Studies on Binary and Ternary Blends of Polypropylene with ABS and LDPE. II. Impact and Tensile Properties

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Synopsis

Studies on impact and tensile properties of binary blend of PP and ABS and ternary blend of PP, ABS, and LDPE are presented. Variation of impact strength and the fracture surface morphology with blend composition is examined and interpreted. Tensile behavior in the yield region is studied and the trends of variation of work of yield and impact strength are compared to ascertain the predominent mechanism of impact toughening in these binary and ternary blends. An analysis of yield-stress data in terms of theoretical models is presented to reveal the differences in these binary and ternary blends, attributable to the role of LDPE component in the ternary blend.

INTRODUCTION

Studies on blends of polypropylene (PP) with acrylonitrile–butadiene–styrene terpolymer (ABS) are mostly confined to patents and quite rarely to the published literature. The paper by Markin and Williams[1] is apparently a pioneering one on PP/ABS blend. We have carried out studies on PP/ABS binary blend and a corresponding ternary blend with LDPE (low-density polyethylene) as the third component. In the first part[2] of this work, we reported rheological properties in molten state of these binary and ternary blends.

In this second part of the work, we present studies on impact and tensile properties of the same binary and ternary blends of PP, ABS and LDPE. Variations of impact strength as function of blend composition, mode of fracture by scanning electron microscopy, and tensile yield behavior as a function of blend composition are studied, and the results are analyzed and interpreted to explain the role of structure and morphology in the properties.

EXPERIMENTAL

Materials

Commercial injection molding grade polymers, PP (Koylene-M3030, melt flow index 3.0) and LDPE (Indothene-22FA 002, melt flow index 0.2) of Indian Petrochemicals Corporation Ltd. and the ABS terpolymer (A:B:S being 16:17:67) of Polychem Ltd., were used.

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Blend Preparation

Blends were prepared by melt mixing in Betol BM-1820 single screw extruder keeping 205, 210, and 215°C as temperatures of the three zones and 40 rpm screw speed. For the case of the ternary blends, blending was done in two steps: (i) a 50:50 blend of ABS and LDPE was prepared and granulated; (ii) this ABS/LDPE blend was then mixed with PP in varying proportions to obtain the ternary blend PP/(ABS/LDPE).

Measurements

Izod impact strength of notched samples was measured in accordance with ASTM D 256 test procedure, on a FIE (Model IT-0.42) impact tester. Injection-molded specimens of dimensions 5 × 1.1 × 0.6 cm with triangular notch of 45° angle and 3 mm depth were used. Ten samples for each composition of the blend were tested.

Tensile tests were carried out on an Instron universal testing machine (Model 1121) using dumbbell-shaped injection-molded specimens in accordance with ASTM D 638. Testing was done at a crosshead separation speed of 20 mm/min for an initial gauge length of 50 mm. At least five samples for each composition were tested.

Electron micrographs of impact fractured surfaces were recorded on a Cambridge Instruments (Model S4-10) scanning electron microscope.

RESULTS AND DISCUSSION

Impact Properties

Binary Blend

Notched Izod impact strength of PP/ABS binary blend is higher than that of PP, implying a positive role of ABS in impact toughening of PP. Variation of impact strength with ABS content is shown in Figure 1. Impact strength of PP is enhanced almost twofold on initial addition of 5 wt % ABS. At 10 wt % ABS content, impact strength passes through its maximum value (2.5 times the value of PP), and then on further addition of ABS the impact strength decreases to reach a value of 1.6 times that of PP at the highest studied ABS content (i.e., 50 wt %). This indicates that impact strength of PP/ABS blend is not simply additive, and its dependence on blend composition implies the influence of blend morphology, state of dispersion, and/or any other structural parameter on impact toughening of this blend. A maximum in impact strength for PP/ABS blend is also reported by Markin and Williams[1] at an identical blend composition.

Occurrence of maximum in impact strength at a particular blend composition may be attributed to the critical size of dispersed phase domains. Domains smaller or larger than the critical size may produce poorer toughening.[3] Thus from the concept of critical domain size and the observation, reported elsewhere,[2] of continuous increase of average domain size with increasing ABS content, it may be stated that at 10 wt % ABS content the average domain size corresponds to its critical value required for optimum

