

Mechanical Properties of Mica-Filled PBT/ABAS Composites

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ABSTRACT: Tensile properties and Izod impact strength of mica-filled composites of poly(butylene terephthalate) (PBT)/polyacrylonitrile-butyl acrylate-styrene (ABAS) were studied at mica concentration range 0 to 0.14 volume fraction, (Φ_f). Tensile properties such as tensile modulus, strength, and breaking strain were normalized by dividing the data with the crystallinity (%) of the major component PBT in the composites and the matrix blends. The normalized relative tensile properties were compared with simple models to evaluate the interphase interactions between the matrix (i.e. PBT/ABAS blend) and the dispersed phase mica. Mica reinforced the blend increasing the tensile modulus and strength with mica concentration while the

strain-at-break was increased marginally up to $\Phi_f = 0.04$ and decreased beyond this Φ_f . The impact strength, however, decreased with increase in Φ_f due to enhanced matrix stiffening and lack of plastic deformation of the matrix. Scanning electron microscopic studies revealed good dispersion of mica in the composites. The effect of surface treatment with a zirconate coupling agent, NZ-97, on the above properties has also been examined. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 672–681, 2010

Key words: PBT/ABAS/Mica composites; zirconate coupling agent; predictive modeling

INTRODUCTION

The thermoplastic polyester poly(butylene terephthalate) (PBT) is extensively used in many fields of applications.¹ However, PBT suffers from notch sensitivity in impact performance which significantly hinders its even wider utilization. One of the most common methods to overcome this drawback is by blending it with other polymers, especially elastomers.^{2,3} However, elastomer modification of PBT lowers its stiffness which may be compensated for by the incorporation of particulate fillers. Fillers have always played an important role in plastics technology to meet the continued demand for improved materials with higher strength, modulus, thermal, and/or electrical properties and chemical resistance.⁴ Significant improvements in physical, mechanical, and frictional properties of PBT by various fillers and reinforcements such as glass fibers,^{5–7} carbon fibers⁸ etc. have been reported.

A plate-like particulate filler mica is of particular interest for electrical insulation applications because of its outstanding insulation properties along with excellent mechanical and thermal properties. It also imparts lower cost to the polymer composites than

glass and carbon fibers.⁴ Muscovite mica is a crystalline 2 : 1 layered aluminosilicate ($K_2 Al_4 (Al_2Si_6O_{20}) (OH)_4$). Each layer consists of two tetrahedral silica sheets sandwiching an alumina octahedral sheet.⁹ Since of four Si atoms in the tetrahedral sheet one Si atom, on the average, is replaced by Al, the layers are negatively charged. These charges are compensated for by interlayer cations, mostly potassium and the layers are held together in stacks by electrostatic and Van Der Waal forces.⁹

The reinforcement of thermoplastics and polymer blends by mica has been the subject of several studies.^{10,11} Mutual miscibility/adhesion of the components are crucial factors influencing the structure and properties of three component polymer systems.¹² Enhancement of mica-polymer interaction by treatment of mica with chlorinated paraffins,¹³ silane and titanate coupling agents,^{14,15} polypropylene matrix modifications by grafting with acrylic acid, acrylic ester, or maleic anhydride^{16–18} has been studied.

In a recent article on PBT/ABAS blends, it was shown that with increase in ABAS content the impact strength was enhanced with a corresponding decrease in stiffness and tensile strength.¹⁹ In such a blend if inorganic particulate filler is added, a balance of important composite properties may be obtained at a reduced cost. This would also enlarge the scope of application of the blend system as well as new technology can be investigated.

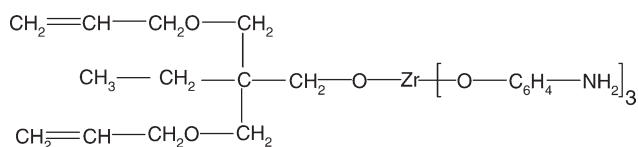
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In the above backdrop, mica flakes were incorporated into the PBT/ABAS blend at a fixed composition of the toughening component (20 phr ABAS) to enhance tensile strength and modulus as well as to widen the scope of application. This blend was selected for the study because maximum impact toughening was obtained at 20 phr ABAS content.¹⁹ The effect of mica concentration on the mechanical properties such as tensile strength and modulus, breaking strain and impact strength of PBT/ABAS blends are reported. Tensile properties were compared with simple theoretical predictions. Izod impact strength data have been analyzed on the basis of mica concentration. Scanning electron microscopy has been used to evaluate the dispersion of mica in the PBT/ABAS blend. The effect of surface modification of mica with a zirconate coupling agent, NZ-97, on these properties have also been studied.

EXPERIMENTAL

Materials

PBT used was LUPOX-HV1010 ($M_n = 25,000$ and polydispersity index = 2.2) of LG chemicals, South Korea. The amount of carboxylic acid in the PBT was $63 \text{ eq}/10^6 \text{ g}$, i.e., 1.6 carboxylic acid units per chain based on M_n .²⁰ ABAS polymer was obtained from Eliokem, France. The polymer was a saturated, precrosslinked polar acrylate terpolymer with functional carboxylic end groups. It has outstanding resistance to thermal and UV degradation.²¹ Mica was obtained from Daruka (Mica), India.²² The average particle size and density of mica was $37.8 \mu\text{m}$ and $2.6 \text{ g}/\text{cm}^3$, respectively. Surface treatment of mica was performed by the use of a neoalkoxy type zirconate coupling agent neopentyl (diallyl) oxy, tri (m-amino) phenyl zirconate (NZ-97) of the following chemical formula:²³



