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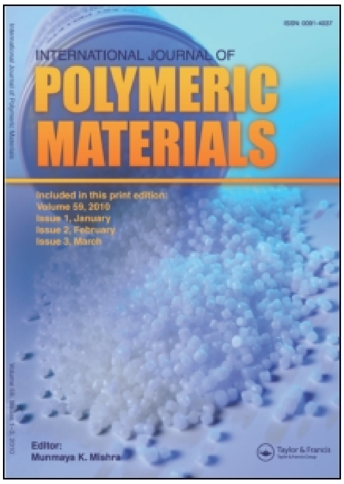

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Mechanical Properties of ABS/CSM Rubber Blends

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Impact behavior and tensile properties of acrylonitrile butadiene styrene (ABS) terpolyer/Chlorsulfonated Polyethylene (CSM) blends are studied at CSM concentrations of 0 to 30.6 vol%. The data are presented as functions of CSM content. Predictive models have been employed to analyze the tensile properties. Impact behavior has been analyzed on the basis of interphase adhesion. Scanning electron microscopy (SEM) has been used to study the adhesion between the matrix and the elastomeric phase.

Keywords: ABS/CSM blends, matrix softening, interphase adhesion, stress-concentration, crazing and shear-yielding

INTRODUCTION

The terpolymer acrylonitrile-butadiene-styrene (ABS) is a versatile thermoplastic possessing a number of useful properties such as excellent toughness, good stiffness, excellent surface quality, high dimensional stability at elevated temperatures, good chemical and stress cracking resistance, and good electrical properties [1–5]. If the impact strength of ABS is further enhanced by blending with a suitable elastomer the resulting blend can be subsequently modified by incorporation of various reinforcing agents to tailor the property profiles and to reduce cost [6]. Chlorinated polyethylene has been used to enhance

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the pliability and impact properties of ABS, which was further modified with $CaCO_3$ [6].

In the present study ABS was impact modified by the incorporation of varying concentrations of chlorosulphonated polyethylene (CSM) rubber. The tensile and impact performance of the blends are reported as functions of CSM contents. Blend morphology was examined by scanning electron microscopy (SEM) studies.

EXPERIMENTAL

Materials

A high flow, high gloss, injection moldable grade of acrylonitrile butadiene styrene (ABS) terpolymer (IM-17A, sp.gr.1.04) was obtained from M/S Bhansali Engineering Polymers Limited, Vadodara [7]. Chlorosulfonated polyethylene (CSM) grade Hypalon 40 (Sp.gr.1.18, chlorine content 35(%)) manufactured by M/s DuPont was used [8]. The viscosity average molecular weight ($\bar{M}v$) of Hypalon 40 measured in toluene solution at 313 K was 78,000 [9, 10]. Tribasic lead sulfate (sp.gr.7.1) and lead stearate (sp.gr.7.23) were procured from M/s Fine Chemicals India Ltd. and M/s Pioneer Chemical Co. Ltd., respectively.

Preparation of Blends

Binary blends of ABS and Hypalon (along with 0.4 phr of both lead sulfate and lead stearate stabilizer) at Hypalon content of zero to 50 phr (0–30.6 vol%) were prepared by melt mixing the components in a Klockner Windsor single screw extruder (Model S × 30, L/D ratio 20:1) at 443–463 K. Initially the Hypalon rubber was cut into small pieces to facilitate homogenization. Thick strands from the extruder were quenched in a water bath and then granulated. The granules were vacuum dried at 343 K for 2 h. The ABS material was also extruded under identical conditions so as to give it the same thermal history as the blends.

Molding of Test Specimens

Samples for the evaluation of mechanical properties were prepared by injection molding in a Windsor SP-1 screw-type machine using temperatures 443, 453, and 463 K at the three zones, respectively. Injection pressure and mold locking pressure were 58.8 Mpa and 1.9 Gpa whereas the mold temperature was 343 ± 2 K.

