STUDIES ON PBT/ABAS POLYMER BLENDS AND THEIR COMPOSITES

by

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Submitted

in fulfillment of the requirements for the degree of Doctor of Philosophy

to the

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polymerizates
composite materials

Dedicated

To

My Parents,

Husband, Dheeraj

Brother, Vineet

&

Daughter, Srinidhi

CERTIFICATE

This is to certify that the thesis entitled **"Studies on PBT/ABAS Polymer Blends and Their Composites"** submitted by **Ms. Neetu Tomar** to the **Indian Institute of Technology, Delhi** for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by her. Ms. Neetu Tomar has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis.

The results contained in this thesis are original and have not been submitted in part or full, to any other university or institute for the award of any degree (or) diploma.

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ABSTRACT

Blends of poly (butylene terphthlate) (PBT) with poly (acrylonitrile- butyl acrylate-styrene) (ABAS) were prepared to improve the impact properties of PBT. PBT and ABAS blends are partially miscible due to transesterification and imide linkage formation which led to improved interfacial adhesion between two phases. Incorporation of ABAS polymer results in enhanced impact properties but decreased the modulus. Mica and nano TiO_2 fillers were added to the PBT/ABAS (20 phr) blend to enhance the modulus. Neoalkoxy zirconate and titanate coupling agents were used in mica- and TiO_2- filled PBT/ABAS composites, respectively, to improve the filler dispersion in the PBT/ABAS matrix.

Various studies have been performed on the blends, composites and nanocomposites. Mechanical properties by tensile, impact and flexural mode of load application have been evaluated. Tensile properties were analyzed with the help of simple theoretical models. Crystallization properties of the major component PBT in the blends and composites were determined by differential scanning calorimetry (DSC) and X-ray diffraction measurements. The degree of crystallinity was correlated with the mechanical properties. Melt rheological properties and morphological properties (by scanning electron microscopy, SEM) also have been studied. Transmission electron microscopy (TEM) has been used to study the morphology of nano TiO_2- filled nanocomposites. The effects of surface modification of mica and nano TiO2 with the coupling agents on the composite properties were also studied.

In PBT/ABAS blends the effects of ABAS concentration on the above properties were evaluated. Tensile strength, elongation at maximum stress (%) and modulus decreased

with increase in ABAS concentration, while impact strength increased up to 0.2 volume fraction of the ABAS, the value then decreased marginally, remaining higher than neat PBT. Flexural modulus and strength also decreased with increase in ABAS contents. The decrease in tensile properties of the blends indicated plastic matrix softening by the use of elastomers which, however, leads to practical advantages since it enhances toughness and increases adaptability of fillers and reinforcements diversifying the end uses of the PBT matrix. Analysis of tensile properties after normalizing the effect of degree of crystallinity indicated phase interaction between the PBT and ABAS. These interactions were substantiated by FTIR spectroscopy results also.

In the DSC melting endotherm of PBT/ABAS blends, the second heating shows a minor melting peak for PBT which originated due to the presence of different morphologies and simultaneous melting and reorganization of the crystallites of PBT. The degree of crystallinity of PBT decreased in the blends. The intermolecular interaction between the two components led to the depression of the crystallization rate, reduction of crystallization temperature, T_c, and increase in the degree of undercooling as were observed in the DSC crystallization (cooling) exotherms.

Thermogravimetric analysis (TGA) also supports the interphase interaction between the two phases as initial degradation temperature increased with ABAS content. The interphase interaction between PBT and ABAS was also observed in the rheological properties of the blends. All the blends show pseudoplastic behavior and follow the power law relation. The viscosity of the blends was higher than the neat polymers, and was maximum at 0.11 volume fraction of ABAS.

SEM studies were carried out on etched samples of the blends to visualize the dispersion of the ABAS and mode of fracture of the blends. Elongated and irregular shape of the dispersed phase was imputed to be due to the elastomer's sensitivity to the complex flow imposed during melt processing coupled with an extent of interphase adhesion. The SEM micrographs also show some whitening around torn and stretched rubber particles, indicating yield of the interface region.