Surface treatment of mica

Mica was added with vigorous stirring to a moisture free solution of NZ-97 (0.4 wt % on the basis of filler) in toluene. The slurry was stirred for 3 h using magnetic stirrer. Toluene was expelled by heating the coated filler for 8 h at 393 K in an air oven followed by vacuum drying at 383 K for 3 h. The hydrophobicity acquired by the filler was confirmed by floating test on water. Although the untreated mica sank immediately in water in a beaker, the surface modified particles spread and floated on the water surface. This technique of filler surface treat-

ment was reported to give uniform coating of the coupling agent.^{15,24} The hydrophobic character of mica clearly demonstrates the presence of an adsorbed hydrophobic species on the mica. It has been proposed that the hydrolyzable neoalkoxy group (RO-) of the coupling agent reacts with available proton on the mica surface giving rise to an organofunctional layer.²⁵ This organofunctional layer on mica also leads to its deagglomeration because of the reaction of coupling agent with available water of hydration and filling of the air voids. The phenyl amine end then react with carboxylic and other polar moieties of the PBT/ABAS blends.

Compounding and molding

The PBT, ABAS, and mica powders were vacuum dried at 383 K for 3 h. For composite preparation, the blend composition selected contained 83.4 wt % PBT and 16.6 wt % ABAS because this blend registered high impact strength.¹⁹ Mica was incorporated in proportions ranging from 0 to 40 phr, (0 to 0.14 Φ_f). The Φ_f values were calculated as follows:

$$\Phi_f = (W_{\text{mica}}/\rho_{\text{mica}}) / [(W_{\text{PBT}}/\rho_{\text{PBT}}) + (W_{\text{ABAS}}/\rho_{\text{ABAS}}) + (W_{\text{mica}}/\rho_{\text{mica}})] \quad (1)$$

where W and ρ denotes the weight (g) and density (g cm^{-3}), respectively, of the components. The ingredients were first tumble mixed and then melt compounded in a corotating twin screw extruder, model JSW J 75E IV-P (L/D = 36, diameter = 30 mm), operated at 246 rpm. The temperature profile was 468 K to 518 K from the feed zone to the die zone. Extruded strands were pelletized and vacuum dried at 383 K for 4 h. These granules were injection molded into dumb-bell shaped tensile specimens and rectangular Izod bars on an L & T- Demag injection molding machine, model PFY 40-LNC 4P. The barrel temperature from feed zone to the nozzle was 353 K to 527 K.

Measurements

Tensile properties were measured according to the ASTM D638 test procedure²⁶ using dumb-bell shaped specimens at a cross-head speed of 20 mm/min and cross-head separation 65 mm on a Zwick universal tester, model 2010. For the Izod impact strength evaluation, notches of 2.5 mm depth, angle 45° and 0.25 mm radius were introduced. The Izod impact strengths of these specimens were determined by impact fracturing on a falling hammer type Ceast Impactometer following the ASTM D256 test method.²⁶ Seven to 10 samples were tested at each composite composition and the average values within $\pm 3\%$ variations are reported. All the tests were performed at ambient temperature $303 \pm 2 \text{ K}$.

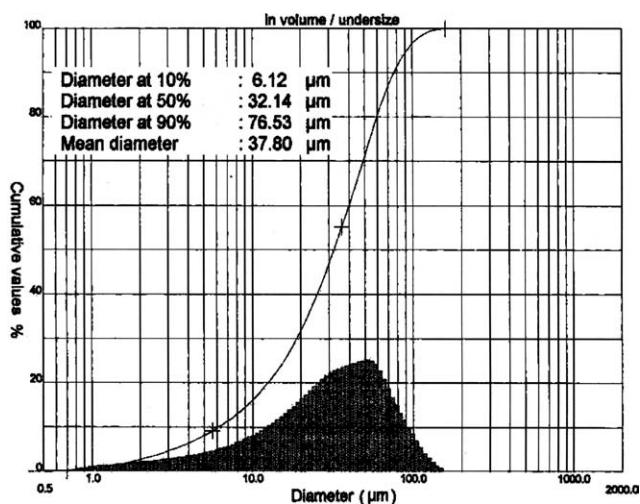


Figure 1 Particle size distribution plot of the mica particles.

Crystallinity (%) of PBT in the matrix blend and the composites were determined by differential scanning calorimetry (DSC) studies using powder samples obtained by filing the injection molded matrix and the composites following standard procedure.²⁷ The samples were heated at a rate of 10 K/min from 303 K to 513 K to obtain the crystal melting thermograms, Figure 1. The enthalpy values (ΔH) from both the peaks were taken into consideration for the estimation of crystallinity (%) data. The ΔH values were corrected by dividing the weight fraction of PBT, w_{PBT} , which were then divided by the enthalpy of 100% crystalline PBT according to eqs. (2) and (3):

$$X_b = [(\Delta H_b/w_{\text{PBT}})/\Delta H_{100}] \times 100 \quad (2)$$

$$X_c = [(\Delta H_c/w_{\text{PBT}})/\Delta H_{100}] \times 100 \quad (3)$$

Here X denotes crystallinity (%) of PBT and the subscripts b and c stand for the blend matrix and the composites, respectively. The weight fraction of PBT in the matrix blend was (83.4/100) while the parameter in the composites, $w_{\text{PBT}(c)}$ was calculated from eq. (4):

$$w_{\text{PBT}(c)} = 83.4/(100 + y) \quad (4)$$

where y is the phr of mica in the composites.

Scanning electron microscopic studies

Cryogenically fractured surfaces of the dumb-bell specimens were scanned on a Stereoscan 360 to examine the dispersion of mica in the PBT/ABAS matrix. The samples were sputter coated with silver before scanning.

Average particle diameter

Particle size distribution of the mica fillers was measured by laser diffraction technique on CILAS

940 instrument in dilute aqueous suspension. The particles varied between 6.1 μm and 76.5 μm , Figure 1. The average particle diameter was 37.8 μm .