Measurement of Mechanical Properties

Tensile properties were measured with a Zwick Universal tester (Model–Z010) using injection molded dumb-bell shaped specimens following ASTM D638 test procedure [11]. The gauge length used was 5 cm and the crosshead speed was 5 cm/min. Izod impact strength of notched specimens were evaluated using a falling hammer-type impact tester (FIE instrument, Model IT-0.42) in accordance with ASTM D256 test method [11]. At least five samples were tested for each blend composition and the average value is reported. All the tests were performed at ambient temperature of $303 \pm 2\,\mathrm{K}$.

Scanning Electron Microscopic (SEM) Studies

Cryogenic fractured surfaces of the specimens were scanned on a Cambridge strecoscan (Model S4-10) to examine the phase morphology of the blends. The fracture surfaces were sputter coated with silver prior to scanning.

RESULTS AND DISCUSSION

Tensile Properties

Tensile parameters were determined from the stress-strain curves (not shown) and are presented in Figures 1–4 as the variations of the ratio of the property of the blends (subscript b) to that of the unblended ABS polymer (subscript m) as functions of volume fraction of the discrete phase (ϕ_d), that is, the blending polymer Hypalon.

Tensile Modulus

Figure 1 exhibits the variations of relative tensile moduli (E_b/E_m) of the blends as a function of elastomer (i.e., Hypalon) volume fraction, ϕ_d. The modulus drops drastically up to $\phi_d = 0.04$ while with further increase in ϕ_d the data level off. The data were compared with the theoretical values calculated on the basis of "rule of mixtures" in composites [12], Figure 1, Eq. 1:

$$E_b/E_m = (E_d/E_m - 1)\phi_d + 1 \tag{1}$$

In these calculations the moduli of ABS (E_m) and the blends (E_b) were determined from the initial straight line portions of the stress-strain curves whereas the modulus value of Hypalon rubber (E_d) was taken at 300% strain [8]. The modulus data of the blends showed negative deviation form the curve calculated from Eq. 1 indicating a significant

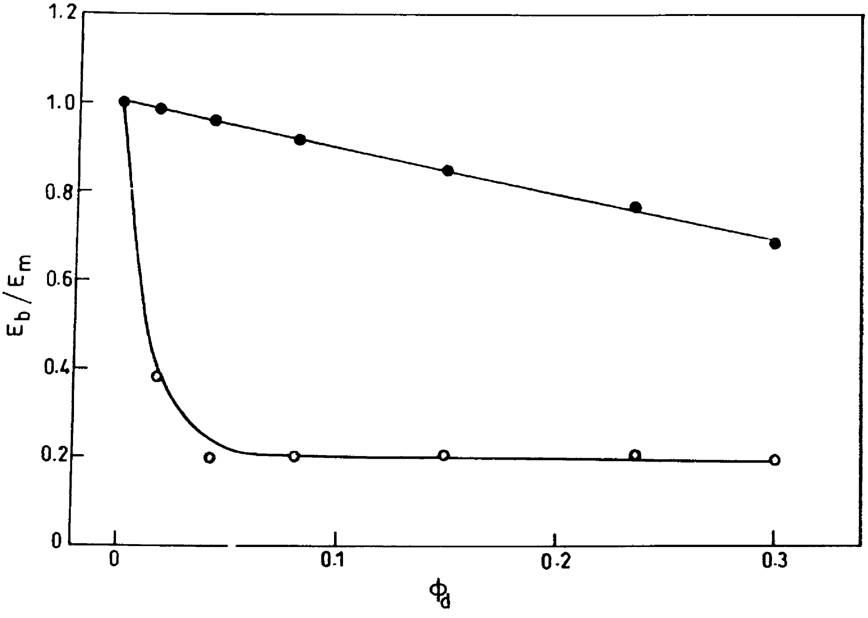

FIGURE 1 Variation of relative tensile modulus (E_b/E_m) of (O) ABS/Hypalon blends and (●) calculated data according to "rule of mixtures" (Eq. 1) vs. ϕ_d.

modification of the ABS on incorporation of Hypalon rubber. The decrease in the modulus of ABS in the presence of the elastomer is, however, quite expected. Hypalon is a low modulus elastomer, the modulus being or 1/100 of that of ABS Polymer so that the plastic matrix becomes highly softened, which facilitates molecular deformability of the latter. This would of course be of some advantage in that the filler adoptability of ABS matrix will be enhanced [6]. Decrease in modulus of polymer materials upon addition of elastomers has been observed earlier [13–15].

