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EFFECT OF UNIAXIAL DEFORMATION, ANNEALING AND CARBON NANOTUBES ON THE MORPHOLOGY AND MECHANICAL PROPERTIES OF POLY (BUTYLENE TEREPHTHALATE) AND PBT NANOCOMPOSITES

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ABSTRACT

The goal of this investigation is to elucidate the interrelations between the strain-induced crystallization behavior, morphology and mechanical properties of poly (butylene terephthalate) PBT and its nanocomposites with multi-walled carbon nanotubes (MWNTs). The mechanical properties of semicrystalline polymers such as PBT depend upon the processing conditions, which affect the crystallization behavior and the resulting crystal morphology developed within the processed sample. PBT is observed to undergo strain-induced crystallization during uniaxial deformation, with concomitant changes in the polymer crystal as a function of the applied strain history. In the current work polymer morphology was investigated with wide angle XRD, differential scanning calorimetry (DSC) and polarized light microscopy (PLM). DSC results indicate an increase in crystallinity due to strain-induced crystallization during uniaxial cold-stretching, which was further confirmed with XRD analysis of the samples. Analyses of the samples under polarized light pre- and post-stretching clearly show that there is a transformation of the spherulitic crystals of the pre-stretch morphology into elongated oblong crystals, as the imposed strain exceeds a critical value. Annealing of PBT was done under different conditions to probe the effects of changes in the crystallinity obtained upon thermal treatment on polymer morphology and mechanical properties. The annealed samples were found to have high crystallinity, high Young's modulus, and low yield stress values as compared to unannealed samples processed under similar conditions.

To investigate the effects of nanoparticle loadings on PBT crystal morphology and mechanical properties, pure PBT was melt mixed with different concentrations of multi-walled carbon nanotubes (MWNTs). Due to the increased nucleation rate effect associated with the incorporation of MWNTs, the PBT crystallization temperature was increased and the crystal size decreased with the increasing concentration of MWNTs. Tensile tests performed on PBT and their nanocomposite samples revealed decreases in the elongation at break values. Research is ongoing to understand the relationship between the MWNT loading levels and mechanical properties along with study of orientation of MWNTs under tensile load and its effect on strain-induced crystallization.

Keywords: Poly (butylene terephthalate), strain-induced crystallization, crystallinity, nanocomposites

INTRODUCTION

Semi-crystalline polymers can be structured upon stretching at a temperature which is below their melting temperature values, "cold-stretching", to enhance their mechanical, chemical and physical properties.[1] Orientation of a semicrystalline polymer produces fiber-like crystals.[2] Furthermore, upon stretching the crystalline as well as the amorphous building blocks are preferentially oriented along the stretch direction, resulting generally in the enhancement of the mechanical properties along the stretch direction as a direct consequence of the preferred orientation of the crystalline and amorphous structural units. Other factors that play a role in the development of the mechanical properties

include the thermo-mechanical history imposed on the polymer during processing, including the procedures used for annealing. The incorporation of various types of nanoparticles is also a popular methodology for the control of the mechanical properties. Such factors affect the morphology developed and the various ultimate properties, including the mechanical properties. Generally, factors which lead to increased crystallinity lead to increases in the stress at failure and the elastic modulus values of polymeric samples

The development of the microstructural distributions and the mechanical properties of semi-crystalline polymers have been studied by various groups.[3, 4] Techniques such as uniaxial stretching have been developed which are capable of producing highly oriented fibers, and films at room temperature. Poly (butylene terephthalate) (PBT) is a semi-crystalline thermoplastic polyester, which can be processed to make fibers and films. We are interested in understanding the effects of uniaxial stretching, annealing and inclusion of low amount of multi-walled carbon nanotubes (MWNTs) on the development of structure and morphology of PBT.

Studies have been conducted to understand the structure development under uniaxial stretching in various polymers such as PET[5-9], PP[10], PVDF[11], PEN-PEI-PEEK ternary blends[12], ethylene-propylene copolymer[13] and syndiotactic-PP[14]. A few studies have been conducted on Nylon-nanoclay[15], PVC-nanoclay[16] and Ethylene-Propylene copolymer-MWNT[17] nanocomposites to understand the orientation of nanoparticles and crystal structure on uniaxial deformation. These studies were done either at room temperature or at a temperature which is higher than glass transition temperature of the polymer. Kawakami et al studied the in-situ structural formation of amorphous PET during uniaxial deformation above glass-transition. They found that the structure and mechanical properties can be divided in three zones as oriented mesophase formation, crystallization initiation and crystal growth.[5] Sevegney et al found that uniaxial strain induced changes in crystal conformation and hence morphology of syndiotactic polypropylene (sPP).[14] Formation of polymorphs (α-β) induced by mechanical deformation is also very interesting, as it affects the mechanical properties of the films.