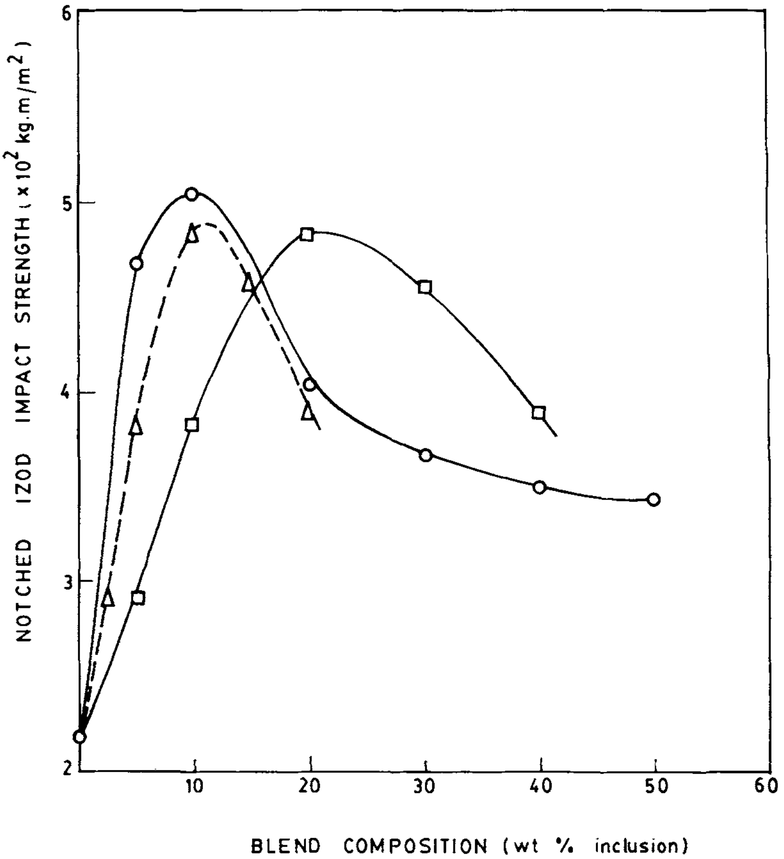


Fig. 1. Variation of notched Izod impact strength with blend composition in terms of weight percent of inclusion in PP/ABS binary and PP/(ABS/LDPE) ternary blend. Inclusion being: (O) ABS in binary blend; (□) (ABS/LDPE) in ternary blend; (△) ABS in ternary blend.

toughening. However, due to our experimental limitation the domain size could not be evaluated with precision.

Furthermore, formation of skin-core morphology in the injection-molded test specimens, as will be discussed in a later section, may also play a role in decreasing the impact strength above 10 wt % ABS content.

Ternary Blend

Impact strength of PP/(ABS/LDPE) ternary blend varies with blend composition as shown in Figure 1. Note that in plotting the data for ternary blend the blend composition may be described in two ways: (1) considering (ABS/LDPE) as the inclusion component and PP as matrix, and (2) considering ABS as inclusion component and (PP + LDPE) as the other component. As a function of (ABS/LDPE) "inclusion" content, the initial increase of impact strength is apparently slower in this ternary blend than in the PP/ABS binary blend, and a maximum in impact strength is observed at 20 wt % "inclusion" content. However, if these data on ternary blend are replotted with blend composition in terms of ABS content, the impact strength curve for the ternary blend (broken line curve in Fig. 1) tends to overlap the curve for the binary blend. This suggests that ABS plays a major role in impact toughening of this ternary blend.

A small adverse effect of LDPE in impact toughening of this ternary blend is apparent at ABS contents less than 10 wt %; impact strength of the ternary blend is lower than that of the binary blend at identical ABS contents. It is somewhat surprising that, though LDPE is much superior in impact properties than PP, its presence as a third component in PP/ABS blend causes a decrease in impact strength. From the changes observed in melt-rheological behavior, the role of LDPE in PP–ABS interface properties was suspected at low blending ratios and a formation of interlocked network morphology with PP matrix at high blending ratios.[2] Such modification in interfacial adhesion beyond a certain desired level may adversely affect the energy dissipation mechanism of the elastomeric domains, hence causing a decrease of impact strength.

Fracture Surface Morphology

Binary Blend

Scanning electron micrographs of impact fractured surfaces of PP/ABS binary blend at various compositions are shown in Figure 2. Characteristic features of shear yielding, such as the advancement of shear lines at angles close to 45° with the stress direction[4–8] and transverse contraction,[9] are apparent in these micrographs at all compositions of the blend. At high ABS content, features of ductile fracture become prominent. Ductile fracture results in plastic flow due to recovery of stresses immediately after fracture. This feature of ductile fracture is quite prominently visible in PP/ABS blend at high ABS content (above 30 wt %). At 20 wt % ABS content the features of ductile fracture are apparent only at the edges of the specimen. Thus the plastic flow pattern, which is almost absent up to 10 wt % ABS content, originates from the outer surface region of the specimen at 20 wt % ABS content and then spreads over the entire fracture surface at higher ABS content. Fracture surfaces at higher than 30 wt % ABS content also show somewhat greater abundance of flow induced pattern at the edges. This indicates the formation of some kind of skin-core morphology during injection molding of the test pieces, of the blend at ABS content 20 wt % or above. Formation of skin-core morphology in injection-molded test pieces of PP/ABS blend is reported by Markin and Williams,[1] where the outer surface (skin) is stated to be rich in ABS at high ABS content, from their perchloric acid treatment test of surface darkening. Appearance of plastic flow features at high ABS content and their origin at the skin region of the specimens confirm the ABS-rich character of the skin region of these injection-molded specimens.

This skin-core morphology of the injection-molded test pieces may have an influence on impact strength. As already stated, the impact strength shows decreasing trend (after passing through a maximum at 10 wt % ABS content as seen in Fig. 1) at a blend composition where skin-core morphology is clearly observed in the micrographs. Thus the decrease in impact strength may be partly an effect of the formation of skin-core morphology, which leaves the major portion of the fracture surface (i.e., the core) poorer in ABS content.

