evidence of coil-stretch transition in polymer crystallization under shear and extension, demonstrating that as the strain rate is increased during deformation there is an abrupt change in birefringence indicative of the formation of a fully-extended chain conformation at the critical strain rate.²⁸ At the moment it is not clear how the oscillatory shear used in our investigation orients and changes the conformation of the entangled polymer melt, and what role the nanotubes play in this coil-stretch transformation.

For all frequencies, the rate of crystallization is higher for the 1% MWNT-PBT nanocomposites in comparison to 0.5% MWNT-PBT, presumably due to the greater number of nucleation sites associated with the greater concentration of nanoparticles. The presence of MWNTs as heterogeneous nucleating agent is presumed to increase the nucleation rate (and hence the overall crystallization rate) in PBT nanocomposites. For pure PBT loss modulus G'' values increased only slightly with time at the higher

frequencies as shown in Figure 4(a), while much more noticeable differences for the PBT nanocomposites are evident (see Figures 4(b) and 4(c)).

For the 0.5 vol% MWNT nanocomposite, the peaks in the G'' curves shift to shorter times as the frequency increases (while a similar result appears to be the case for the 1% MWNT samples, data at longer times could not be collected for these samples due to the increased viscosity of the samples and torque limitations of the instrument). Figure 5 shows a fast decrease in tan delta with increasing frequency, due to an increase in crystallization rate which increases the storage modulus of the melt at a greater rate in comparison to the rate of increase of the loss modulus, emphasizing the greater role played by the elasticity in comparison to viscous dissipation with increasing degree of crystallinity.

Figures 6-9 show the variation of G' , η^* , G'' , and tan delta for PBT and PBT nanocomposite melts with time at different strain amplitudes (from 0.5 to 5%) at a constant temperature of 210°C and a frequency of 4 rps. There is only a modest increase of the linear viscoelastic properties with time for pure PBT, which is noticeable only at the

higher strain amplitude (see Figure 6(a) and Figure 7(a)); it is not clear whether this modest change can be attributed to the flow-induced crystallization of the pure PBT within the time scales of these experiments. For the 0.5% MWNT-PBT nanocomposite samples, Figure 6(b) and Figure 7(b) indicate that the rate of crystallization is not affected by the strain amplitude in the range considered.

In Figures 6-9 it appears that the 1% MWNT-PBT nanocomposites demonstrate a reduction in induction time for crystallization at the largest strain amplitude studied here (5%). However, at the moment it is unclear whether such changes are indeed the result of differences in crystallization behavior for these samples at this strain amplitude, or whether such changes are the result of non-linear viscoelastic effects becoming more evident in these samples at this level of strain. In either case, it is interesting to note that the incorporation of nanoparticles in general, and specifically the MWNTs studied here, introduce subtle but significant changes in the rheology and properties of the polymer nanocomposite melt in comparison to the behavior of the pure polymer in the melt state.