RESULTS AND DISCUSSIONS

Crystallinity of PBT

The major phase PBT in these composites is a crystalline polymer. Thus, any variation in this parameter would play a significant role in the composite properties. Figure 2(A,B) presents the DSC thermograms of the PBT/ABAS/Mica and PBT/ABAS/Mica/NZ-97 composites whereas the crystallinity (%) of PBT in the composites estimated from the thermograms are shown in Table I. The parameter decreased with increase in the mica concentration which may be attributed to the mechanical restraints imposed by mica particles which restricts the chain mobility of PBT. An extent of chemical reaction the hydroxyl groups on mica and carboxylic groups of PBT may also contribute to this decrease in PBT chain mobility hindering its crystallinity (discussed later). Surface treatment of mica also brings about decrease in PBT crystallinity which decreases with increase in Φ_f . The data were comparable with those in the PBT/ABAS/Mica system. Since upon incorporation of mica, the crystallinity of the major phase PBT decreases the composite properties were normalized by dividing with the crystallinity data in the subsequent analysis of the results.

Tensile properties

The tensile properties e.g., the tensile modulus (E_c), breaking strength (σ_c), elongation-at-break ($\epsilon_c(\%)$) of PBT/ABAS/Mica composites were determined from the stress-strain plots (data not shown). These parameters are presented in (Figs. 2-5) as variations of the ratio of the normalized property of the composites (subscripts c) to that of the unfilled blend (subscript b) vs. volume fraction, Φ_f of the dispersed phase, mica.

Tensile modulus

The variations of the normalized tensile moduli, $(E_c/X_c)/(E_b/X_b)$, are presented in (Fig. 3) against Φ_f . The modulus of PBT/ABAS/Mica composites increased significantly with Φ_f the increase was about 1.2 to 2.6 times that of the blend depending on the Φ_f . Surface treatment of mica with the zirconate coupling agent exhibits almost similar variations of the data. The modulus data were compared with predictive models for two phase systems which consider the packing fraction and the shape of the dispersed phase as well as interphase interaction between the

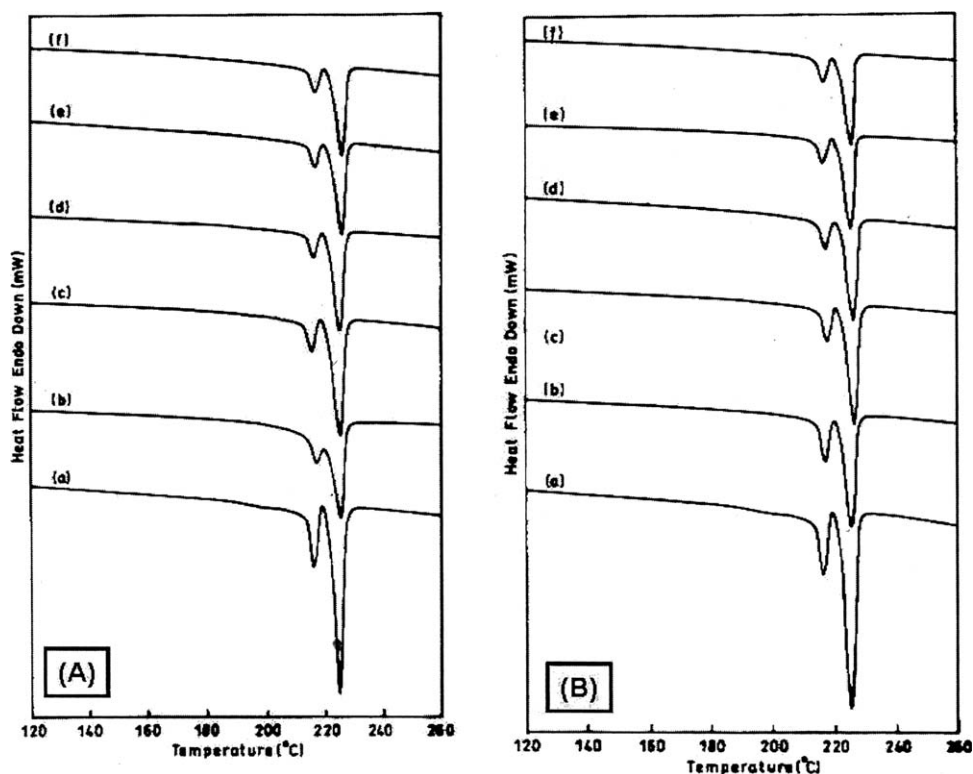


Figure 2 DSC thermograms of PBT/ABAS/Mica (A) and PBT/ABAS/Mica/NZ-97 (B) composites.

matrix and the inclusion, (Fig. 3). Curve A represents Guth-Smallwood model,²⁸⁻³⁰ eq. (5), whereas curve B describes Kerner expression,^{24,31} eq. (2), for filled polymer composites with Poisson ratio, ν_p , for PBT/ABAS blend taken as 0.37.³²

$$(E_c/X_c)/(E_b/X_b) = 1 + 2.5\Phi_f + 14.1\Phi_f^2 \quad (5)$$

$$(E_c/X_c)/(E_b/X_b) = 1 + [15(1 - \nu_p)/8 - 10 \nu_p] \times [\Phi_f/1 - \Phi_f] \quad (6)$$

The data did not exhibit good agreement with the models. The moduli of both types of the composites were much higher than the theories. Nevertheless, the increase in the modulus in the mica-filled composites indicates an increase in the rigidity through

the imposition of restrictions in the mobility/deformability of the blend system through introduction of mechanical restraint which is dependent on the particulate spacing and the properties of the particles and the matrix.²⁸ The mechanical restraint may be a result of the enhanced surface interaction between the polymer and the filler phases in view of quite large surface area of the dispersed phase mica with an average particle diameter of 37.8 μm along with mechanical interlocking between the phases due to differential shrinkage.²⁴ Other works also

