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Morphology and properties of Nylon6/ poly (butylene terephthalate) in situ microfibrillar reinforced blends: influence of blend ratio

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Abstract: Microfibrillar reinforced composite (MFCs) have been prepared by reactive melt-extrusion of Nylon6 and Poly (butylene terephthalate) in different blend ratio. These composites have been generated by a series of process, which include reactive extrusion in a twin-screw extruder, followed by melt spinning and drawing (nanofibrillation). These composites have been investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and mechanical testing. The microstructure of blend as revealed by SEM, showed fine dispersion of minor phase and PBT fibrils in PA6 matrix.This enhanced fibrillation of PBT was attributed to Polar-polar interactions of amid-ester group as modifier to improve interfacial adhesion of phases and fibrillation. This improvement in structure altered mechanical properties by transferring stress between matrix and PBTnanofibril reinforcement.

Keywords: Blend, Microfibrillar, Morphology, Nylon6/PBT.

Introduction

Polymer blending has been successfully used as a modification technique to produce new polymeric materials with desired properties. One type of polymer blends named microfibrillar reinforced composite or blend, which consists of a thermoplastic polymer as a matrix and in situ thermoplastic polymer microfibrils as reinforcement [1-4]. The microfibrils in the blends are of miraculous role, such as application of gas barrier: the microfibrils increase the channel length of gas or vapor passing through the materials, The enhancements of mechanical properties in which the transcrystallites are formed and the skin-core structure can be well suppressed by the microfibrils network [5-8]. The fiber spinning is the most conductive method to create fibril morphology because the elongational force field exiting in the spinning process is more effective than the shear force field existing in other processes. The interface between polymer considered as the third phase, plays a predominant role in the improvement of properties of the blend fibers [9-13]. The aim of the present study is to follow and distinguish between the contribution of physical and chemical processes to the structure and properties of Nylon6/ Poly (butylene terephthalate) blend fibers [14, 15].

Results and discussion

Morphology:

A comparative study of the phase morphologies of the blends was performed by SEM. Nylon6 and Poly (butylene terephthalate) are miscible polymers together, and the PBT appeared as dispersed phase with irregular shape in the PA6 matrix. Figure **1** shows that the compounding system has important effect on resulting morphology whereas it can control the microstructure by improving interaction between phases via compounding condition. SEM micrographs of the Nylon6/Poly (butylene terephthalate) blend containing 40% PBT with appropriate compounding

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system at three different magnifications (Figure **2**) indicates that even by incorporation of 40% PBT, disperse phase disappeared which resulted that two phases were completely compatible. Figure **3** shows the Nylon6/Poly (butylene terephthalate) blend containing 30% PBT before and after being Nylon6 matrix etched by formic acid. In this Figure the internal network of PBT phase have been noticed. PBT phase is distributed all over the matrix to enhance the final properties of resulting blend.

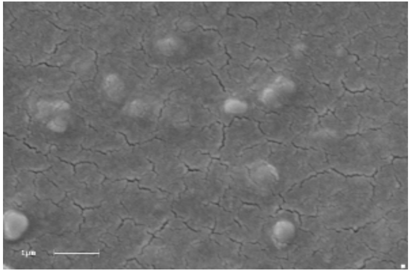


Figure 1. SEM micrographs of Nylon6/Poly (butylene terephthalate) blend containing 20% PBT without appropriate compounding system

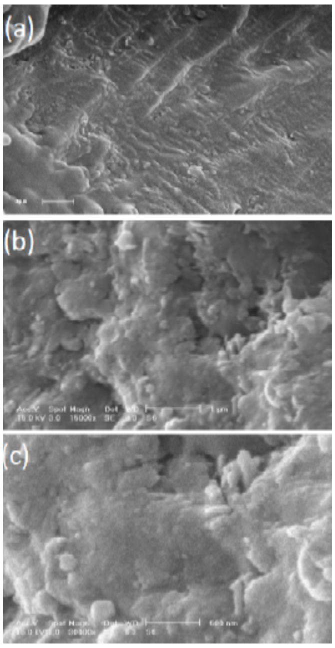


Figure 2. SEM micrographs of the Nylon6/Poly (butylene terephthalate) blend containing 40% PBT with appropriate compounding system at three different magnifications

Strain existed below the spinneret, which could deform the PBT phase in nanofirils plays a significant role in improving of properties of blend fiber via reinforcement matrix by fibrillar morphology development. As can be seen in Figure **4** fibrils oriented in fiber axis could have enhanced mechanical properties by transferring stress towards fibrils and decreasing fibrils diameter by stretching via drawing. It is well known that when the melt flow through the entrance of a capillary die i.e. spinneret, the melt would undergo the elongatioanal flow field because of the convergence effect at the entrance. Single spherical particle deformation and coalescence process of elongated particles at the entrance and inside of the spinneret are the crucial steps in the formation of microfibrillar hybrid morphology under melt spinning condition. It can be formed the whole microfibril was comprised of elongated singles particles together. The PBT fibrils with the submicron diameter were obtained during melt spinning of PA6/PBT miscible blends which indicates that the elongational flow during fiber spinning can deform PBT droplets into the fibrils in each blend ratio. Furthermore, the interface as a transition layer often acts to transmit the stress from one phase to the other and efficiency of stress transfer continuity depends on the nature of the transition layer in other words, the appropriate dispersion can improve the adhesion, and consequently improve fibril formation.