Tensile Strength

Relative tensile strength (σ_b/σ_m) of ABS/Hypalon blends are shown in Figures 2 and 3 as functions of ϕ_d. Tensile strength of ABS polymer decreased upon addition of Hypalon; the data continued to decrease with increase in ϕ_d. This implied that the elastomer weakens the polymer structure due to the reduction of the effective matrix cross-section caused by the elastomer phase, similar to other studies [13–17]. Tensile strength data were analyzed using predictive models, Eqs. 2 and 3, in order to estimate weakness/discontinuity in the blend structure

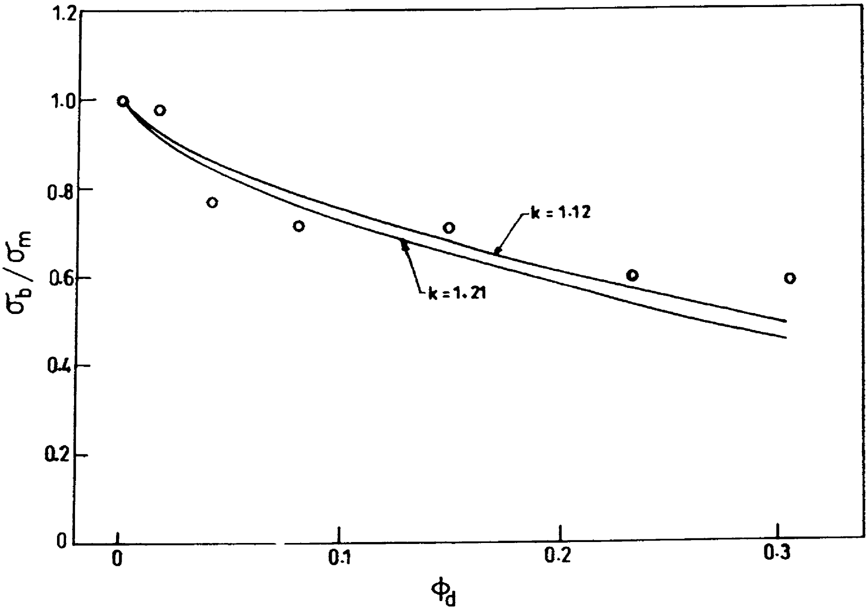

FIGURE 2 Relative tensile stress σ_b/σ_m of (O) ABS/Hypalon blends and (–) predicted behavior according to Eq. 2 with K = 1.12 against ϕ_d.