TABLE I
Values of DSC Crystallinity (%) in the PBT/ABAS/Mica and PBT/ABAS/Mica/NZ-97 Composites

Composite composition Φ_f	Crystallinity (%)	
	PBT/ABAS/Mica	PBT/ABAS/Mica/NZ-97
0	27.2	27.2
0.02	22.2	25.2
0.04	21.4	22.3
0.07	17.9	20.6
0.11	18.0	16.3
0.14	15.9	16.5

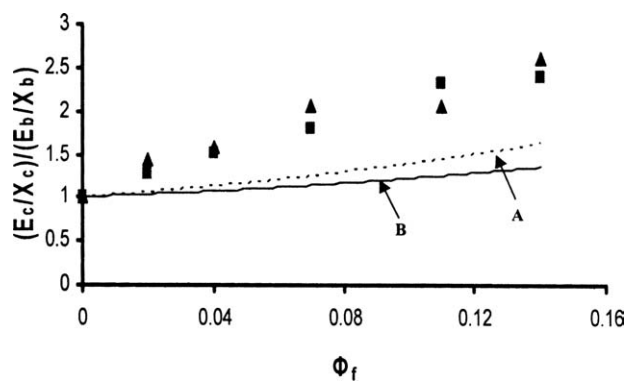


Figure 3 Plot of normalized relative tensile modulus, $(E_c/X_c)/(E_b/X_b)$, of PBT/ABAS/Mica (\blacktriangle) and PBT/ABAS/Mica/NZ-97 (\blacksquare) composites and “Guth-Smallwood model” (---), [eq. (5)], and “Kerner expression,” (—) [Eq. 6], against Φ_f .

reported modulus increase in polymers in presence of rigid particulate fillers even in the absence of strong interaction with the matrix.^{9,33,34} Hindrance in diffusion of the polymer in the presence of solid particles was shown by Baumgarter and Muthukumar.³⁵ However, in the PBT/ABAS/Mica system some chemical interaction between surface hydroxyl groups of mica and the carboxylic acid and ester groups of PBT/ABAS blends may also takes place which would contribute in matrix immobilization in the interlayer.⁹ Similar behavior was observed in other systems too where the polymer matrix was modified with acrylic acid or acrylic esters.^{17,36} Because the decrease in crystallinity of the PBT component in the PBT/ABAS blend due to the impediment of the matrix mobility with increase in Φ_f Table I, has been accounted for by normalizing the relative modulus data, this increase in the interphase interaction appears to be quite high which enhances the modulus of the matrix.

It has been reported that in ternary composite systems two dominating structures can form: (1) separate dispersion of the elastomer and the filler in the plastic matrix or (2) encapsulation of the filler by the elastomer.^{12,37,38} Mutual wettability and the adhesion of the components have been shown to be the most important factors which determine the structure and the properties of these composites.¹¹ In the PBT/ABAS/Mica system, the presence of the carboxylic acid groups in PBT and the acrylate groups in the ABAS should increase the polarity of the matrix (PBT/ABAS blend) leading to possible adhesion with inorganic filler, mica. Thus, mutual wettability presumably results in the structure in which separate dispersion of filler is possible in the plastic PBT and elastomeric ABAS polymer.

In comparison with the two component polymer system, the modulus describes well the structure in a three component polymer system.³⁹ If the dispersed phase is separately dispersed in the blend components the composition dependence of the modulus can be predicted by theories. In case of filler encapsulation in the elastomer component, the modulus will be lower than the predictions because the reinforcing effect of the filler is decreased by the surrounding elastomer layer. From the variation of the modulus data in (Fig. 3), it appears that the filler interacts with both the components in the blend and is not wholly encapsulated in the elastomer phase.

Surface treatment of mica does not make any noticeable difference on this low solid displacement property. Some of the hydroxyl groups of mica would now bond with the coupling agent and the latter would also function partly as plasticizer/lubricating agent tending to decrease the modulus. The crystallinity of PBT also decreased with increasing Φ_f to a comparable extent to that of the untreated

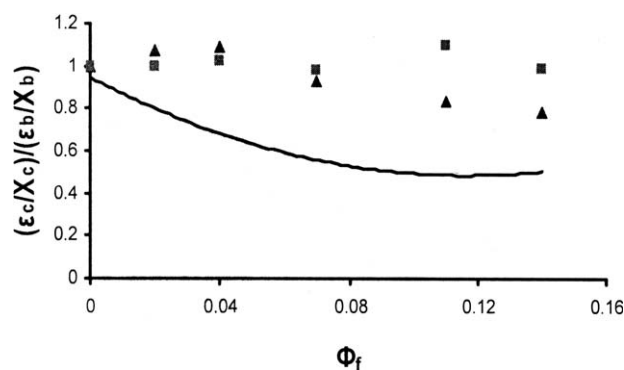


Figure 4 Variations of relative normalized elongation-at-break, $(\epsilon_c/X_c)/(\epsilon_b/X_b)$, of PBT/ABAS/Mica (▲) and PBT/ABAS/Mica/NZ-97 (■) composites and Nielsen's model (—) [Eq. 7], as a function of Φ_f .

mica-filled systems, Table I, which would tend to decrease the modulus of the matrix. Despite these opposing factors, the modulus enhanced with Φ_f which may be due to predominant matrix immobilization arising out of mica particles adhering with both the PBT and ABAS polymers similar to the untreated mica-filled systems.