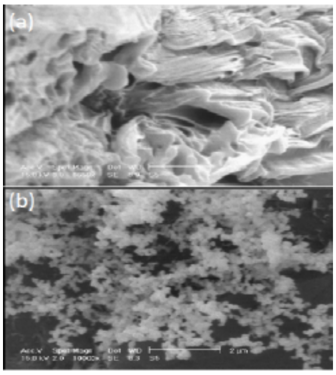
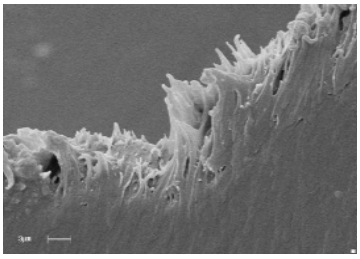


Figure 3. SEM micrographs of the Nylon6/Poly (butylene terephthalate) blend containing 30% PBT (a) before being etched, (b) after being etched

Figure 4. SEM micrographs of the Nylon6/Poly (butylene terephthalate) blend fiber containing 40% PBT fibril phase



Microstructural parameter:

An extensive analysis of crystallization behavior was carried out on pure nylon6 and its nanocomposites in form of fiber. To rightfully compare pure nylon6 material with its blend, it was necessary to extrude and melt spin polyamides under the same processing conditions used to form the blend fibers. Figure **5** shows the crystallization behavior of virgin nylon6 and its blends fibers with different blend ratio prepared with appropriate melt compounding. The temperature of melting and the length of time held in molten state will also determine the amount of stable nuclei remaining prior to recrystallization. The higher crystallization seen in the blend fiber containing higher amount of disperse phase is due to the ability of disperse phase nucleation which allows polymer chains to be incorporated into smaller cell growing crystal.