Semi-crystalline polymers such as PVDF and PP have been studied to understand the polymorphism under uniaxial load[11]. In PBT it has been found that the crystal phase transition is reversible and the detailed mechanism of this solid-state transition has been studied in details.[18] Song et al have studied the formation of polymorphic structure in uniaxially and biaxially stretched PBT films.[19, 20] Annealing is another process variable which affects the polymer crystallinity and hence mechanical and barrier properties of the polymer[21-24]. Annealing of a semi-crystalline polymer such as PET[21], PEN[25], PP[22-24] and Nylon-11[26] leads to development of different crystalline morphologies. Annealing time and temperature affect the crystal size, crystal structure and overall crystallinity of the polymer.

The presence of a nanofiller also affects the polymer crystal size and crystallinity.[23,27-29] Carbon nanotubes are promising nanofillers for polymer nanocomposites due their excellent mechanical, electrical, and thermal properties.[30, 31] The overall improvement in these properties depends not only on the presence on nanoparticles, but also on the polymer used. The polymer microstructure and interface are strongly influenced by presence of MWNTs in a semi-crystalline polymer as MWNTs act as nucleating agents for polymer crystals. Ryan et al have suggested that nanotubes act as reinforcing agents in PVA and hence affect the crystallinity and mechanical properties, in quiescent nanocomposite samples.[28, 32] Here we have studied the effect of different process variables on PBT morphology and mechanical properties, with an ultimate goal of understanding the uniaxial deformation behavior of PBT nanocomposites.

EXPERIMENTAL

Materials

PBT pellets were obtained from Ticona Polymers (NC). PBT pellets were dried in a vacuum oven at 125^0C for 4h to remove moisture prior to their use. MWNTs (Trade name: MWNT-A-P) 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/cm^3. To examine the size and shape distributions of the MWNTs samples a LEO 1550 scanning electron microscope (SEM) operated at 15kV was used. Figure 1 shows a typical scanning electron micrograph of MWNTs. The scale bar is 1 μm .

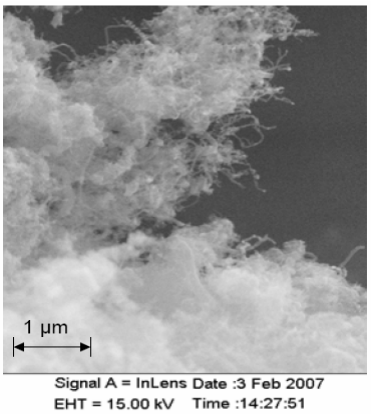

FIGURE 1. SEM micrograph of MWNTs

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 (shown in Figure 2). 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 245^0C for 8 minutes at 32 rpm. The loading levels of the nanocomposites

were 0.01 and 0.1% (by volume) of MWNTs. After mixing the nanocomposite was removed and sealed within polyethylene bags. For mechanical testing dog-bone shaped samples (ASTM D-638 standard) were compression molded using a Carver hot press at 245^{0}C for 5 minutes, followed by cooling employing water (at ambient temperature) circulation in the mold. For the annealing study, the moldings were kept in vacuum oven at desired annealing temperature and time.

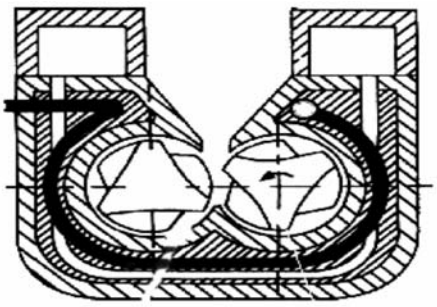

FIGURE 2. Haake torque rheometer

Thermal Analysis and WAXD Analysis

Differential Scanning Calorimetry (DSC) studies were conducted using a TA Instruments (New Castle, DE) DSC model Q1000 on pure PBT and PBT nanocomposites under a dry N_2 environment. The DSC samples were ramped from 25 to 250^{0}C, and maintained at isothermal conditions for 5 minutes at 25 and 250^{0}C. The heating and cooling rates were 10^{0}C/min. The melting point was measured as the samples were heated to 250^{0}C, while crystallization temperatures were determined as the samples were cooled to 25^{0}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 (142 J/g).[33] Wide angle X-ray (WAXD) analysis was performed on the samples using a Rigaku Miniflex diffractometer in conjunction with a CuK_α radiation source operated at 30kV.