Breaking strain

The normalized strain-at-break, $(\epsilon_c/X_c)/(\epsilon_b/X_b)$, of PBT/ABAS/Mica composites at first shows a marginal increase up to $\sim \Phi_f = 0.04$, the value then showed a continuous decrease with further increase in Φ_f (Fig. 4). The data remained almost unaltered at all the Φ_f values. Nielsen's model for strain with perfect adhesion between the matrix and the inclusion,^{24,26} eq. (7), exhibits lower values than those of the composite:

$$(\epsilon_c/X_c)/(\epsilon_b/X_c) = 1 - \Phi_f^{1/3} \quad (7)$$

The values of relative breaking strain higher than eq. (7) indicates that the filler does not exhibit perfect adhesion with the matrix because the relative decrease in the parameter is lesser. The marginal increase in elongation-at-break of the PBT/ABAS/Mica composites up to $\Phi_f = 0.04$ may be attributed to the inappreciable predominance of the matrix softening due to decrease in crystallinity of PBT, Table I, over the interference of the deformation by the discrete phase through imposition of mechanical restraint through an extent of chemical interaction as well as physical interaction described previously. On the other hand, the decrease in elongation beyond $\Phi_f > 0.04$ may be due to the predominant effect of matrix immobilization by enhanced concentration of mica over the matrix softening.

In the surface modified mica containing systems, the strain values become almost equal to unity at all

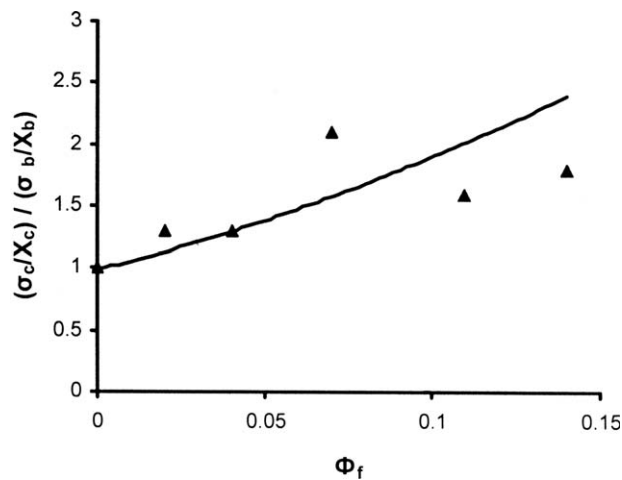


Figure 5 Dependence of normalized relative tensile strength, $(\sigma_c/X_c)/(\sigma_b/X_b)$, of PBT/ABAS/Mica composites (▲) and Pukanszky model (–) [eq. (8)], with $B_\sigma = 10.4$, vs Φ_f .

Φ_f values, the curve runs higher than Nielsen’s model, Figure 4. Although mica adheres with both the PBT and ABAS polymer in the matrix, it causes matrix softening through an extent of decreased crystallinity of the PBT, the softening taking effect at large deformations. In addition, the coupling agent NZ-97 appears to function, at least in part, as a lubricant/plasticizer, which enables a leveling off of the relative strain data striking an even balance between the mechanical restraint and the matrix softening.

Tensile strength

It has been shown that the properties measured at large deformations present structural changes and phase interactions of the components in polymer blends and composites.³⁷ Tensile stress is determined by the decrease of effective load bearing cross-section and the load carried by the inclusion in a composite, which, in effect, is a measure of phase interaction.⁴⁰⁻⁴² Thus, normalized relative tensile breaking strength was used to analyze interphase interaction in these systems:

$$(\sigma_c/X_c)/(\sigma_b/X_b) = [1 - \Phi_f/1 + 2.5 \Phi_f] \exp(B_\sigma \Phi_f) \quad (8)$$

where σ_c and the σ_b are the tensile breaking stress of the composite and the matrix polymer blends, respectively, and B_σ stands for the proportion of the load carried by the dispersed phase. The term B_σ is described⁴² as:

$$B_\sigma = \ln(C_\sigma E_f/E_b) \quad (9)$$

where E_f is the modulus of the dispersed phase mica and C_σ is the proportionality constant related to stress transfer. Because the stress transfer is a func-

tion of the size and the thickness of the interphase, C_σ is a measure of the interphase interaction which can be described as a reinforcing parameter.^{40,18} Rearranging eq. (9):

$$C_\sigma = (E_b/E_f) \exp B_\sigma \quad (10)$$

from which the reinforcement factor C_σ can be calculated from the B_σ values which in turn can be estimated from comparing the experimental normalized σ_c/σ_b data following eq. (8).

The normalized relative tensile strength values, $(\sigma_c/X_c)/(\sigma_b/X_b)$, of the PBT/ABAS/Mica composites are plotted in (Fig. 5) as functions of Φ_f . The tensile strength increases up to $\Phi_f = 0.07$ and flattens beyond this filler concentration. Thus, up to $\Phi_f=0.07$ the mica particles reinforce the blend matrix. The normalized relative tensile strength data were compared with eq. (8) to estimate the values of B_σ . The E_f for mica¹⁸ used for these calculations was 30 GPa, whereas E_b was 614.5 MPa.¹⁹ Using eq. (10), the reinforcement factor C_σ was calculated, Table II. It may be noted that in the untreated mica-filled composites the C_σ values up to $\Phi_f = 0.07$ show a wide dispersion. This indicates that the interaction between mica and PBT/ABAS matrix depends greatly with composite composition. This may arise due to enhanced availability of hydroxyl groups attached with mica particles. The composition dependence of the value of C_σ has been shown in other works also.^{18,43} The data up to $\Phi_f = 0.07$ agreed well with eq. (8) with $B_\sigma = 9.7$, whereas the values beyond this Φ_f deviated, Figure 5. The interaction between mica and the PBT/ABAS matrix is quite strong as indicated by the C_σ values up to $\Phi_f = 0.07$, Table II. As indicated earlier this interaction is a result of chemical type of reactions between the hydroxyl groups of mica and carboxylic and ester groups of PBT/ABAS blends which make the interphase strong even at large deformations. The strong interphase absorbs a portion of the energy enhancing the energy of fracture.¹⁸ However, the chemical interaction