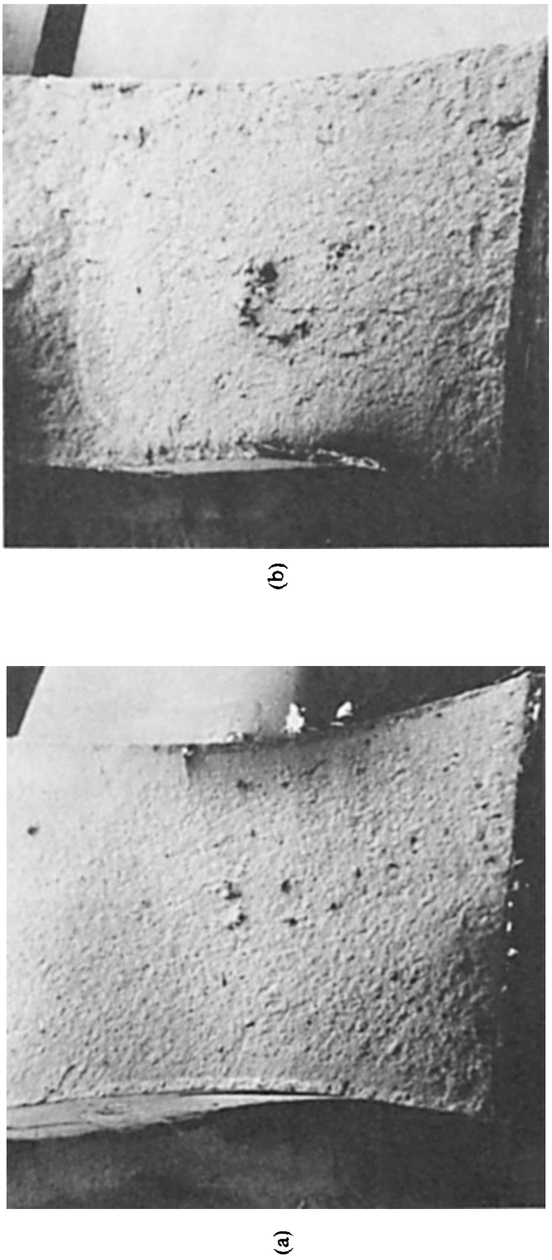
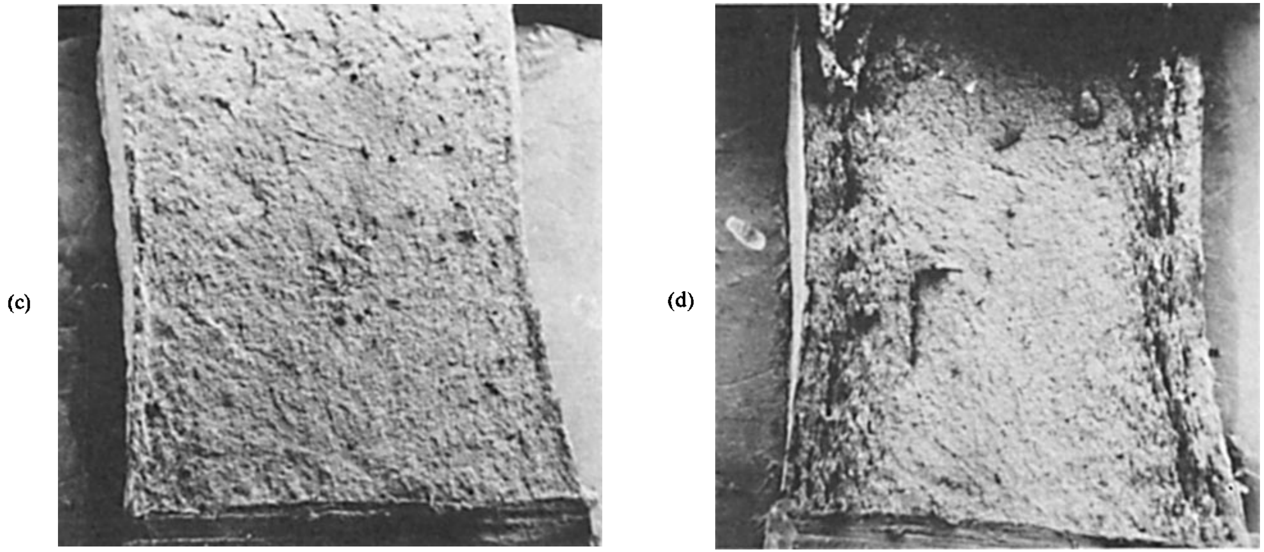


Fig. 2. Scanning electron micrographs of impact fractured surfaces of PP/ABS binary blend, at varying ABS content (wt %): (a) 0; (b) 5; (c) 10; (d) 20; (e) 30; (f) 40.