Uniaxial tensile testing and microstructural analysis

An INSTRU-MET floor model Instron with Testworks material software was used to test dog-bone samples. All tests were performed at room temperature. The deformation rates were 1.27, 2.54 and 12.7 mm/min. For microstructural analysis, PBT and nanocomposite samples were microtomed using a LKB Ultrotome. Figure 3 shows the locations on the dog-bone samples from where the specimens were taken for analysis. Thin microtomed slices (cut thickness: 2-4μm) were placed between two glass slides, and studied under a polarized light microscope (Nikon) to probe the crystal structure.

RESULTS AND DISCUSSION

Uniaxial deformation and change in crystal morphology

A typical stress-strain curve collected at a nominal stretch rate of 1.27 mm/min is shown in Figure 4. As the nominal strain increases the crystal structure changed from spherulite to elongated oblong crystals. It was found that this change in the crystal morphology occurred at a critical strain value along with an increase in crystallinity due to strain-induced crystallization.[10,34, 35] At 20% strain the crystals are ellipsoidal, which become fiber-like at 90% strain as typical for this type of testing and shown in Figure 4. It can be seen that the fiber-like crystals are highly oriented in the direction of stress. Prior to the strain reaching the yield point (up to 10% strain) the crystals were spherulitic, and no changes in crystallinity were observed. The increase in crystallinity with applied strain (which was revealed on the basis of the DSC experiments) was confirmed with WAXD analysis of the same samples (shown in Figure 5). It can be seen that all major peaks transformed to one single peak (with increase in strain). No new peaks were observed from WAXD analysis of undeformed and deformed sample. A change in the crystal conformational structures can be seen.

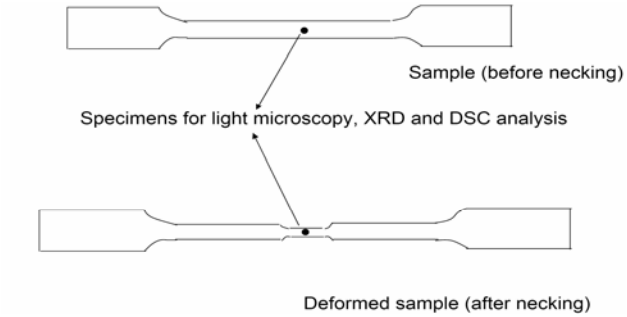

FIGURE 3. Sample location for structural analysis

To investigate the effect of the deformation rate on the development of the crystal structure transitions and mechanical properties, the uniaxial stretching experiments were performed at different deformation rates (1.27, 2.54 and 12.7 mm/min). The results are as shown in Figure 6. The deformation rate employed does not affect the principle deformation behavior (in the range investigated), although the yield stress increased and the strain at break decreased with the increasing deformation rate.[11] A change in crystal structure, from spherulitic to elongated oblong crystals, and an increase in crystallinity from 21 to 34% were observed in the samples deformed at the highest stretch rate of 12.7 mm/min.

Effect of annealing on morphology and mechanical properties

The effects of the annealing time and temperature on PBT crystallinity are shown in Figure 7. At higher temperatures the crystallinity values increased along with an increase in the rate of crystallinity increase with annealing time. It can be seen that the crystallinity of PBT samples annealed at 200^{0}C for 300 minutes increased by 8%, whereas the crystallinity increased by only 2% in PBT samples annealed at 100^{0}C for 300 minutes. The samples annealed at 200^{0}C for 300 minutes exhibited the highest crystallinity values. Annealing of Nylon-11 has shown the similar behavior.[26] It has been suggested that at high annealing temperatures large impinging spherulites

