Morphological and Mechanical Properties of PP/ABS Blends Compatibilized with PP-*g*-acrylic Acid

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ABSTRACT: Polypropylene (PP) and acrylonitrile–butadiene–styrene (ABS) blends were prepared by a melt extrusion process. PP-*g*-acrylic acid was used as a compatibilizer. Blends with various compositions of PP, compatibilizer, and ABS were prepared and studied for morphological and mechanical properties. PP-rich ternary blends showed good morphological and mechanical properties. The use of 5 wt % PP-*g*-acrylic acid as a compatibilizer resulted in a fine and homogeneous dispersion of the ABS phase in the PP phase. The experimental data of the tensile modulus showed good agreement in PP-rich compositions with that generated from Kerner's model with perfect adhesion. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1731–1741, 2001

Key words: polypropylene; ABS; compatibilizer; blends; morphology

INTRODUCTION

In recent years, polymer blending has been considered a convenient route for the development of newer polymeric materials with a wide range of properties.[1–3] The improvement of the physical and mechanical properties of the blends mainly depends on the extent of adhesion at the interface and how fine the dispersion is of one phase into another.[2–4]

The blending of polypropylene (PP) with commercially available polymers such as polycarbonate, polystyrene, polyethylene, and nylon 6 is of commercial interest.[5] However, some of these blends are less compatible and, hence, do not exhibit desirable properties. Attempts have been made to decrease the interfacial tension between

PP and polycarbonate,[6] PP and polyethylene,[7] PP and nylon 6,[8] and PP and polystyrene[9] with graft copolymers such as PP-*g*-maleic anhydride, PP-*g*-acrylic acid, and styrene–ethylene–butadiene–styrene (SEBS) block copolymers to achieve improvement in the compatibility. PP has poor impact strength but high elongation and also good chemical resistance, whereas acrylonitrile–butadiene–styrene (ABS) has poor elongation but high impact strength.[10] Hence, the blending of PP/ABS or incorporation of ABS in a PP matrix would be desirable to achieve higher impact strength without losing important properties of PP.

A few reports[11–18] and patents[19–23] are available on PP/ABS blending. Markin and Williams[11] thoroughly examined mechanical properties and morphology of binary PP/ABS blends. They observed improved impact strength with the addition of ABS to a PP matrix. Maiti et al.[12,13] reported an improvement in the compatibility of PP/ABS blends with the addition of polyethylene to the binary blend. The use of SEBS block copolymers as compatibilizers was reported by Froun-

chi and Burford.[14] However, many patents were reported where more than one compatibilizer was used in PP/ABS blends.[19–23]

We undertook the synthesis of a series of graft copolymers with variable hydrophilic/hydrophobic ratios by selecting the monomers. The first in this series was PP-*g*-acrylic acid, which was used as a compatibilizer in PP/ABS blends.

EXPERIMENTAL

Materials

Isotactic PP of M0030 koyelene grade with a density of 0.93 g/cm³ and a melt-flow index of 10 g/10 min was supplied by Indian Petrochemicals Corp. Ltd. (Vadodara, India).

ABS of 100*N* grade with a density of 1.05 g/cm³ and a melt-flow index of 10 g/10 min was a gift sample from Bayer-ABS India Ltd. (Vadodara, India).

Acrylic acid was obtained from National Chemicals (Vadodara, India) and was used after vacuum distillation. Benzoyl peroxide (BPO) from Fluka (Switzerland) was used without further purification.

AR-grade toluene and methanol were used without further purification.

Synthesis of PP-*g*-acrylic Acid

The grafting of PP with acrylic acid was carried out in a five-necked reaction kettle equipped with a mechanical stirrer, a condenser, a thermopocket, a nitrogen gas inlet, and dropping funnels. The temperature was maintained at 110 ± 1°C. A known amount of accurately weighed PP (5 wt %) was dissolved in toluene at 110°C. The reaction mixture was deoxygenated by nitrogen purging before the addition of initiator and monomer. To this homogenized solution, BPO (0.21 mmol/g of PP) and acrylic acid (1:1 w/w PP) dissolved in toluene were added simultaneously over a period of 1 h. The reaction was continued further for 5 h. The reaction mixture was poured into a threefold to fourfold excess of methanol under vigorous stirring. The precipitated graft copolymer was isolated and washed several times with water and extracted with hot water for 2 h to remove the homopolymer of acrylic acid. Finally, the products were dried under reduced pressure at 80°C to a constant weight.

Table I   Composition of PP/ABS Blends (w/w)

Number	PP/ABS/PP-*g*-Acrylic Acid
1	100/0/0
2	90/10/0
3	85/15/0
4	75/25/0
5	25/75/0
6	15/85/0
7	10/90/0
8	100/0/0
9	90/10/2.5
10	85/15/2.5
11	75/25/2.5
12	25/75/2.5
13	15/85/2.5
14	10/90/2.5
15	90/10/5
16	85/15/5
17	75/25/5
18	25/75/5
19	15/85/5
20	10/90/5
21	90/10/7.5
22	85/15/7.5
23	75/25/7.5
24	25/75/7.5
25	15/85/7.5
26	10/90/7.5

The grafting percentage was determined by the acid titration method[24] and by gravimetry.