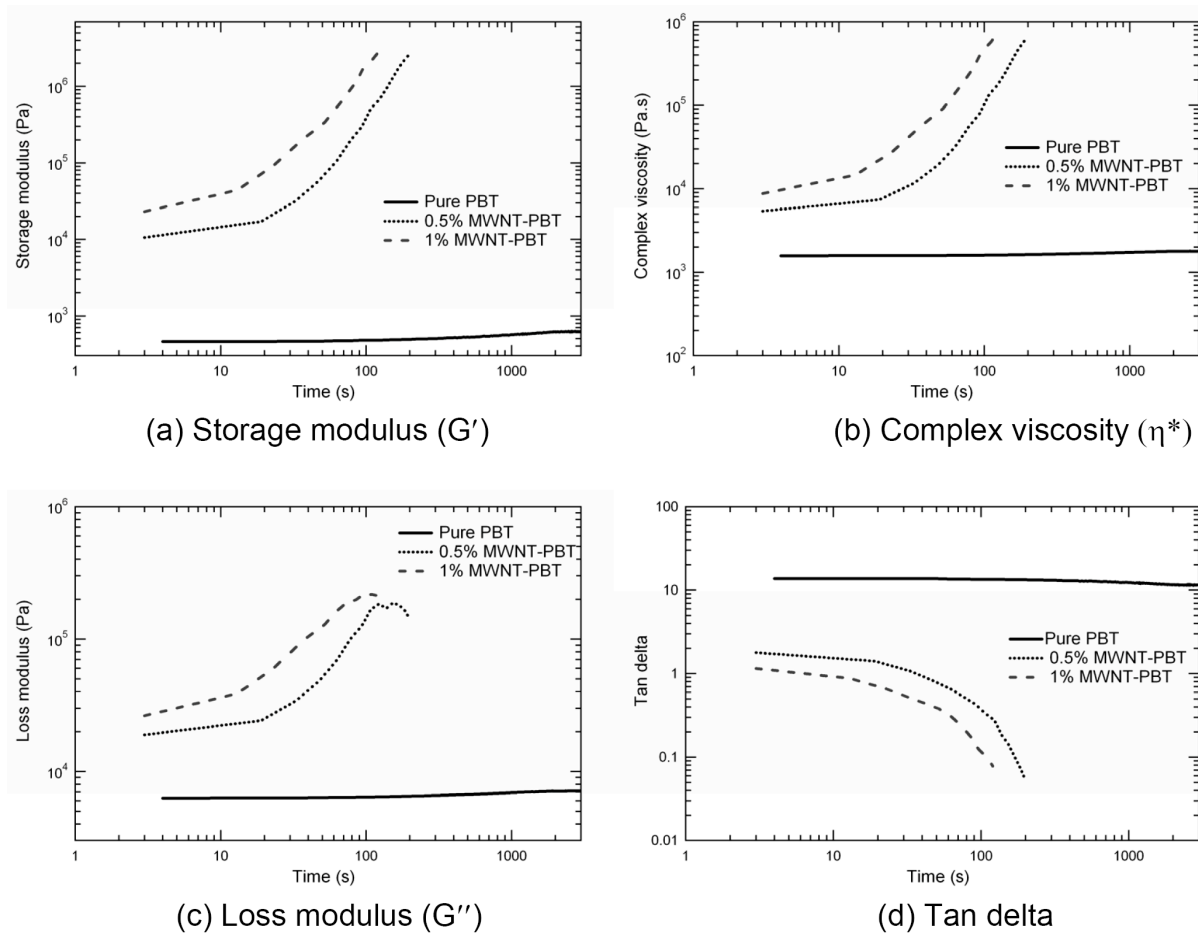
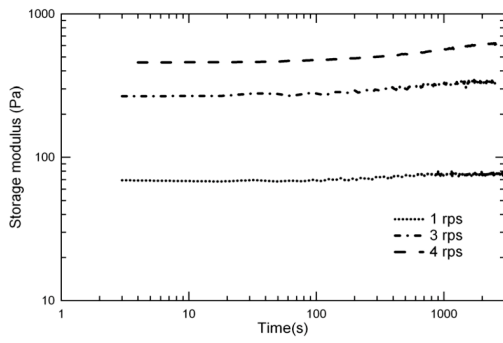
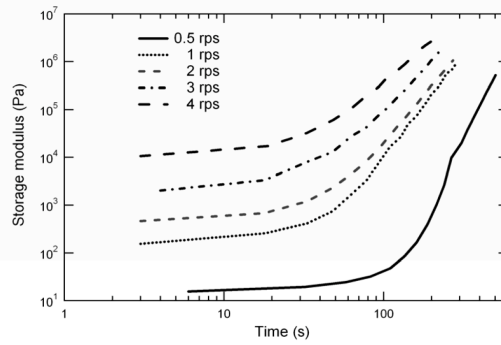


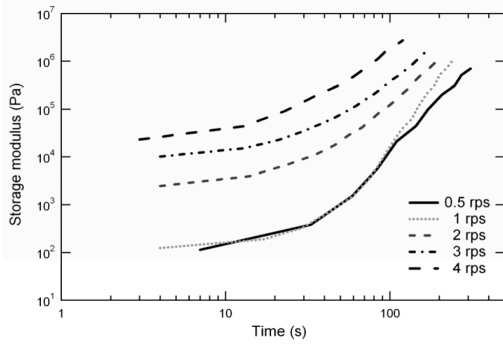
FIGURE 1. Variation of G' , G'' , η^* , and tan delta with time at 4 rps, 5% strain, 210°C