TABLE II
Values of Interaction Parameter, B_σ , eq. (6), and Stress Transfer Constant, C_σ , eq. (7), in PBT/ABAS/Mica and PBT/ABAS/Mica/NZ-97 Composites

Φ_f	B_σ		C_σ	
	PBT/ABAS/ Mica	PBT/ABAS/ Mica/NZ-97	PBT/ABAS/ Mica	PBT/ABAS/ Mica/NZ-97
0	—	—	—	—
0.02	16.8	12.7	2.1×10^4	3.14×10^2
0.04	9.97	9.9	25.5	24.4
0.07	13.7	8.8	1380	8.9
0.11	7.6	8.7	3.2	10.3
0.14	7.4	7.1	2.9	6.3

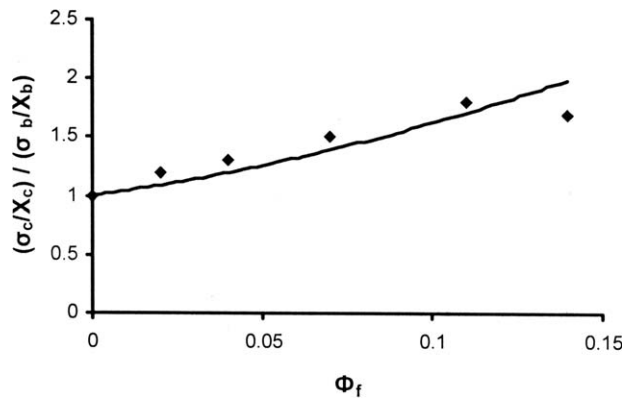


Figure 6 Variations of normalized relative tensile stress, $(\sigma_c/X_c)/(\sigma_b/X_b)$, (◆), and Pukanszky model, [eq. (8)], $B_\sigma = 8.8$ for PBT/ABAS/Mica/NZ-97 (–) composites against Φ_f

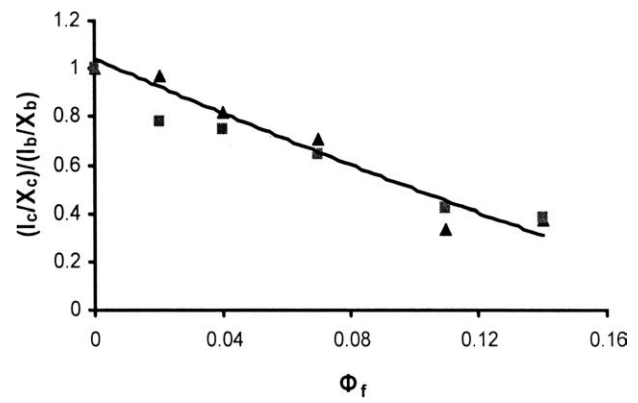


Figure 7 Plot of normalized relative impact strength, $(I_c/X_c)/(I_b/X_b)$, of PBT/ABAS/Mica (▲) and PBT/ABAS/Mica/NZ-97 (■) composites vs. Φ_f .

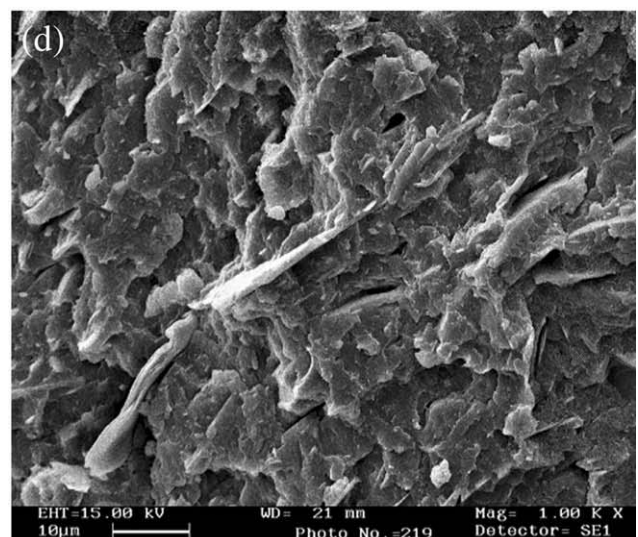
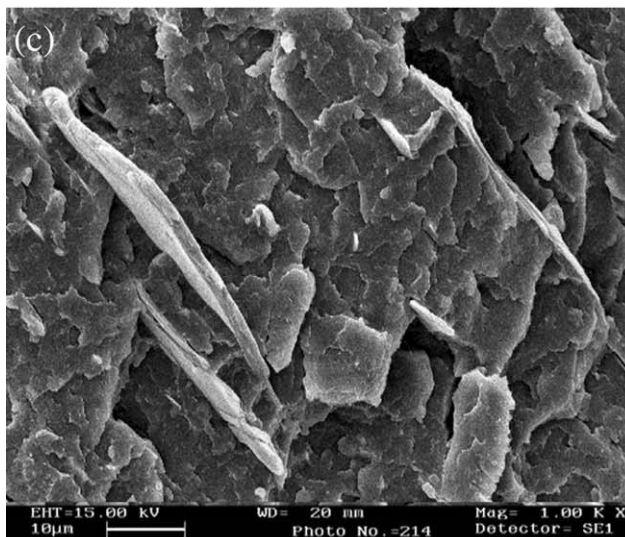
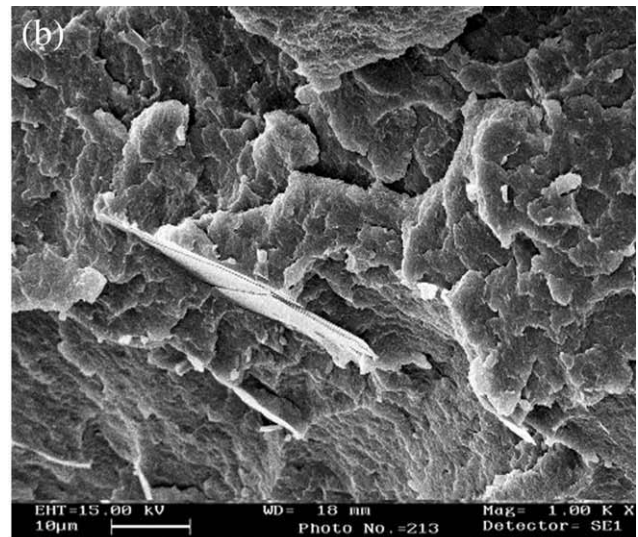
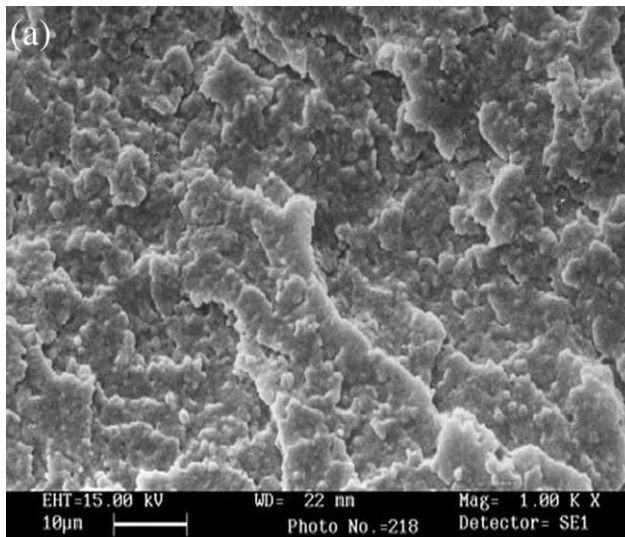