(c) (d)

Fig. 2. *(Continued from the previous page.)*

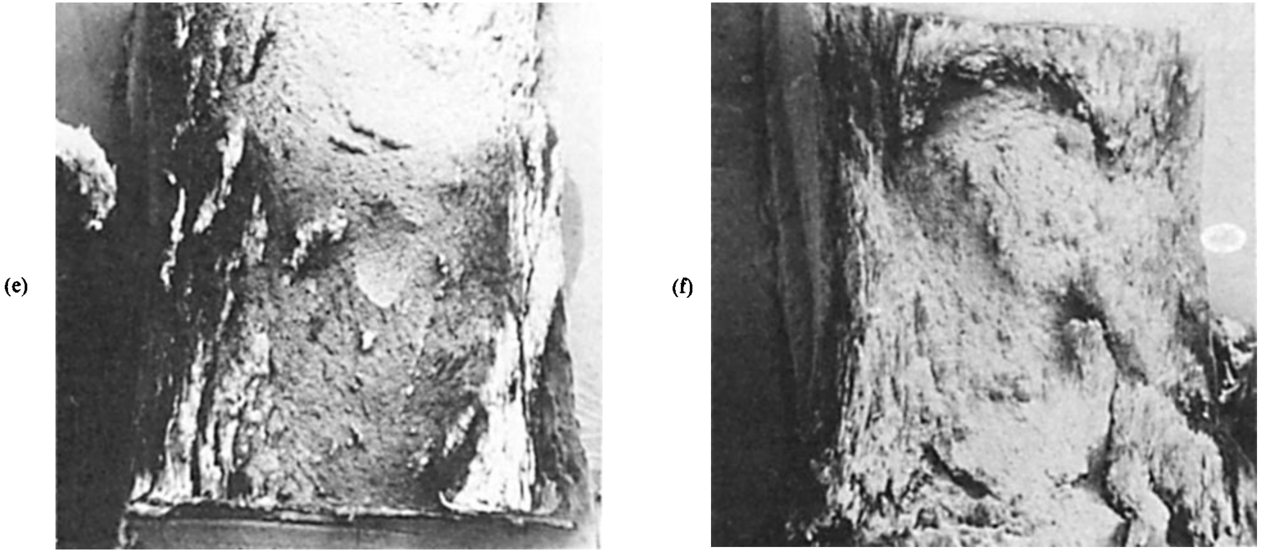
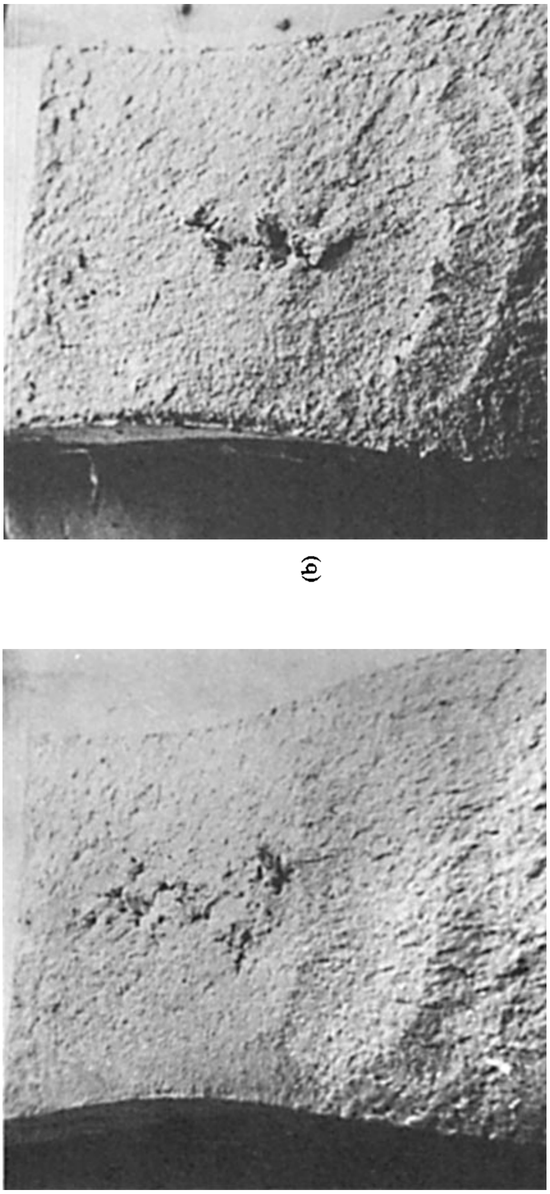
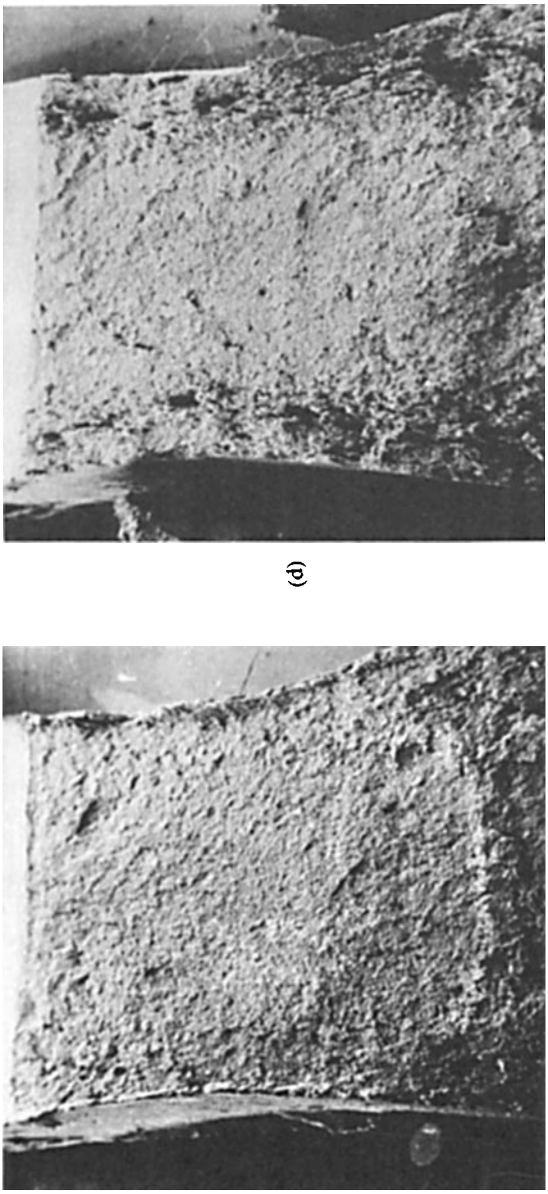