form quickly, while at lower temperatures many small spherulites continue to grow for a longer time before impingement occurs.[21] The spherulite sizes (as revealed by the Maltese cross patterns under the polarized light) for PBT annealed at 200^0C for 300 minutes are shown in Figure 8. An increase in the spherulite size can be seen to occur upon annealing. It can also be seen that there is significant variation in the sizes of the spherulites. Tensile testing was performed on the dog bone samples annealed for different conditions and on unannealed samples at similar deformation rate (to act as control samples). The results are summarized in Table 1. Changes in mechanical properties occurred as a function of annealing time at 200^0 C. The changes should be associated principally with the increase of the crystallinity with increasing annealing time, as well as the altered crystalline morphology. It is expected that the formation of larger spherulites will lead to the development of stress concentration points to reduce the toughness of the samples (area under the stress versus strain curve). The tensile strength at yield generated a maximum at two hours of annealing, and elongation at break decreased with the increasing of the annealing time. These results are indicative of the brittle behavior of samples annealed for 5h. The modulus increased with the increase of the annealing time.

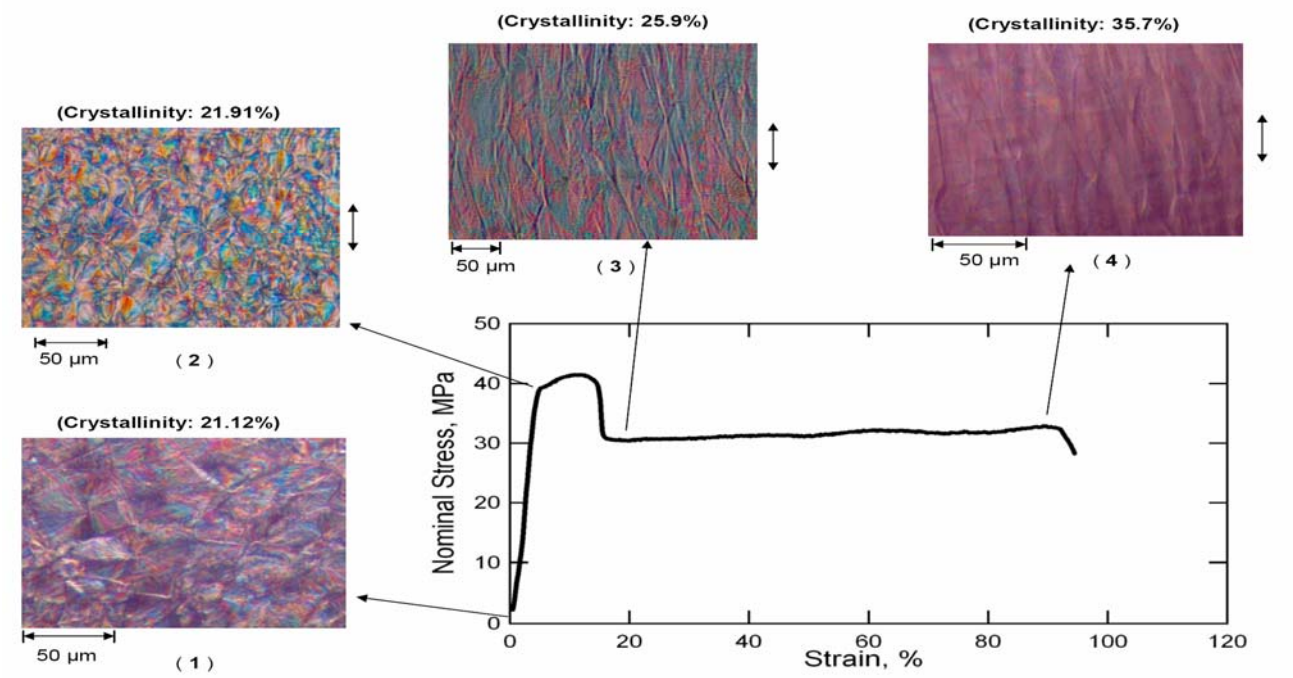

FIGURE 4. The typical development of the stress-strain curve and the associated changes in the crystallinity and crystal morphology during uniaxial stretching of PBT. The deformation rate is 1.27 mm/min. The arrow indicates the load direction.