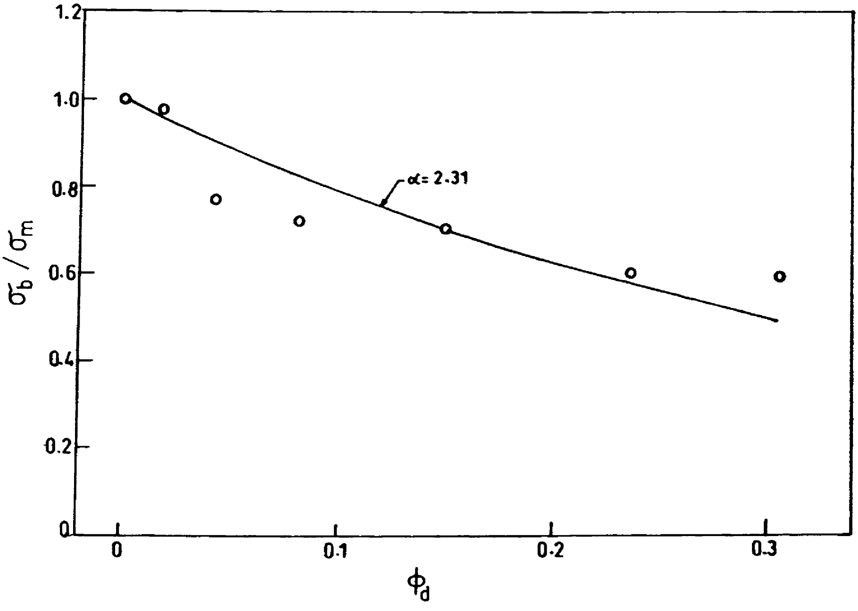

FIGURE 3 Plot of σ_b/σ_m of (O) ABS/Hypalon blends and (–) predicted behavior according to Eq. 3 with $\alpha = 2.31$ vs. ϕ_d.

generated by the matrix softening on blending Hypalon elastomer. Similar models represented by Eqs. 2 and 3, have been employed in other blend/composite systems also to determine weakness in the structure [16–19]. In these equations

$$\sigma_{\mathrm{b}}/\sigma_{\mathrm{m}} = (1 - \mathrm{K}\phi_{\mathrm{d}}^{2/3}) \tag{2}$$

$$\sigma_{\mathrm{b}}/\sigma_{\mathrm{m}} = \exp(-\alpha\phi_{\mathrm{d}}) \tag{3}$$

No-adhesion type of blend structure is assumed, which depends on either area fraction or volume fraction of the discontinuous phase [16, 19–21]. In the two-thirds power law model, Eq. 2, where the dispersed phase area-fraction is considered operative, the interphase interaction constant K, which is also known as weightage factor, depends on the blend structure [22–23]. For hexagonal packing of the discrete phase in the plane of highest density $\mathrm{K} = 1.1$. In the extreme case of poor adhesion when the dispersed phase is spherical, minimum cross-section is generated between spherical practices and the value of K is equal to 1.21 [21–24]. $\mathrm{K} = 1$ stands for strain consideration [25]. The value of $\mathrm{K} = 0$ describes the upper pound for interphase adhesion and stands for the unblended polymer. Values of K less than 1.21 imply occurrence of adhesion between the phases, the lesser the value the better the adhesion [26, 27]. In the porosity model, Eq. 3, the dispersed phase resembles pores/voids in metals and ceramics [28] as well as two-phase polymer systems [29]. The pores/voids are assumed not to exert any influential role on the mechanical properties of the two-phase systems on account of non-adhesion at the phase boundaries. The parameter α is a measure of weakness in the structure in the form of stress concentration [21], the higher the value of α the higher the degree of stress concentration.

By comparing the experimental tensile stress data with the theoretical models (Eqs. 2 and 3) values of the parameters K and α at each individual blend composition were evaluated (Table 1). According to the Nicholais–Narkis model, Eq. 2, the stress concentration parameters were either less than or greater than unity depending on ϕ_{d}. This indicates quite a significant weakness in the blend structure, similar to other systems [16–17, 30]. According to the porosity model a significant weakness in the blend structure is indicated, the values of α being significantly higher than unity.

The tensile strength data were compared with the predictive models, Eqs. 2 and 3, in Figures 2 and 3, respectively. The data do not exhibit good fit with the Nicholais–Narkis model, Eq. 2; however, the data lie scattered around a curve with average $\mathrm{K} = 1.12$, Figure 2.

TABLE 1 Values of adhesion parameter K (Eq. 2), and Stress Concentration Parameter α (Eq. 3) in ABS/HYPALON Blends

ϕ_d (%)	K	α
0	—	—
1.73	0.334	1.300
4.22	1.800	6.040
8.09	1.513	4.111
14.98	1.027	2.282
23.57	1.049	2.170
30.58	0.902	1.698
Mean value	1.123	2.312

Due to data variations, the mean value was determined excluding the values at some data points, for example for K at ϕ_d (%) $= 1.73$ and 4.22; for α at ϕ_d (%) $= 4.22$.