Fig. 2. (*Continued from the previous page.*)



(a) (b)

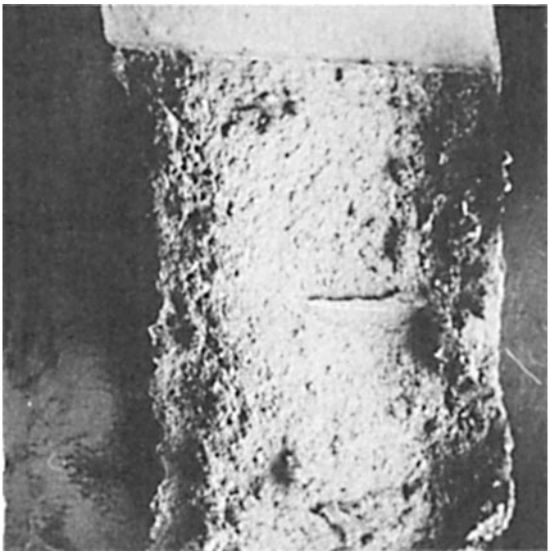
Fig. 3. Scanning electron micrographs of impact fractured surfaces of PP/(ABS/LDPE) ternary blend, at varying ABS content (wt %): (a) 2.5; (b) 5; (c) 10; (d) 15; (e) 20.



(c)

(d)

Fig. 3. *(Continued from the previous page.)*



(e)

Fig. 3. (*Continued from the previous page.*)

Ternary Blend

Scanning electron micrographs of the ternary blend PP/(ABS/LDPE) at various blending ratios are shown in Figure 3. Features of shear yielding and plastic flow pattern resulting from recovery of stresses in ductile fracture are quite similar to those described above for the PP/ABS binary blend. The effect of skin-core morphology becomes quite prominent at 15 wt % ABS content [Fig. 3(d)] in these ternary blends. A comparison of micrographs of binary [Fig. 2(d)] and ternary [Fig. 3(e)] blends on identical ABS content (20 wt %) shows a wider skin zone in the ternary blend than in the binary blend. Furthermore, coarseness of the fracture surface is much less in the ternary blend than in the binary blend at identical blending ratios, which seems to be an effect of interaction of LDPE and PP and/or formation of network or interlocked morphology accounting for an enhanced dissipation of energy in the matrix and thus less deformation of the fracture surface.

Tensile Behavior

Binary Blend

Stress–strain curves in the yield region of the PP/ABS binary blend at various blending ratios are shown in Figure 4. After the initial linear increase of stress with strain, the curve passes through the yield region where the stress decreases with increasing strain. The stress–strain curve in the yield region gives an appearance of a broad peak, called "yield peak." The yield peak is very broad in case of the two samples with lowest ABS content. At higher ABS content, yield peaks are apparently incomplete as the samples break in the yield region. Breaking elongation decreases with increasing ABS content as shown in Table I.

The yield stress (σ_y), i.e. the stress at the highest point of the yield peak, decreases with increasing ABS content (Table I), suggesting that ABS domains facilitate yielding of PP. Similar ease of yielding of PP was observed on blending with SEBS elastomer.[10,11]

Area under the yield peak, which is a measure of "work of yield" or the energy absorbed in the process of yielding, is quite high up to 10 wt % ABS content. Narrowing of yield peak with increasing ABS content is clearly apparent in these incomplete yield peaks (Fig. 4) at higher ABS content. This indicates a decrease of "work of yield" with increasing ABS content above 10 wt %. Thus work of tensile yield and impact strength vary with blend composition quite similarly, suggesting that shear yielding is the major mechanism of impact toughening in PP/ABS blend. Furthermore, we also observed in these tensile tests that at initial stages of deformation the stress whitening bands were inclined at approximately 45° angle with the stress direction, which is a characteristic of shear bands. Shear bands propagate along lines of zero strain rate whose direction depends on the properties of the material; an angle of inclination about 45° with stress direction is calculated[8] for an ideal isotropic material.