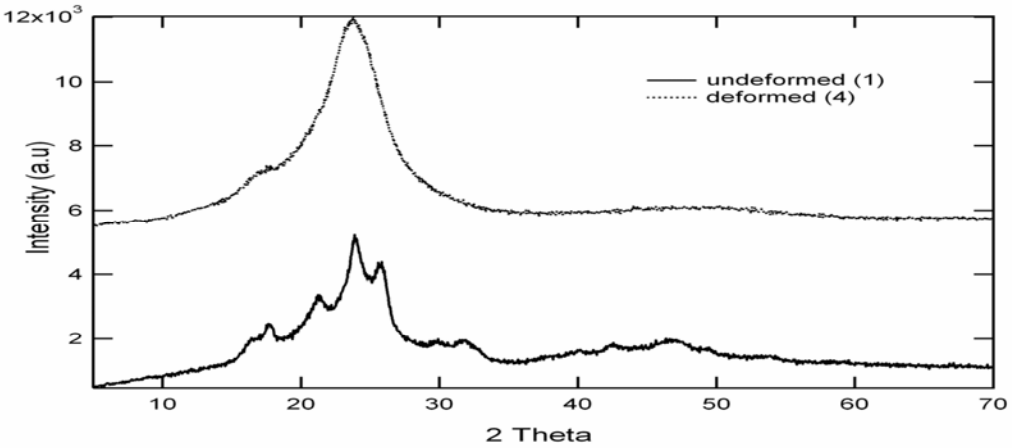

FIGURE 5. WAXD patterns of the samples collected during uniaxial testing of PBT (Deformation rate 1.27 mm/min). Samples were taken from the same location on the dog-bone specimen indicated in Figure 3. Note that (1) and (4) in the legend refers to the stages of the stress-strain curve shown in Figure 4.

Sample	Annealing Time (h)	Crystallinity (%)	Young's Modulus (GPa)	Tensile Strength at yield (MPa)	Elongation to break (%)
PBT	0	20.36	0.47	41.36	94.95
PBT-200C-2h	2	26.80	0.65	45.22	12.11
PBT-200C-5h	5	29.01	0.85	22.78	2.70

TABLE 1.Effect of annealing on the development of the mechanical properties of PBT. Annealing temperature: 200^0C, Deformation rate: 1.27 mm/min