The value of $K = 1.12$ is slightly less than 1.21, which is the value for no-adhesion with spherical inclusions [21]. This indicates an inappreciable degree of interphase adhesion in the blends, the adhesion arising out of the possible interaction of chlorosulfonated polyethylene with the acrylonitrile moiety of the ABS polymer. Nevertheless, the interphase of the blend becomes weak and cannot sustain the load, leading to failure failing at large deformations, similar to other polymer composites and blends [16, 17, 30, 31].

The σ_b/σ_m data show a reasonably good fit with the porosity model with an average α value of 2.31, Figure 3, Table 1. As mentioned earlier, a higher value of α denotes significant stress concentration in the blends, as reported in other works [16–19, 31].

Elongation-at-Break

The relative elongation at break, E_b/E_m, of the ABS/Hypalon blends are plotted as function of ϕ_d in Figure 4. The elongation of ABS polymer increased upon the addition of Hypalon and increased ϕ_d; the enhancement was by $\sim$250% compared to the value of ABS up to $\phi_d = 0.08$, whereas with further increase in ϕ_d the data level off. This indicates that ABS matrix is significantly softened by the elastomer, which facilitates molecular movement/deformability of the former. The matrix softening was also observed in the decrease in modulus data in the presence of Hypalon. Increase in breaking elongation and decrease in modulus indicate toughening of ABS so that higher energy will be needed to break the plastic material, similar to other systems [32, 33].

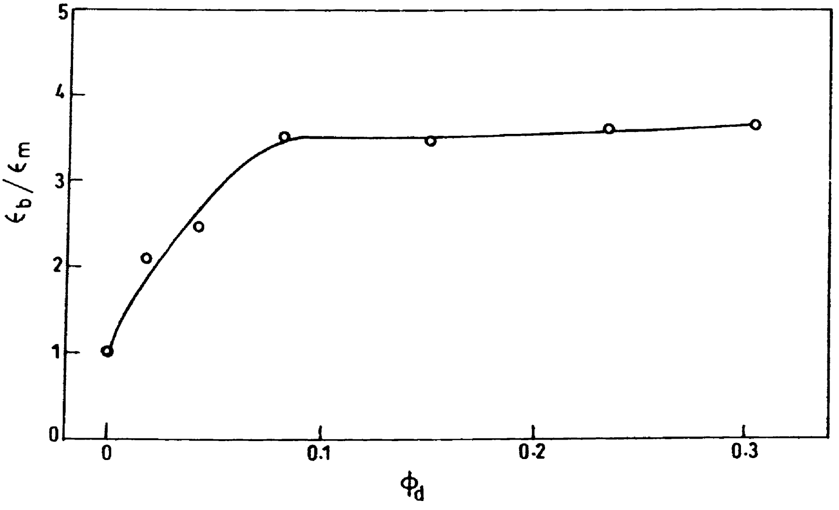

FIGURE 4 Variation of relative elongation-at-break element of $\in_b/\in_m$ of ABS/Hypalon blends as functions of ϕ_d.

Impact Behavior

Figure 5 exhibits the relative Izod impact strength (I_b/I_m) values of the blend system as functions of ϕ_d. Upon incorporation of Hypalon the value at first decreases by ~23% at $\phi_d = 0.017$ showing a minimum here. The impact value increased with further increase in ϕ_d, the value remaining below that of ABS up to $\phi_d = 0.08$, however; and at $\phi_d = 0.15$ the impact strength increases by ~38% over that of ABS, the data level off with further increase in ϕ_d.