PBT/ABAS (20 phr) blend was chosen for further studies on the basis of its maximum impact strength. Mica and nano TiO_2 fillers were incorporated to improve the tensile strength and modulus reduced following the incorporation of ABAS into PBT.

The tensile strength of the mica filled PBT/ABAS composites increased up to 0.07 volume fraction (Φ_f) of mica. The modulus of the mica filled composites increased continuously with filler content, however the elongation–at-yield and impact strength decreased with increase in the volume fraction of filler. The rigidity of the composites remains almost unaffected up to Φ_f=0.04, the values of the flexural strength and modulus increased beyond this Φ_f. Surface treatment of mica either retains most of the properties of PBT/ABAS or enhances the same except flexural properties and thermal stability. The flexural properties of PBT/ABAS/Mica/NZ-97 registered lower values compared to PBT/ABAS/Mica composites. The thermal stability of both types of composites were lower than those of the blend matrix, however the initial degradation temperature remain marginally higher than neat PBT. Increased char yield was observed in both types of composites.

Analysis of the tensile properties and their comparison with the theoretical predictions after eliminating the effect of crystallinity indicates interphase interaction between the filler and matrix up to a critical filler concentration 0.07 volume fractions.

The overall decreases in crystallinity of the composites determined by X-ray and DSC measurements have shown good agreement. The degree of crystallinity decreased with increase in the filler concentration. Surface treatment of mica also followed similar trend of PBT crystallinity was exhibited by PBT/ABAS/Mica/NZ-97 composites as was in the untreated mica filled systems.

The results of melt rheological properties of the composites show that the composites are pseudoplastic in nature and follow the power law relation. The melt viscosity of mica filled composites decreased up to a certain level of filler concentration, the value then increased. The decrease in viscosity at low filler concentration of mica is due to flow orientation behavior of flaky mica. The viscosity of treated mica filled composites registered higher values as compared to those for untreated mica filled composites, the data, however, follows the same trend. The melt elasticity parameter decreased up to Φ_f= 0.07 with increase in shear rate showing a minimum at γ_w = 1352 s^{-1}, the value then increased with further increase in γ_w. On the other hand the extrudate swell of the composites with Φ_f >0.07 increased with γ_w. In the presence of the coupling agent, variations of apparent melt viscosity were less pronounced whereas the melt elasticity decreased at Φ_f=0.04 and remained almost unaltered with increase in Φ_f.

The size of most of the mica particles is clearly higher than the particle size of the dispersed phase ABAS, the mica particles appear dispersed in the PBT/ABAS matrix with some extent of polymer residues adherent on the particles. Upon surface treatment

of mica with the zirconate coupling agent the state of dispersion appears marginally increased and the fracture surface looks smoother to an extent.

Mineral fillers enhance the tensile modulus but adversely affect the impact strength of polymer matrix. With enormous surface area the nanoparticles possess many special properties that are different from those of other particles. Therefore, in order to evaluate the effect of incorporation of nanofiller into PBT/ABAS blend nano TiO_2 filler was added into the matrix.

Nanocomposites were prepared by varying filler concentration up to 2.2 volume percent (9 phr). Increase in tensile modulus, tensile strength and Izod impact strength were observed up to a certain filler concentration, the properties decreased with further increase in the filler concentration. The elongation-at-break showed a continuous decrease with increase in TiO_2 content. The surface treated TiO_2 filled composites showed lower rigidity as compared to untreated TiO_2 filled composites as they registered lower values of flexural properties compared to the blend matrix and the untreated TiO_2 filled composites.

The tensile properties compared with simple predictive models indicated good phase interaction in both types of composites which may be due to the reaction of functional groups of the matrix with surface hydroxyl groups of TiO_2 surface. The effect of good phase interaction was observed in melt rheological properties also where surface treated TiO_2 filled composites registered higher apparent viscosity.

Morphology of both types of composites studied by TEM indicated enhanced dispersion in the case of surface treated TiO_2 filled systems.

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