Ternary Blend

Stress-strain curves of PP/(ABS/LDPE) ternary blend, shown in Figure 5, differ from those of the PP/ABS binary blend at low ABS content up to 10 wt % of ABS content, the breaking elongation is 15–20% for the ternary blend as against 40–50% for the binary blend. This indicates that the addition of LDPE causes a reduction in breaking elongation of PP/ABS binary blend. However, the addition of LDPE produces little change in the yield stress at low blending ratios. This is surprising, because if LDPE is believed to introduce weaker points in the structure, then yield stress should also decrease along with the reduction of elongation at break. Another observation from a previous work[2] relevant to the role of LDPE in ternary blend is that this ternary blend showed lower viscosity of the melt than this binary blend at identical ABS content.

At higher ABS content the observed weakening (i.e., smaller yield stress and smaller elongation at break) of the ternary blend in comparison to the binary blend might be due to any one or more of the three kinds of interfaces present, viz., PP-LDPE, PP-ABS, and ABS-LDPE.

Above 10 wt % ABS content, the decrease of breaking elongation of the ternary blend with ABS content is much less than that observed for the binary blend, which seems to be an effect of formation of network type dispersion of LDPE in PP matrix.

Furthermore, yield peaks are incomplete (even up to the breaking elongations) in these ternary blends of ABS contents up to 10 wt %. At higher ABS content the yielding is complete, and stress begins to rise, at above 18% elongation. Variation of area under yield peak with blend composition suggests a lowering of "work of yield" at ABS content 15 wt % and above, which is similar to the variation of impact strength of these ternary blends with

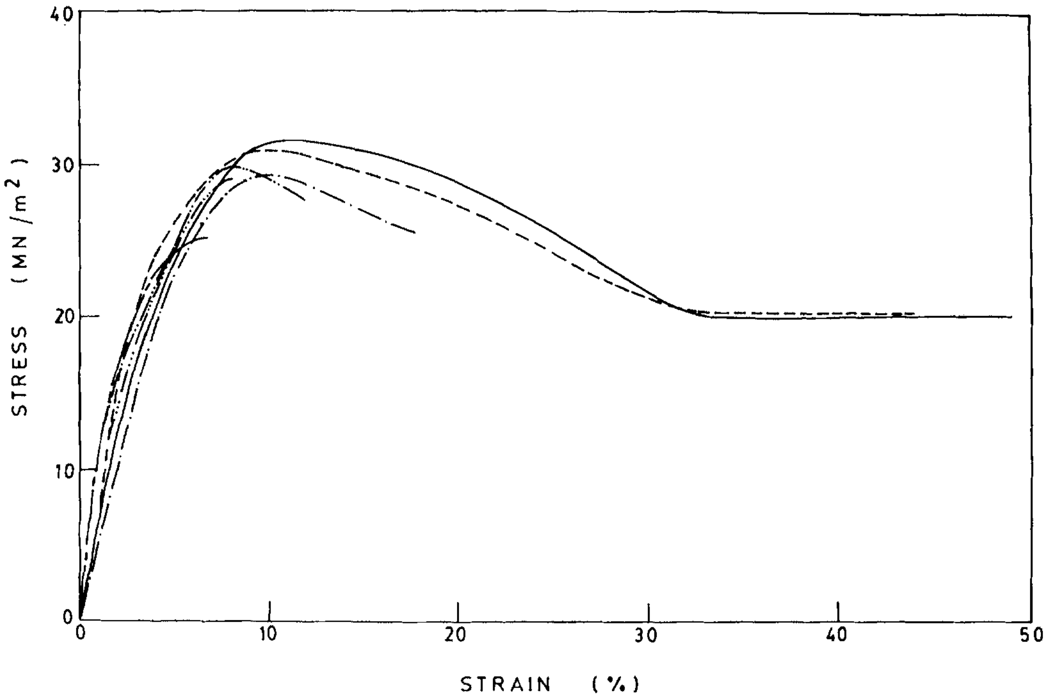


Fig. 4. Stress–strain curves of PP/ABS binary blend at varying ABS content (wt %): (—) 5; (---) 10; (-·-) 20; (-··-) 30; (- ···· -) 40; (---) 50.

TABLE I
Tensile Properties of PP/ABS Binary and PP/(ABS/LDPE) Ternary Blend

Blend	ABS content (wt %)	LDPE content (wt %)	Modulus (MN/m^2)	Breaking elongation (%)	Yield stress (MN/m^2)	Yield strain (%)
PP/ABS	5	—	5.17	49.6	31.5	10.6
	10	—	7.50	44.0	30.7	10.0
	20	—	4.69	17.6	29.7	9.8
	30	—	8.87	12.0	29.8	8.0
	40	—	8.75	7.6	[a]	[a]
	50	—	9.31	6.6	[a]	[a]
PP/(ABS/LDPE)	2.5	2.5	4.86	16.1	32.0	9.6
	5	5	5.71	17.1	30.0	9.6
	10	10	5.48	20.0	29.0	8.8
	15	15	4.44	22.4	26.5	10.8
	20	20	4.81	20.8	24.5	10.4

[a] Breaking occurs before reaching of yield peak.