The variation of impact strength data shows a qualitative resemblance with that of the elongation values, although the latter increased significantly up to $\phi_d = 0.08$ before leveling off. The decrease of impact strength of ABS at low ϕ_d values may be attributed to the formation of thicker ligaments than a critical thickness T_c in the matrix, which does not facilitate shear yielding leading to brittle failure [34, 35]. The formation of thicker ligaments seems quite possible in these systems at the low ϕ_d values where interphase adhesion is negligible. At around $\phi_d = 0.15$ and above, adhesion of ABS with the elastomer increases, which gives better dispersion of the discrete phase and smoother surface features (shown in the morphology section later). This would generate ligament thickness $< T_c$, which can facilitate shear yielding, which in turn increases the impact strength. The shear yielding may be initiated at the region of high stress

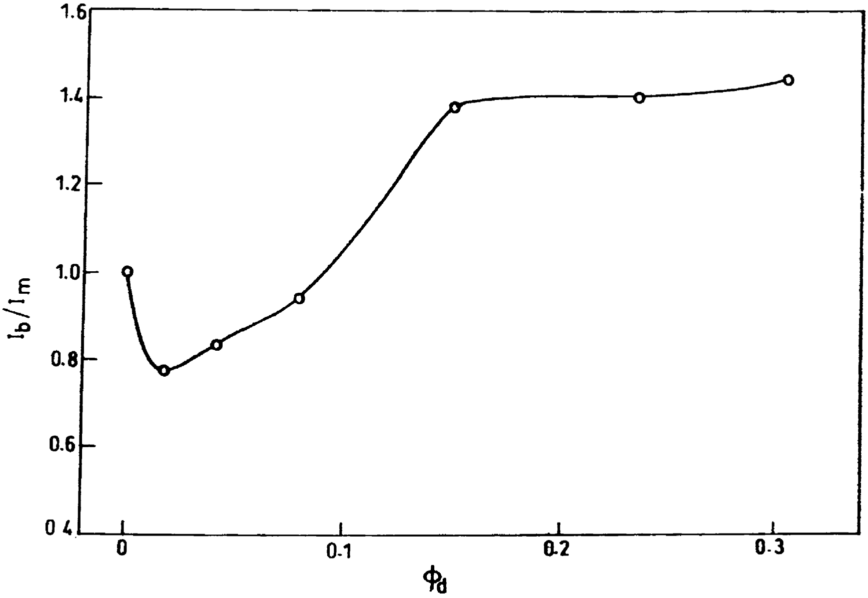

FIGURE 5 Plot of relative Izod impact strength (I_b/I_m) of ABS/Hypalon blends vs. ϕ_d.

concentration, giving rise to local strain in homogeneities [32, 33]. Generation of significant extent of stress concentration by the Hypalon phase was indicated in an earlier analysis of tensile stress data of the blends.

Crazing mechanics also seems operative in these blend systems. Up to $\phi_d = 0.08$ poor interphase adhesion leads to failure by craze termination giving rise to early failure, decreasing the impact strength of the blend. Shear yielding cannot initiate before termination of crazes and formation of larger crazes leading to brittle failure of ABS. At and beyond $\phi_d = 0.15$, because adhesion is enhanced, craze size is controlled and craze termination is facilitated at the interphase. Furthermore, shear yielding can initiate at the craze tips, which can also absorb some energy from the craze, increasing the impact strength of the blend [32, 33].

Fracture Surface Morphology

Scanning electron microscopy (SEM) studies on the fracture surface morphology of ABS and ABS/Hypalon blends are presented in Figure 6a–d. Because ABS polymers and Hypalon rubbers have common