Blend Preparation

PP, PP-*g*-acrylic acid, and ABS were dried in a hot-air oven at 70°C for 24 h prior to extrusion. The blends were prepared at the Indian Petrochemical Corporation Ltd. (Boroda, India) by the melt extrusion technique with a Brabender single-screw extruder with an length/diameter (L/D) ratio of 20. All the blends were prepared by a two-step mixing technique. In the first step, PP and PP-*g*-acrylic acid (1:1 w/w) were premixed in the extruder; the temperature was kept in the four zones at 190, 200, 210, and 220°C, and the screw speed was kept at 50 rpm. The resultant mixture was pelletized, and in a second step, a calculated amount of it was mixed with ABS and PP and extruded at 200, 220, 230, and 225°C for PP-rich compositions and at 220, 230, 250, and 240°C for ABS-rich compositions. The various blend compositions that were prepared are given in Table I. The extrudates were cut into pellets.

The blend pellets were injection-molded with an ARBURG allrounder 220-90-350 injection-molding machine at NCL (Pune, India) to obtain the test specimen for the measurements of mechanical properties according to ASTM standards.

Characterization

Mechanical Properties

The measurement of the tensile properties of the dumbbell-shaped samples was carried out at NCL with an Instron 4204 testing machine using the ASTM D638 procedure. Notched impact strength was measured using the ASTM D256 procedure with a Ceast impact testing machine at NCL. At least five specimens for each analysis were tested at room temperature, and the average value was considered for the study.

Morphology

The morphology of room-temperature fractured surfaces etched with methyl ethyl ketone (MEK) for ABS extraction was examined with a scanning electron microscope (Leica Cambridge, UK Stereoscan) at 10 kV at NCL. The samples were gold-coated at NCL (50 μm thick) with an automatic sputter coater (Polaron Equipment Ltd., United States of America) to avoid surface charging.

## RESULTS AND DISCUSSION

Synthesis of PP-*g*-acrylic Acid

The grafting of acrylic acid onto PP in solution resulted in a grafting weight percentage of 7.2%. The Fourier transform infrared spectrum of the grafted PP exhibited a carbonyl stretching band for poly(acrylic acid) at 1720 cm^{-1}. The grafting percentage determined through acid titration was observed to be in agreement with that obtained gravimetrically.
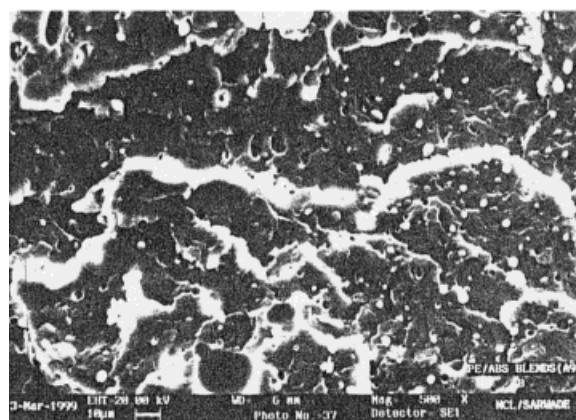
PP-*g*-acrylic acid was further used in the preparation of PP/ABS blends with different compositions, as given in Table I. The blends were characterized for their morphology and mechanical properties.

Morphology

As expected, blends containing no compatibilizer exhibited coarse and heterogeneous dispersions of the phases, as seen in scanning electron micro-
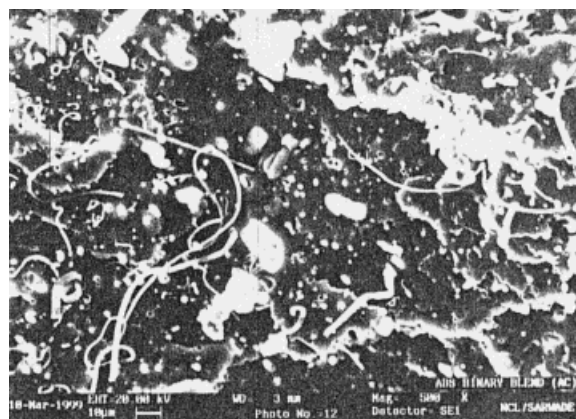
(a)

(b)

Figure 1 Scanning electron micrographs of impact fractured surfaces of blends: (a) 90/10 PP/ABS and (b) 90/10/2.5 PP/ABS/PP-*g*-acrylic acid.

graphs of the 90/10 PP/ABS blend [Fig. 1(a)]. PP-rich binary blends exhibited coarsely dispersed ABS particles in a PP matrix. After the addition of 2.5% PP-*g*-acrylic acid as a compatibilizer, the blend compositions showed a finer and more homogeneous dispersion of ABS particles in the PP matrix [Fig. 1(b)].