(a) Pure PBT

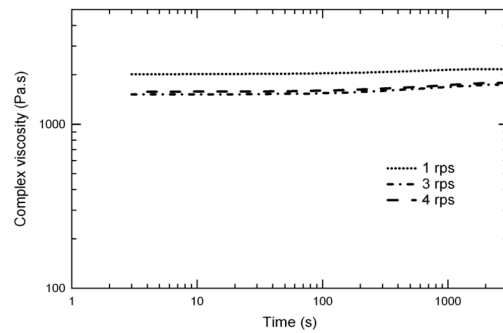


(b) 0.5% MWNT- PBT

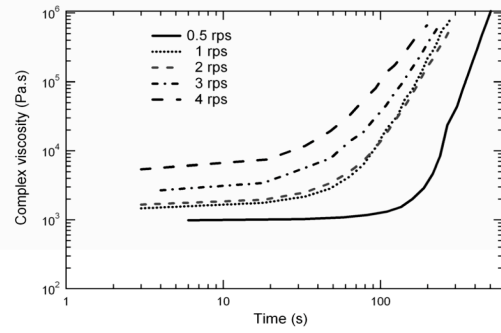


(c) 1% MWNT-PBT

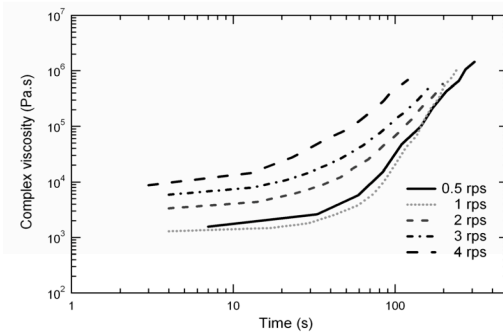
FIGURE 2. Variation of storage modulus G' with time at different frequencies and 5% strain amplitude, 210°C



(a) Pure PBT

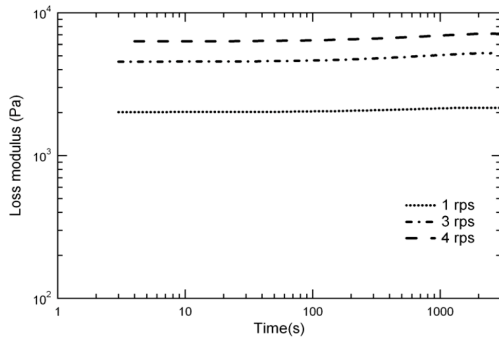


(b) 0.5% MWNT-PBT

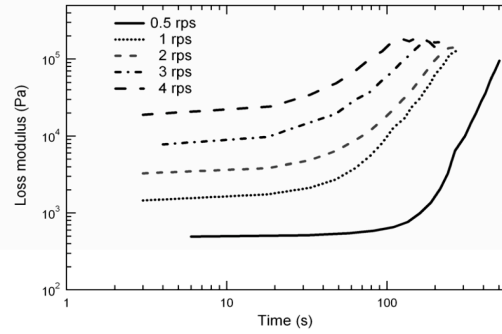


(c) 1% MWNT-PBT

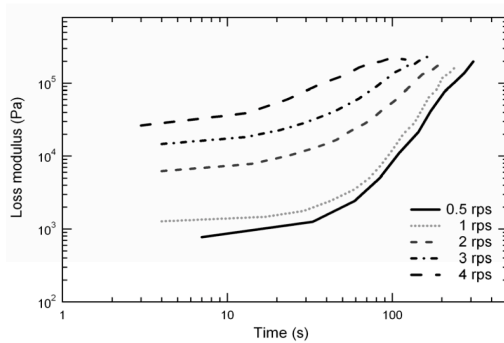
FIGURE 3. Variation of complex viscosity η^* with time at different frequencies and 5% strain amplitude, 210°C