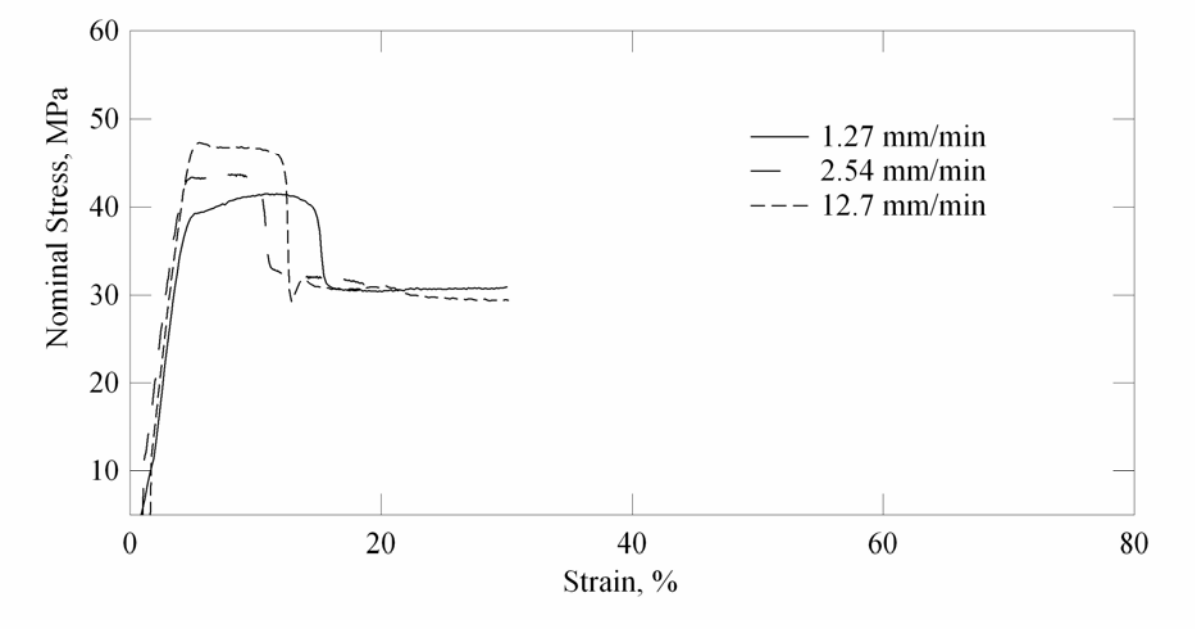

Figure 6. Uniaxial stretching of PBT at different deformation rates

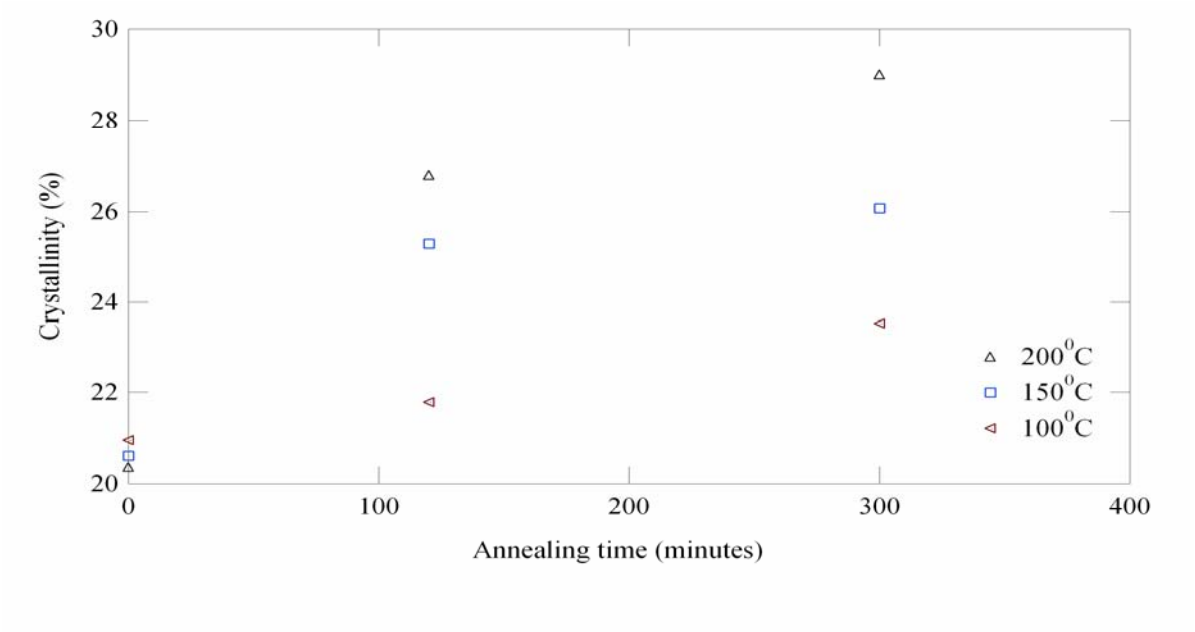

Figure 7. Effect of annealing temperature and annealing time on PBT crystallinity.

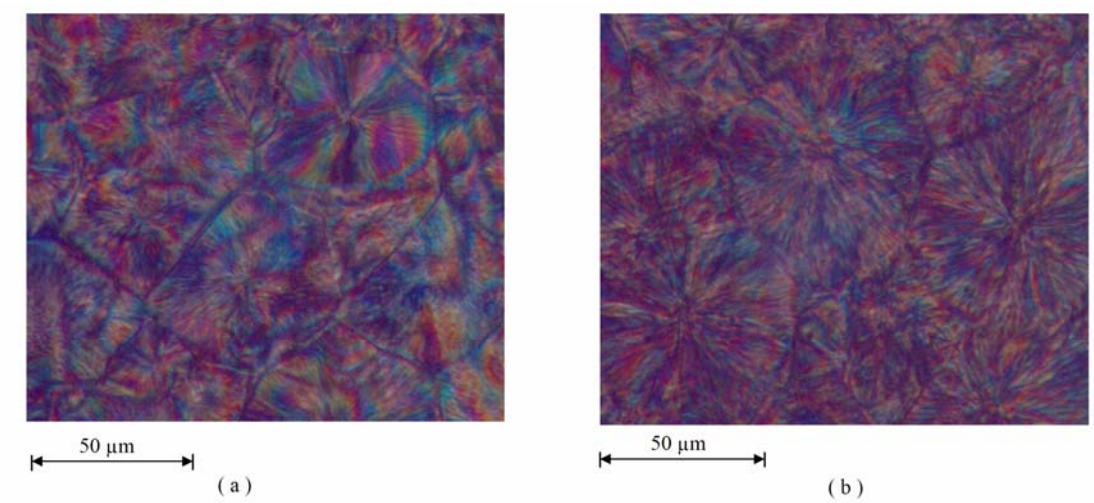

FIGURE 8. Effect of annealing on PBT crystal size: (a) not annealed, (b) annealed at 200^0C for 5 h