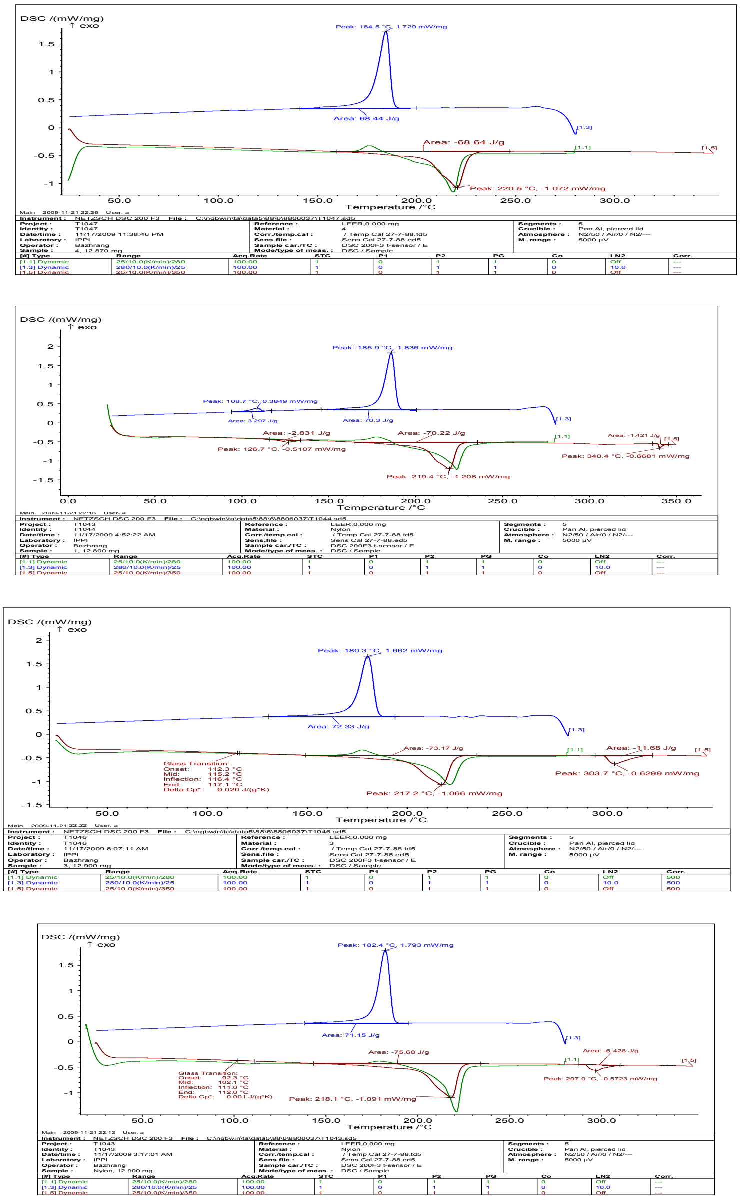


Figure 5. DSC thermograms of samples 1, 3, 4 and 5 up to down respectively

In other word, the presence of higher concentration of dispersed phase in form of fibril prevents large crystalline domains from forming duo to limited space and restrictions imposed on polymer chains by a high number of nucleating agent (PBT sphere and fibril); this leads to smaller crystalline cell. However, addition of disperse phase, results in a marginal increase in crystallization temperature of nylon6 thus confirming that PBT phase acts as a nucleating agent and contributes to rise of the crystallization temperature and reduction of crystal size of matrix of polymer blend.

Figure **6** shows the X-ray patterns of neat PA6 and its blend fibers to compare the crystallization of each phase in multi-blend system in which phases have the same melting point. As can be seen in this Figure incorporation of PBT disperse phase can improve crystal formation process by increasing the extent of matrix phase crystalline. By increasing minor phase in the blend system duo to the compatibility of phases, polymeric chains of PBT phase attract PA6 chains to be in the small crystal cell. This behavior attributed to the lower mobility of PBT chain and higher crystallization temperature of it which can increase the total crytallinity of system.

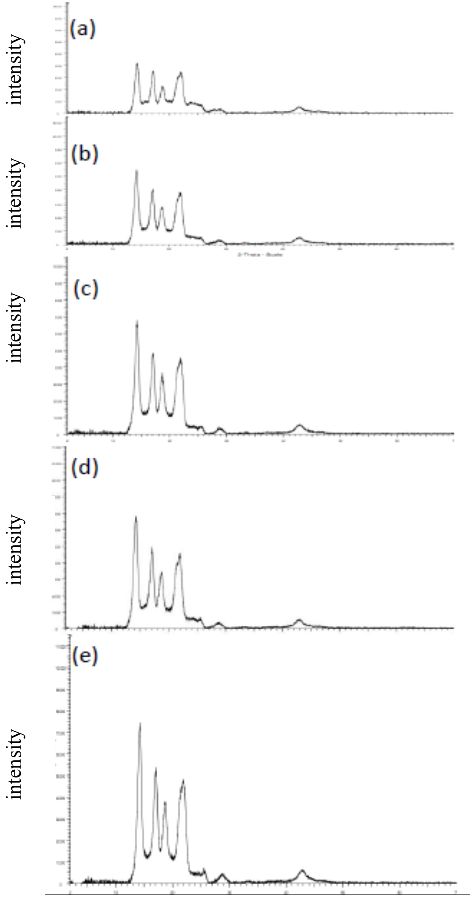


Figure 6. X-ray diffraction of samples 1,3,4,5 and 6 up to down respectively

Mechanical properties:

Tensile strength, modulus, and elongation at break of different PA6/PBT blend fibers varying in composition are listed in Figure **7**. The ultimate tensile strength of the hybrid fibers were found to increase with increasing disperse phase content up to 30% and then decreased. The initial modulus of the hybrid fibers were also found to increase with increasing PBT content, where increase in content from 0 to 30%, resulted in linear improvement in the modulus which is about more than the modulus of pure PA6. This increase in the tensile modulus of the blend fibers are thought to the dependent on the interactions between the PA6 and PBT chains as well as on the rigidity of the resulting nanofibrils are themselves. Presence of two components in the hybrid blend fibers caused the acceptable increase in the elongation at break which suggested chain slippage of two polymeric phases instate of chain breakup. The extent of dispersion of PBT phase in the matrix improved the mechanical properties, fine dispersion of nanofibrils in fibers manufactured by modified compounding system have led to nanofibril structure without any defect.