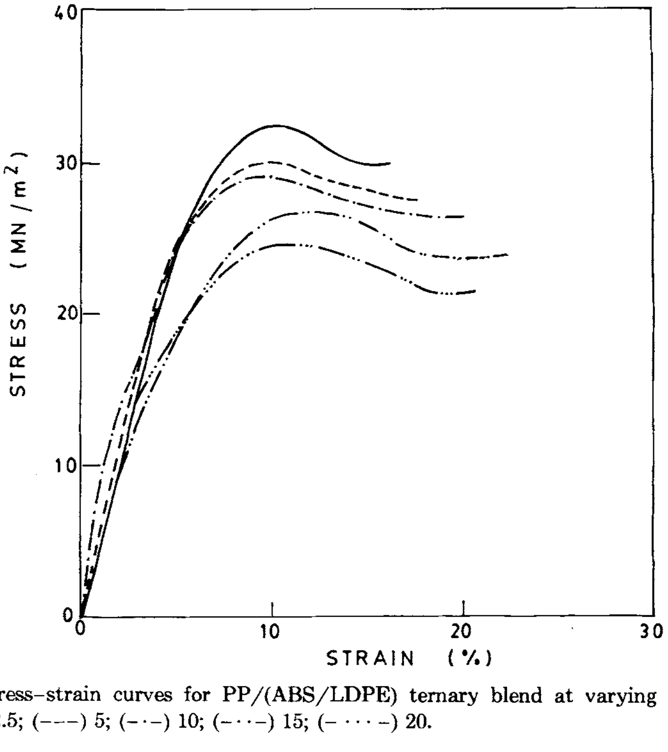


Fig. 5. Stress-strain curves for PP/(ABS/LDPE) ternary blend at varying ABS content (wt %): (—) 2.5; (---) 5; (-·-) 10; (-··-) 15; (-···-) 20.

ABS content. Thus, like the case of the binary blend, the ternary blend shows similar trends of variation of both impact strength and work of yield.

Analysis of Yield-Stress Data

Analysis of these tensile yield stress data in terms of theoretical models for blends and composites reveals some differences in behavior of the binary and ternary blends. Theoretical models describing the decrease of tensile property

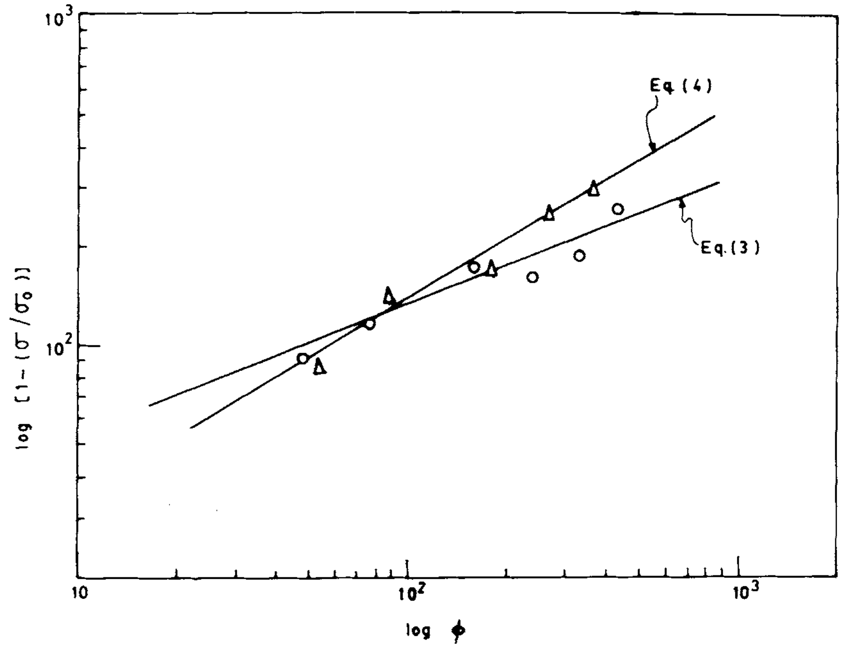


Fig. 6. Variation of $\log(1 - \sigma/\sigma_0)$ as function of $\log \phi$ for PP/ABS binary blend (○) and PP/(ABS/LDPE) ternary blend (△).

as a function of volume fraction of the inclusion are generally based on two-thirds power of the volume fraction, as, for example, the Nielsen's equation[12] [eq. (1)] and Nicolais and Narkis' equation[13] [eq. (2)] given below:

$$\sigma/\sigma_0 = (1 - \phi^{2/3})S \tag{1}$$

$$\sigma/\sigma_0 = 1 - 1.21\phi^{2/3} \tag{2}$$

where σ and σ_0 denote the property (yield stress) of the blend and the matrix respectively, ϕ is the volume fraction of the inclusion, and S is a parameter which is unity or a fraction. S is indicative of the stress concentration such that a decrease of S implies an increase of stress concentration and its highest value unity corresponds to the case of no stress concentration.