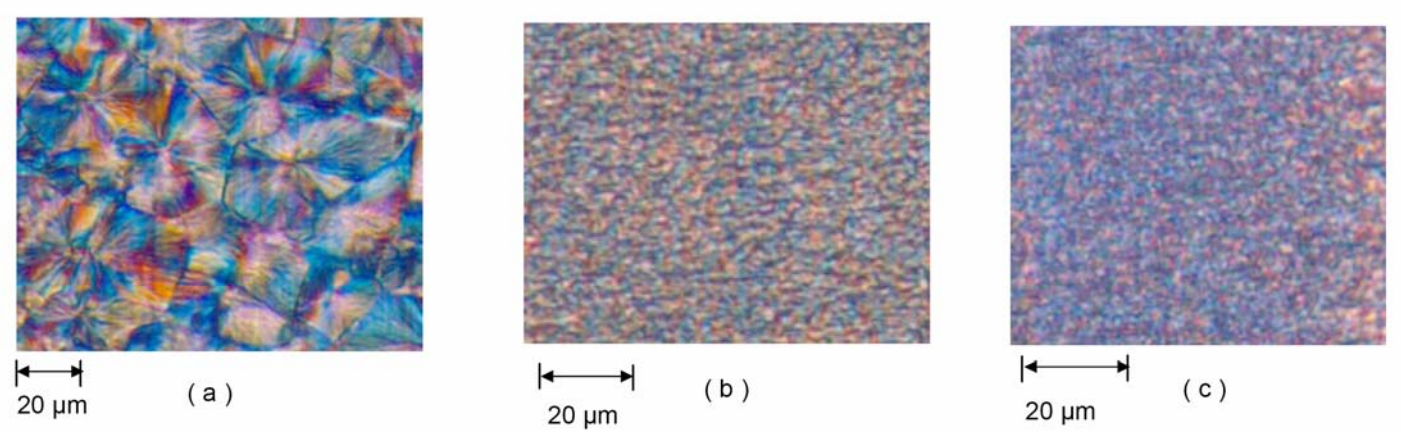

FIGURE 9. Effect of MWNTs loading on PBT crystal size: (a) Pure PBT (b) 0.01% MWNT-PBT (c) 0.1% MWNT-PB**T**

Sample	T_m (°C)	T_c (°C)	ΔH_m, J/g	X_c,%	Crystal size, µm
PBT	227.21	178.02	27.5	19.36	50-55
0.01% MWNT-PBT	227.43	198.11	27.63	19.45	4-6
0.1% MWNT-PBT	226.84	201.38	29.8	20.98	2-4

TABLE 2. Crystallization temperature, melting temperature and crystallinity for PBT and MWNT-PBT nanocomposites. T_m = melting temperature, T_c = crystallization temperature, ΔH_m = melting enthalpy, and X_c = percentage crystallinity.