(a) Pure PBT

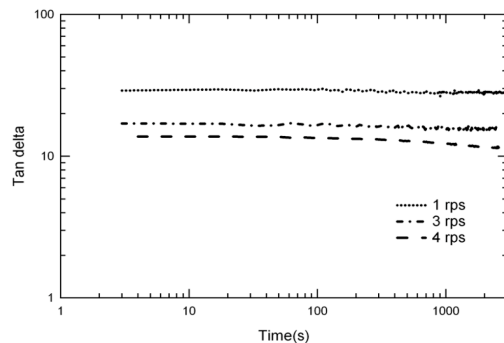


(b) 0.5% MWNT-PBT

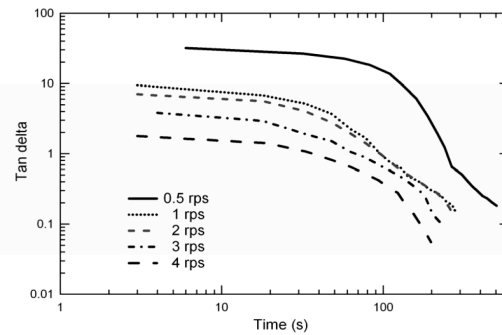


(c) 1% MWNT-PBT

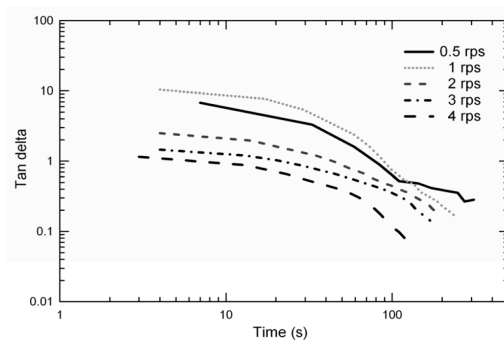
FIGURE 4. Variation of loss modulus G'' with time at different frequencies and 5% strain amplitude, 210°C



(a) Pure PBT

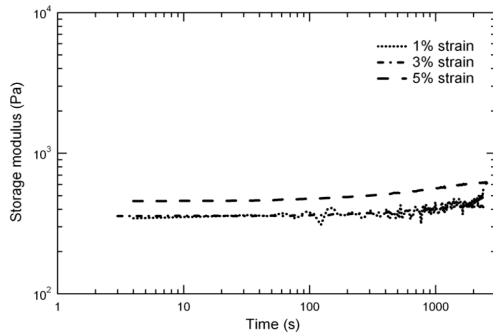


(b) 0.5% MWNT-PBT

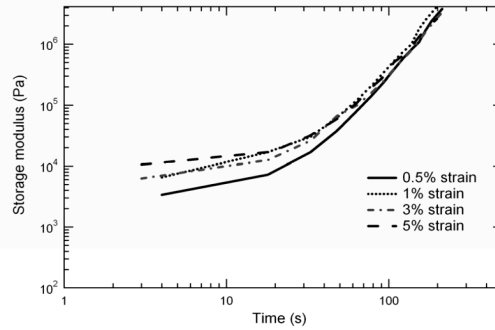


(c) 1% MWNT-PBT

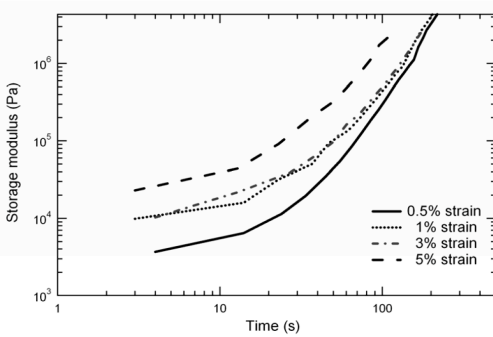
FIGURE 5. Variation of tan delta with time at different frequencies and 5% strain amplitude, 210°C



(a) Pure PBT

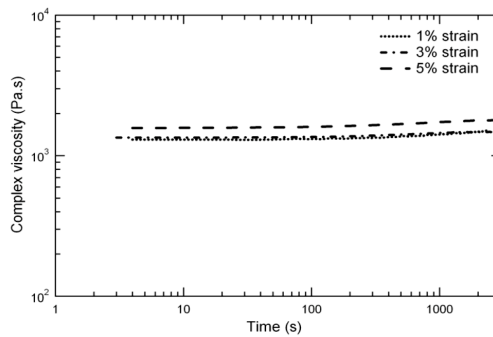


(b) 0.5% MWNT-PBT

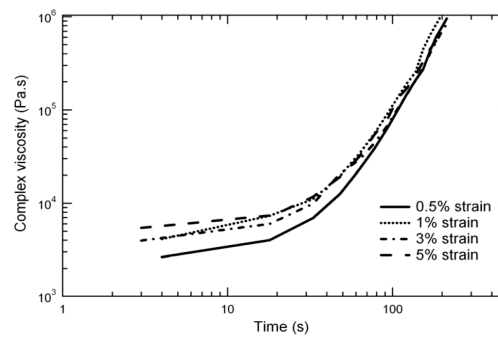


(c) 1% MWNT-PBT

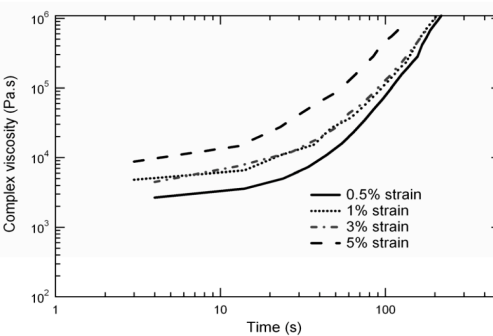
FIGURE 6. Variation of storage modulus G' with time at different strain amplitudes, 4 rps, 210°C