Figure 8 SEM photomicrographs of PBT/ABAS blend (a) and PBT/ABAS/Mica composite at varying Φ_f : (b) 0.02; (c) 0.07; (d) 0.14.

possibly reaches its maximum at $\Phi_f = 0.07$ where the equivalence of the reactive groups on mica and those available on the PBT/ABAS polymer blend is attained. Beyond $\Phi_f = 0.07$, although the filler particles will have additional hydroxyl groups the fixed content of the matrix will not provide extra reactive groups for the interaction. Thus, voids may form around the excess filler particles in the stretch direction which eventually grow to initiate the crack and fail the structure.¹⁸

Upon surface treatment of mica by NZ-97 the normalized relative strength data showed quite similar variation with Φ_f (Fig. 6) as in the PBT/ABAS/Mica system. The strength data agreed well with eq. (8) with an average value of $B_\sigma = 8.6$ up to an enhanced Φ_f value of 0.11 with higher C_σ values, Table II. This may be due to partial blockage of some of the hydroxyl groups on mica by the coupling agent so that an extent of enhanced mica concentration is needed for interaction with the fixed concentration of PBT/ABAS polymer. Thus, the interphase interaction reaches a maximum at higher filler concentration of $\Phi_f = 0.11$. A degree of better filler distribution between the phases may be facilitated due to expulsion of occluded air from the filler clusters. The reinforcement factor, however, decreased beyond $\Phi_f = 0.11$ due to attainment of saturation in the interphase interactions similar to the PBT/ABAS/Mica composites. An extent of the coupling agent's lubricating/plasticizing function will also contribute partly to this decreased reinforcement factor.

Impact strength

Variation of the normalized relative notched Izod impact strength, $(I_c/X_c)/(I_b/X_c)$, vs. Φ_f is shown in (Fig. 7). The strength decreases drastically with increase in the filler content, the value decreases to ~ 0.45 at $\Phi_f = 0.11$. This may be attributed to the resultant effect of immobilization of the matrix by the filler and sequential matrix softening by decrease in crystallinity. However, at this high rate of loading the interphase eventually fractures before sufficient plastic deformation. The immobilization is due to matrix-filler interaction which increased the tensile strength and modulus and decreased the strain-at-break. Thus, the decrease in crystallinity in this system, Table I, which provides a degree of enhanced free volume, is overridden by the matrix immobilization in presence of the filler. In the PBT/ABAS/Mica/NZ-97 composites also the impact strength showed similar decrease in impact strength with increase in Φ_f (Fig. 7). Surface treatment of the filler with zirconate coupling agent does not appear to alter this balance of matrix immobilization and matrix softening in the impact property. The effect of lubricating/plasticizing function of the coupling agent