Though 2/3 is widely used as the value of the exponent of ϕ, Piggott and Leidner[14] have described reasons for the value of this exponent different from 2/3. Hence in our analysis of these data the value of the exponent is determined through the slopes of $\log(1 - \sigma/\sigma_0)$ vs. $\log \phi$ plots. The straight line extrapolations shown in Figure 6, are consistent with the following relationships for these binary [eq. (3)] and ternary [eq. (4)] blends:

$$\sigma/\sigma_0 = 1 - 0.4\phi^{0.5} \quad \text{(binary)} \tag{3}$$

$$\sigma/\sigma_0 = 1 - 0.5\phi^{0.6} \quad \text{(ternary)} \tag{4}$$

Decrease of σ/σ_0 as a function of volume fraction ϕ (on linear scale) for these binary and ternary blends are shown in Figure 7, along with the theoretical curves corresponding to eqs. (3) and (4). The exponent of ϕ in these

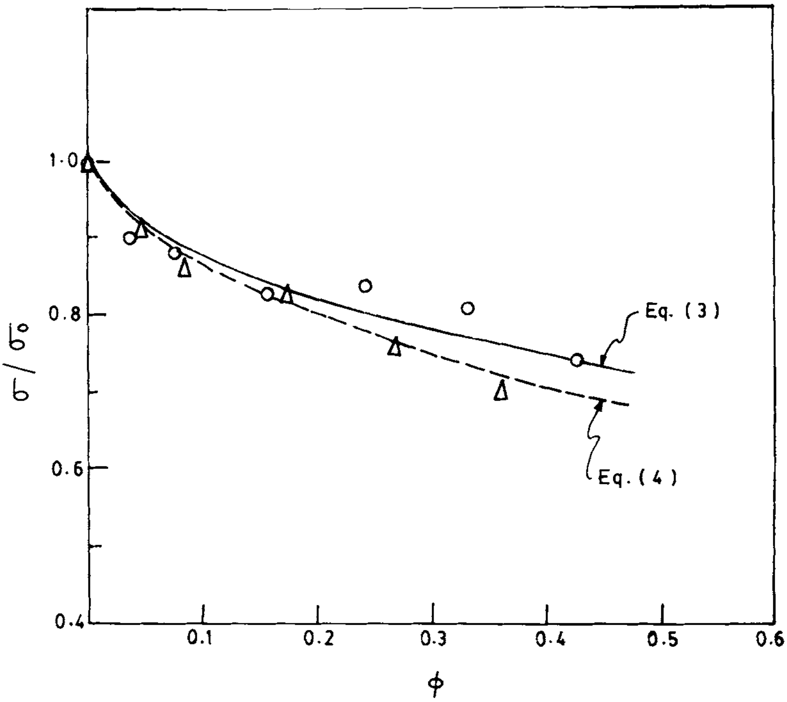


Fig. 7. Variation of σ/σ_0 as function of the ϕ binary blend (○) and PP/(ABS/LDPE) ternary blend (△). Predicted variations from eqs. (3) and (4) are solid and broken line curves, respectively.

equations is less than the conventional value 2/3; the binary blend has smaller value (i.e., 0.5) than the value for ternary blend (i.e., 0.6). According to Piggott and Leidner,[14] the exponent value is 1/3 or 2/3, depending on whether the length fraction or volume fraction (respectively) of the inclusion is considered operative in the concerned mechanical property. This viewpoint and the above-stated observed values of the exponent suggest greater significance of length-fraction dependence in the binary blends and of area-fraction dependence in the ternary blends.

The dispersed domains are of ABS component in both binary and ternary blends, and LDPE in the ternary blend is situated either as mixed phase with PP matrix or on the boundary region of ABS and PP. In any case, the LDPE seems to modify the surface properties of the ABS domains, by probably interacting with any of the three components, A, B, or S of ABS. The dispersed ABS domains seem more elongated in the absence of LDPE so as to account for lower value of the exponent of ϕ for the binary blend. Whereas, in the ternary blend LDPE seems to modify the surface properties such that they become effectively less elongated and their area fraction becomes more predominent in the property of the blend.

CONCLUSIONS

Considerable impact toughening of PP is achieved by blending it with ABS. The critical blend composition for maximum impact strength is 10 wt % ABS content for both PP/ABS binary and PP/(ABS/LDPE) ternary blends. Thus a low cost dilution with LDPE is admissible without hampering the impact properties at 10 wt % ABS content.

Shear-induced fracture with ductility increasing with increasing ABS content is observed in these binary and ternary blends. Features of ductile fracture originate at the outer edges of fracture surface electron micrographs, providing an additional experimental support to the findings of Markin and Williams[1] regarding skin-core morphology of PP/ABS blend.

Yield stress decreases with increasing ABS content, and the variation of work of yield with blend composition is quite similar to the variation of impact strength, thus justifying shear yielding as the principal mechanism of toughening in these blends. An analysis of these yield stress data revealed some influence of LDPE on surface characteristics of ABS domains, which are less elongated in the ternary blend than in the binary blend.

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