(a) Pure PBT

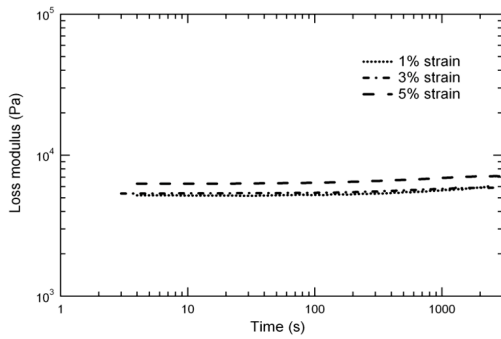


(b) 0.5% MWNT-PBT

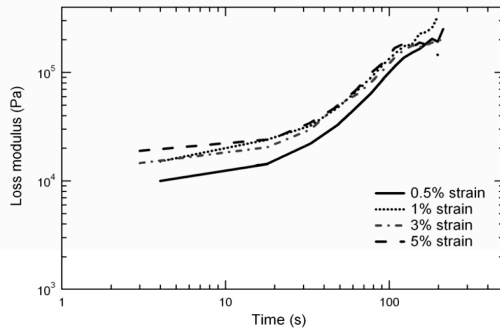


(c) 1% MWNT-PBT

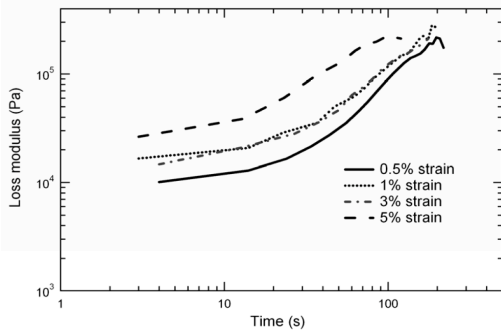
FIGURE 7. Variation of complex viscosity η^* with time at different strain amplitudes, 4 rps, 210°C



(a) Pure PBT

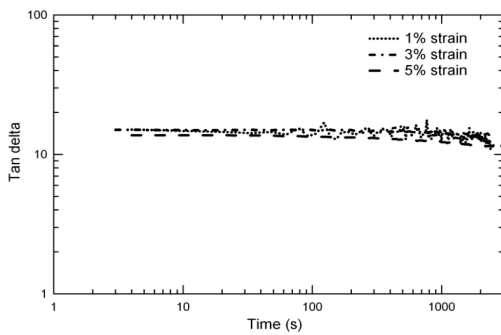


(b) 0.5% MWNT-PBT

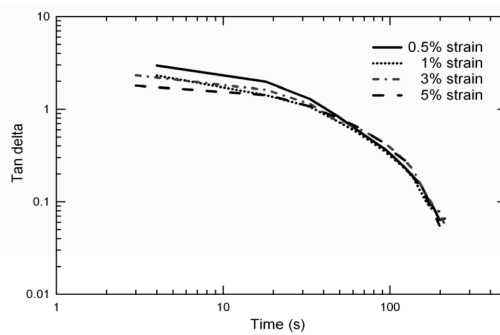


(c) 1% MWNT-PBT

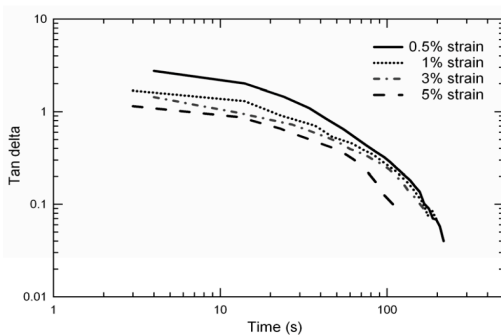
FIGURE 8. Variation of loss modulus G'' with time at different strain amplitudes, 4 rps, 210⁰C



(a) Pure PBT



(b) 0.5% MWNT-PBT



(c) 1% MWNT-PBT

FIGURE 9. Variation of tan delta with time at different strain amplitudes, 4 rps, 210⁰C