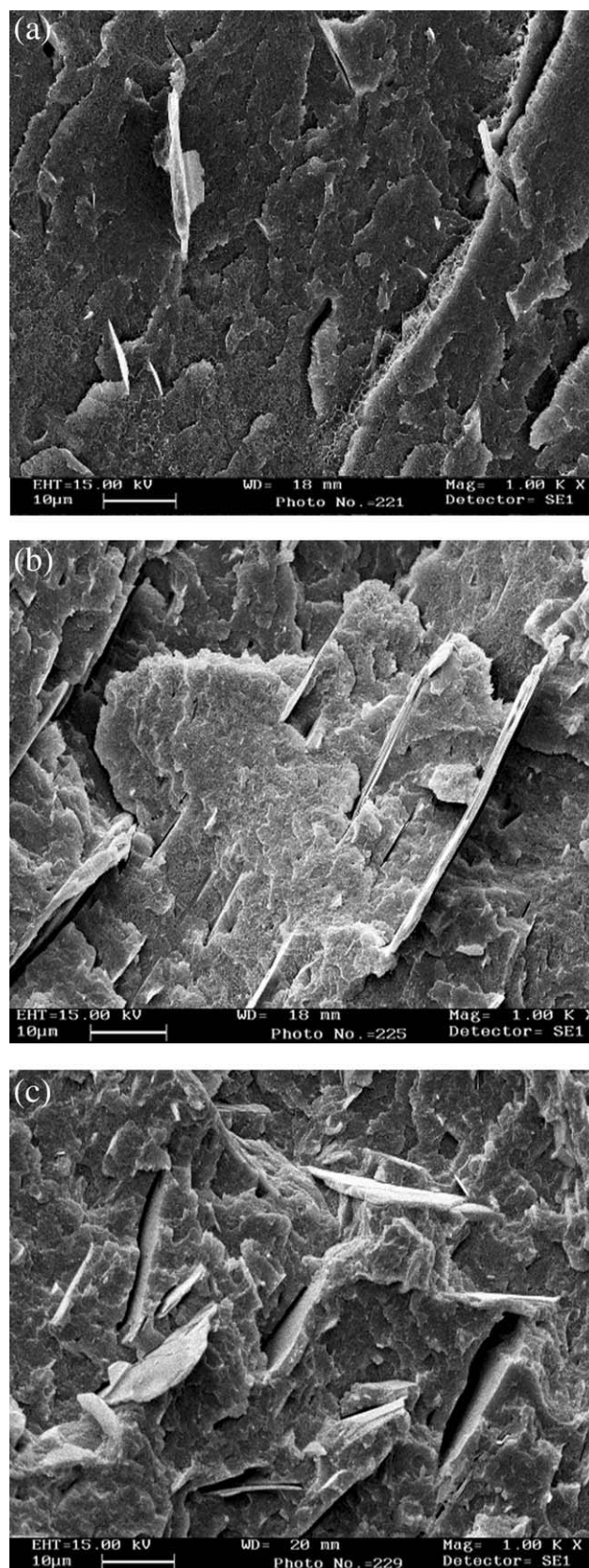


Figure 9 SEM photomicrographs of PBT/ABAS/Mica/NZ-97 composite at varying Φ_f : (a) 0.02; (b) 0.07; (c) 0.14.

may be considered overridden by the matrix immobilization.

State of dispersion

The scanning electron microscopic studies of the PBT/ABAS/Mica composites are shown in Figure 8(a–e). The matrix polymer blend is clearly a two phase system where the ABAS phase is seen in the form of well-adhered globules with the major phase PBT, Figure 8(a). There are some whitening on the fracture surfaces which may be due to shear yielding at the PBT/ABAS interphase.¹⁹ In the presence of mica flakes, the appearance of phase morphology changes toward that of a brittle material with conchoidal fracture surfaces [Fig. 8(b–d)]. The long dimensions of the mica flakes are discernible. Because the size of most mica particles is clearly higher than the particle size of the ABAS¹⁹ the mica particles appear dispersed in the PBT/ABAS matrix with some extent of polymer residues adherent on the particles [Fig. 8(b,c)]. At the highest Φ_f value, a few mica flakes appear dislodged from the matrix [Fig. 8(d)]. The conchoidal fracture surface and lack of shear yielding indicate that mica introduces restrictions in the matrix deformation which was noted in the tensile properties of the composites. However, the filler decreases drastically the notched impact strength.

Upon surface treatment of mica with the zirconate coupling agent the state of dispersion appears marginally better and the fracture surface looks smoother to an extent, Figure. 9(a–c). This may be attributed to the expulsion of occluded air from the filler surface in presence of the coupling agent.²⁵ However, the fracture surfaces retain their conchoidal structure and absence of shear yielding [Fig. 9(a,b)]. At the highest Φ_f , the composites show a large number of mica flakes dislodged, from the PBT/ABAS matrix, Figure 9(c). The lubricating/plasticizing effect of the coupling agent may be responsible for the expulsion of mica flakes from the matrix. The brittle fracture promoting surface morphology leads to enhanced stiffness and accounts for significant decrease in impact strength of the composites similar to the untreated mica-filled systems.

CONCLUSIONS

Mica particles modify the properties of PBT/ABAS matrix to a significant extent acting as reinforcing filler. The normalized relative modulus showed an increase in of 1.2 to 2.6 times compared with neat matrix, indicating significant interaction between the matrix and the filler. The matrix polarity plays a sig-

nificant role in the dispersion of mica in the plastic and elastomer component of the blend. Surface treatment of mica brings about inappreciable variation in the low deformation properties. The normalized tensile strength showed an increasing trend up to $\Phi_f = 0.07$. Beyond this Φ_f value saturation of chemical interaction levels off the reinforcement activity of the filler. Surface-treated mica-filled composites showed a similar trend, however, the reinforcement by mica continued up to $\Phi_f = 0.11$. The normalized elongation-at-break marginally enhances up to $\Phi_f = 0.04$, the values then showed a decreasing trend which may be attributed to the predominant effect of matrix softening and matrix immobilization, respectively. The coupling agent NZ-97 appears to function as lubricating/plasticizing agent. Decreased impact strength at all the compositions of both types of composites may be due to matrix immobilization in presence of the filler. Dispersion and adhesion of mica flakes were good in the untreated mica-filled composites while upon surface treatment of mica the dispersion improved to an extent. However, due to the coupling agent's lubricating/plasticizing function some mica flakes are dislodged from the matrix at higher filler contents.

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