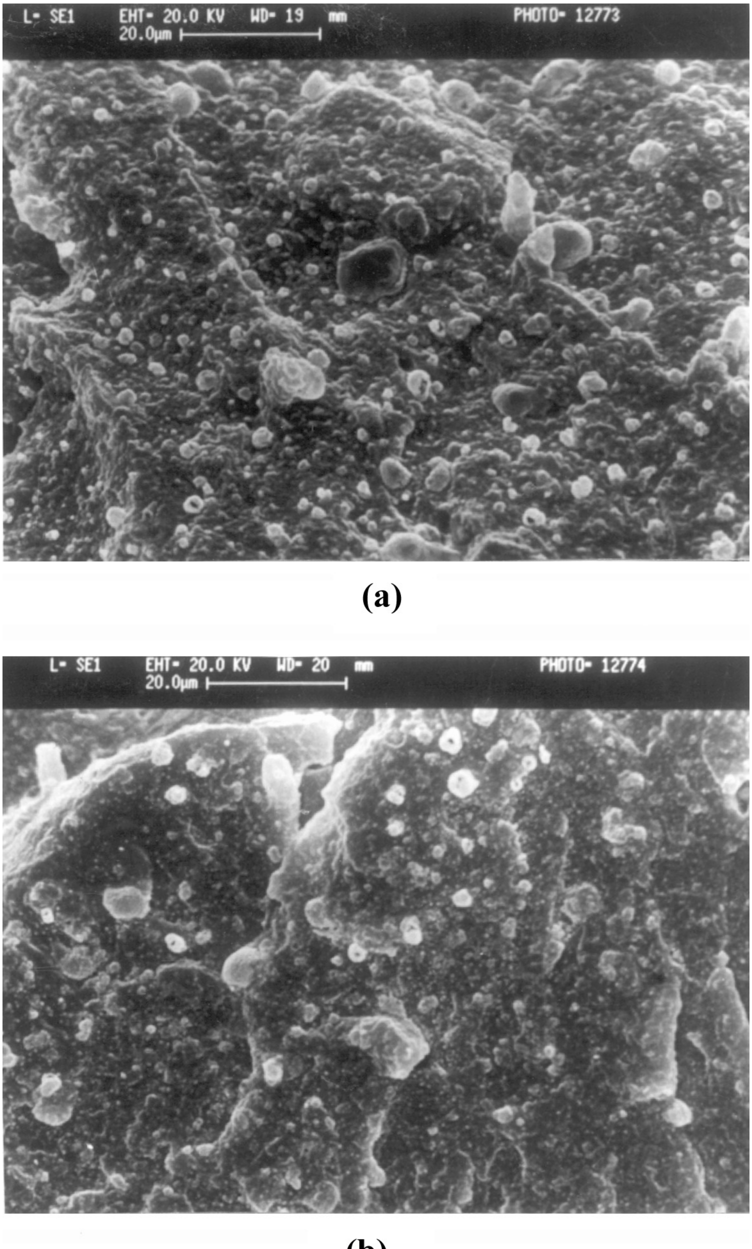

FIGURE 6 Scanning-electron micrographs of (a) ABS and ABS/Hypalon blends at varying ϕ_d; (b) 0.04; (c) 0.15; (d) 0.30.