Quiescent crystallization Behavior of PBT and MWNT-PBT nanocomposites

The effect of MWNTs on the crystallization of PBT under quiescent conditions was further analyzed with DSC experiments. The non-isothermal crystallization and melting thermograms obtained for neat PBT and its nanocomposites are shown in Figure 10. The crystallization peak (T_c), apparent melting temperature (T_m), and degree of crystallinity (X_c) of the samples as a function of MWNT concentration are reported in Table 1. For degree of crystallinity, a value for the

heat of fusion for 100% crystal PBT (140 J/g) was obtained from the literature.²⁹ The observed crystallization behavior shows the effect of MWNTs on the crystallization kinetics of PBT under quiescent conditions, and the behavior is consistent with the reports in the literature.^{3,6,8,9} In particular, the values shown in Table 1 confirm that the addition of MWNTs to the PBT produces an increase in the crystallization temperature T_c . Similar results have been found by others as well.³⁰⁻³² The relative shift of T_c is quite evident at the lowest concentration of MWNT, while the relative change in T_c from 0.5% to 1% MWNTs is much smaller.

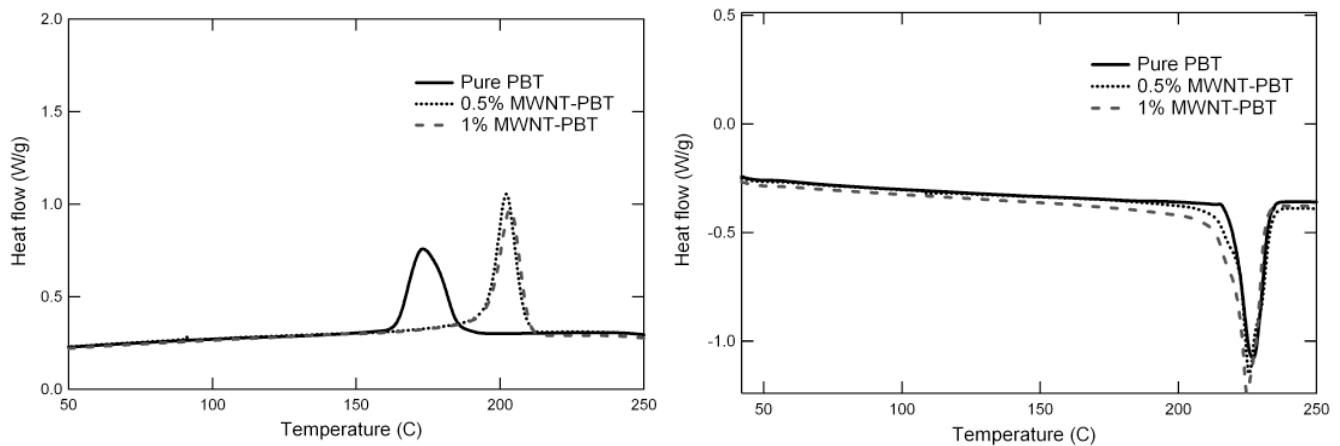


FIGURE 10. (left) Non-isothermal crystallization curves for PBT and MWNT-PBT nanocomposites. $\Delta T = -10^\circ\text{C}/\text{min}$. (right) Melting curves for PBT and PBT-MWNT nanocomposites. $\Delta T = +15^\circ\text{C}/\text{min}$.

Sample	T_m ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	ΔH_m , J/g	X_c (%)
PBT	227.2	173.3	24.6	17.55
0.5% MWNT – PBT	225.6	202.0	28.4	20.25
1% MWNT – PBT	224.8	203.5	32.2	22.98

TABLE 1. Crystallization temperature, melting temperature and crystallinity for PBT and PBT-MWNT nanocomposites. T_m = melting temperature, T_c = crystallization temperature, ΔH_m = melting enthalpy, and X_c = percentage crystallinity.

CONCLUSIONS

The addition of MWNTs to PBT gave rise to shear-induced crystallization of the PBT at temperatures which are greater than the crystallization temperature of PBT. The increasing concentration of MWNTs increased the rate of crystallization and decreased the induction time for crystallization in PBT nanocomposites. An increase in frequency increased the crystallization rate and decreased the induction time for crystallization of the PBT

nanocomposites, whereas similar changes were not observed for pure PBT under identical conditions. These results suggest that nanocomposite rheology and processability can be significantly influenced by flow-induced crystallization effects induced by the presence of the nanoparticles. The resulting microstructural distributions resulting from the change in state of crystallinity within the polymer nanocomposite can significantly affect the development of various ultimate properties of the nanocomposites and must be investigated further.

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