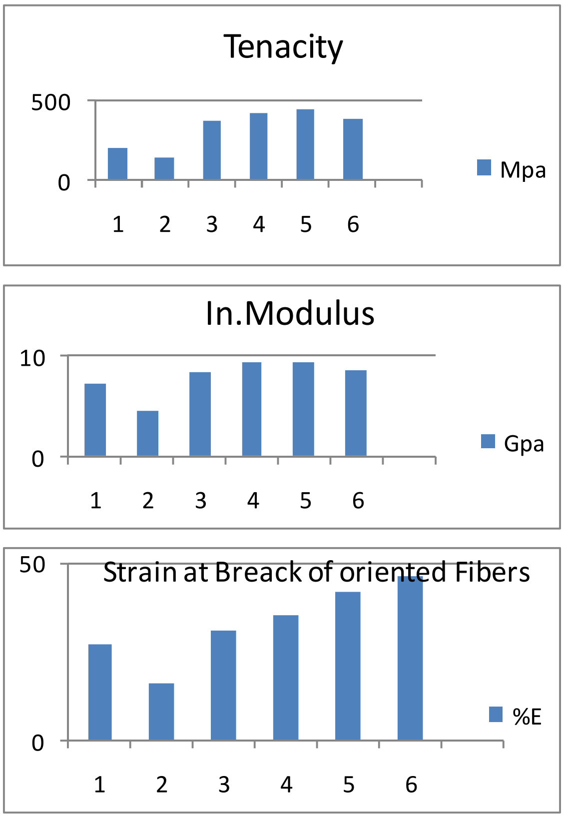


Figure 7. Tensile properties of hybrid blend fibers

Conclusion

In this study, the effect of incorporation of different amount of PBT dispersed phase (different blend ratio) on the morphology and properties of miscible Nylon6/ Poly (butylene terephthalate) blend fibers were investigated. A novel in situ microfibrillar blend fibers based on Nylon6/ Poly (butylene terephthalate) was developed by using melt interaction followed by melt spinning process. PA6/PBT blends showed two phases in which PBT appears as a dispersed phase. The results of this investigation indicate that the degree of fractionated crystallization is dependent on the interface of disperse phase and surrounding medium which could be controlled by nucleating effect of dispersed phase and surpassing chain motion by blend ratio as these are influenced by PBT dispersion in the PA6 matrix. The PBT phase in the blend was found to have great nucleating effect on crystallization of PA6 in fibrils forms in the blend fibers. Results also indicated that by incorporation of compatible polar component in the matrix and enhancement of morphology and microstructure via designing appropriate formulation, compounding and melt spinning process, mechanical properties duo to relationship between microstructure and properties can be improved.

Experimental

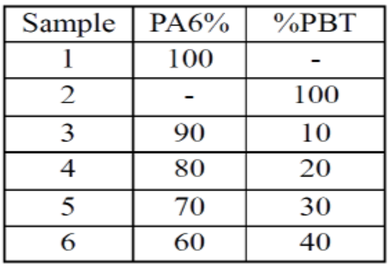
Materials:

A commercial fiber grade Nylon6 supplied by Parsilon petrochemical Co., Iran and Poly (butylene terephthalate) (Pocan) received from Bayer chemical company were used as matrix and dispersed phase.

Specimen preparation:

The PA6/PBT blend samples in different weight ratio were considered (Table **1**). All the samples were melt compounded in a co-rotating twin screw extruder and then melt spun into the fiber using a single screw extruder equipped with a spinneret.

Table 1. Blending compositions



Sample	PA6%	%PBT
1	100	-
2	-	100
3	90	10
4	80	20
5	70	30
6	60	40

As can be seen in Table **1** blend nanocomposite samples were prepared by using different blend weight ratio. Melt spinning was performed on a single-screw (L/D=25) Brabender melt extruder with a spinneret containing 20 orifices, each of 1 mm diameter. The extruder was set with four different temperature zones 220,240,240 and 230, respectively, at the feed, metering, die and spinneret sections. A drawing apparatus was also employed to perform hot drawing of the blend fibers.

Characterization:

Scanning electron microscopy (SEM):

SEM images were taken to study the morphologies of PA6/PBT blend and blend fibers. SEM micrographs were taken from cryogenically fractured surface of samples after submersion in liquid nitrogen for 1hour. The surface was then sputter coated with a layer of gold-palladium. The fractured surfaces of the fibers were investigated in a SEM instrument, LEO 440, operating at 20 KV.

Thermal analysis:

Differential scanning calorimetry (DSC) spectra were recorded on a Perkin-Elmer DSC Pyris-I. Differential scanning calorimeter calibrated the temperature with indium and the crystallization behavior can be obtained. The DSC was performed under nitrogen atmosphere. In this experiment about five milligrams of dried sample was heated quickly from 50 to 300 at 10°C/min and hold for 5min after reached the 300°C in order to eliminate the influence of thermal history. After that the samples were cooled from 300 to 10°C (at- 5°C/min).

X-ray diffraction analysis (XRD):

A Siemens X-ray diffraction unit operated at 30 KV and 20 mA with Cu element and nickel filter was used to find the changes in Crystallization behavior of blend components.

Mechanical testing:

The tensile properties of the PA6/PBTblend fibers were determined at room temperature using Instron mechanical tester with a crosshead speed of 20mm/min. The experimental uncertainties in the tensile strength and modulus were averaged over 30 different determinations to give correlation values of ± 0.01MPa and ± 0.05 GPA, respectively.

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