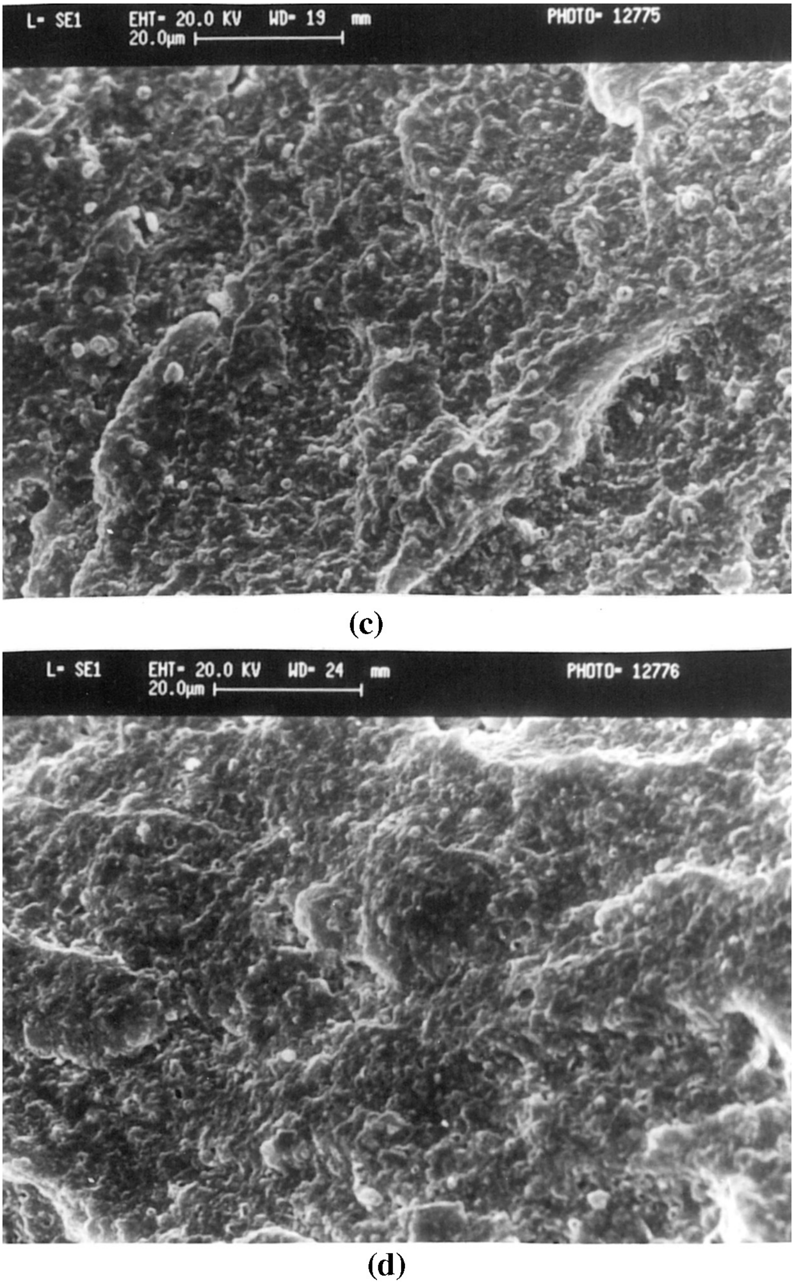

FIGURE 6 Continued.

solvents, preferential etching could not be performed for better phase contrast. Unblended ABS polymer shows two phase morphology where fine droplets of average diameters 1.5–2.5 μm of the SAN component are found dispersed in polybutadiene matrix (Figure 6a). At $\phi_d = 0.04$ quite a large number of smaller globules disappeared and the fracture surface becomes close to conchoidal typical of a more brittle material (Figure 6b). Here, a weak phase boundary is indicated. On application of impact force fracture initiates at these weak interphase and then propagates through these weak spots deceasing the impact strength as observed earlier. At $\phi_d = 0.15$ and above the phase morphology exhibits significant smoothness and the globular phases almost disappear, which is typical of a ductile type of material (Figures 6c and d). This indicates a significant degree of interphase adhesion. Such enhanced adhesion facilitates arresting a propagating craze [33–35]. Furthermore, shear yielding can initiate at these craze tips increasing in the process the impact strength of the blends, as was observed earlier.

CONCLUSIONS

Addition of Hypalon improves the impact strength of ABS, showing a decrease on initial low Hypalon content. At low rubber contents up to 0.08 volume fraction, due to inappreciable interphase adhesion, brittle type fracture occurs, whereas at higher rubber contents adhesion enhances, which in turn increases the impact strength.

However, tensile properties (tensile modulus and strength) of ABS decrease and breaking elongation increases on addition of Hypalon. The rubber causes a matrix softening. Analysis of variation of tensile properties with blend composition in terms of the various models proposed, provides information about interphase adhesion and introduction of stress concentrations in the matrix polymer.

Scanning electron microscopy studies indicate a two-phase morphology in ABS polymer. At low Hypalon content the morphology shows brittle type conchoidal surface fracture whereas at higher rubber contents ductile type fracture occurs, revealing enhanced interphase interaction.

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