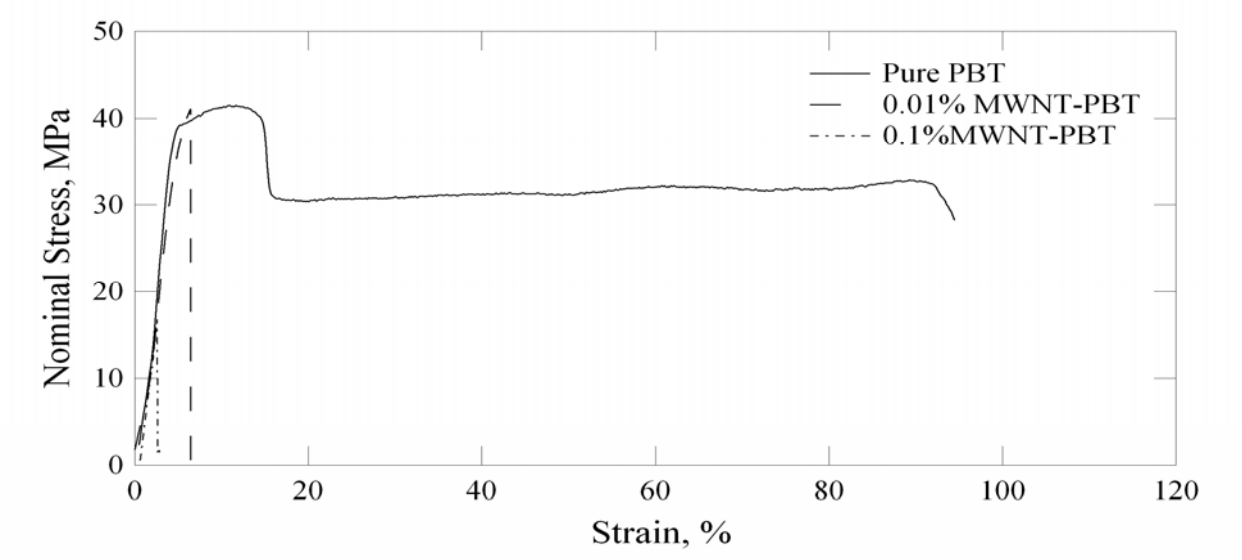

FIGURE 10. Stress-strain relationship of PBT and MWNT-PBT nanocomposites. Deformation rate: 1.27 mm/min

Effect of MWNT loadings on PBT morphology and mechanical properties

Melt-mixed PBT nanocomposite samples with 0.01 and 0.1% of MWNT loadings were subjected to the same analysis undertaken for virgin PBT. The effect of the incorporation of the MWNTs on PBT spherulite size can be seen very clearly from Figure 9. The PBT spherulite size decreased from 50 to 4 μm, upon the addition of 0.01% MWNTs. The crystal size decreased further with addition of 0.1% MWNTs.

Thermal analysis (DSC) was performed on pure PBT and nanocomposite samples to understand the effect of MWNTs on PBT crystallization temperature. The results are shown in Table 2. The increase in PBT crystallization temperature with the incorporation of MWNTs suggests that MWNTs are acting as nucleating agents even at the relatively low loading level of 0.01%. Similar results have been obtained by other researchers, at very low loading of MWNTs.[28,30-32,36-40] However, the bulk crystallinity values were not significantly affected. Tensile testing was also carried out on the nanocomposite samples at the rate of 1.27 mm/min. The results (Figure 10) show that the modulus and the yield stress were not affected by the presence of the MWNTs for the 0.01%MWNT-PBT sample, but elongation to break decreased significantly. Similar results have been obtained by Bhattacharya et al[31] and McNally et al.[37] An increase in the toughness of the composite is expected with the addition of MWNTs[41]. However, there is the difficulty of dispersing the nanoparticles to separate them from each other[42], i.e., the break up of the agglomerates of the MWNTs but such agglomerates were not readily observable using SEM or polarized microscopy. The pictures taken from optical microscope do not show any MWNT agglomerates which might act as the stress concentration points. For nanocomposite samples, the yield stress and the elongation to break decreased upon the incorporation of 0.1%MWNTs, along with an increase in crystallization temperature and decrease in crystal size. Ryan et al studied the mechanical properties of PVA nanocomposites with different kinds of nanotubes at very low concentrations.[28] It was suggested that the improvement in overall mechanical properties depend on the nanotube loadings and the crystallinity developed within the sample. Obederni et al suggested that the material properties are affected by the increase in crystallization temperature in the presence of nucleating agent.[23] From experiments conducted under controlled conditions they found that the fracture toughness of the polymer is not affected significantly by the crystal size, but is affected by the changes associated with the changes in the crystallization temperature and its implications on tie molecule configurations. Additional studies will be carried out to understand better the relationship between the nanocomposite morphology and the development of the mechanical properties.

CONCLUSIONS

It is observed that the PBT crystalline morphology changes from spherulite to fiber-like under uniaxial tensile loading. Beyond the yield point the crystallinity increases due to strain-induced crystallization. Annealing increases the bulk crystallinity of the polymer. Changes in crystallinity, molecular orientation and the changes in the crystalline morphology affect the development of the mechanical properties. Annealing for a relatively long time at a relatively high temperature decreases the elongation to break (giving rise to brittle failure). The MWNTs appear to be acting as nucleating agents even at the low concentration of 0.01%.The overall toughness decreased with increase in the concentration of the MWNTs. At low MWNT loading level an increase in the crystallization temperature and decrease in crystal size was observed in comparison of virgin PBT samples. Further study is required to explain the observed decrease in the toughness of the nanocomposites upon the incorporation of the MWNTs

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