The effect of compatibilizer concentration on blend morphology was examined in a 75/25 PP/ABS blend with 0, 2.5, 5, and 7.5 wt % PP-*g*-acrylic acid. Figure 2(a) shows that larger and coarsely dispersed cavities developed because of the extraction of ABS from the 75/25 PP/ABS blend. A small decrease in particle size was observed with the incorporation of 2.5 and 5 wt % compatibilizer. A further increase of the compatibilizer to 7.5% resulted in an increase in the size of dispersed particles. This was due to the fact
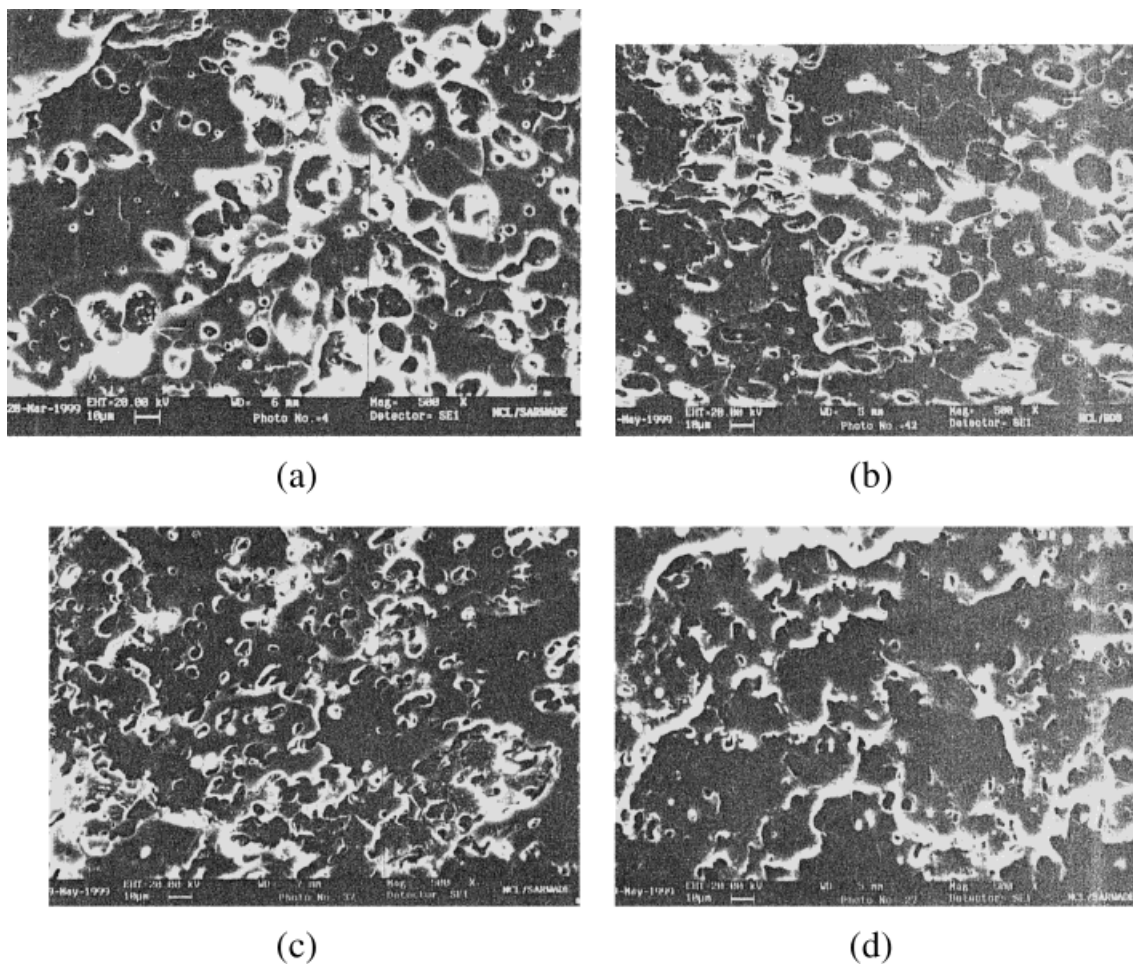
Figure 2 Scanning electron micrographs of impact fractured surfaces of 75/25/X PP/ABS/PP-g-acrylic acid (X) blends after etching of ABS in MEK: (a) X = 0%, (b) X = 2.5%, (c) X = 5%, and (d) X = 7.5%.

that the formation of aggregates of compatibilizer in bulk at high concentration causes less availability of it at the interface. This can lead to larger dispersed particles. The particle size of the dispersed phase decreased to some extent with an increase in compatibilizer concentration up to 5 wt % [Fig. 2(c)]. A further increase in compatibilizer concentration did not decrease the size of

Table II Particle Size and PDI in Blends

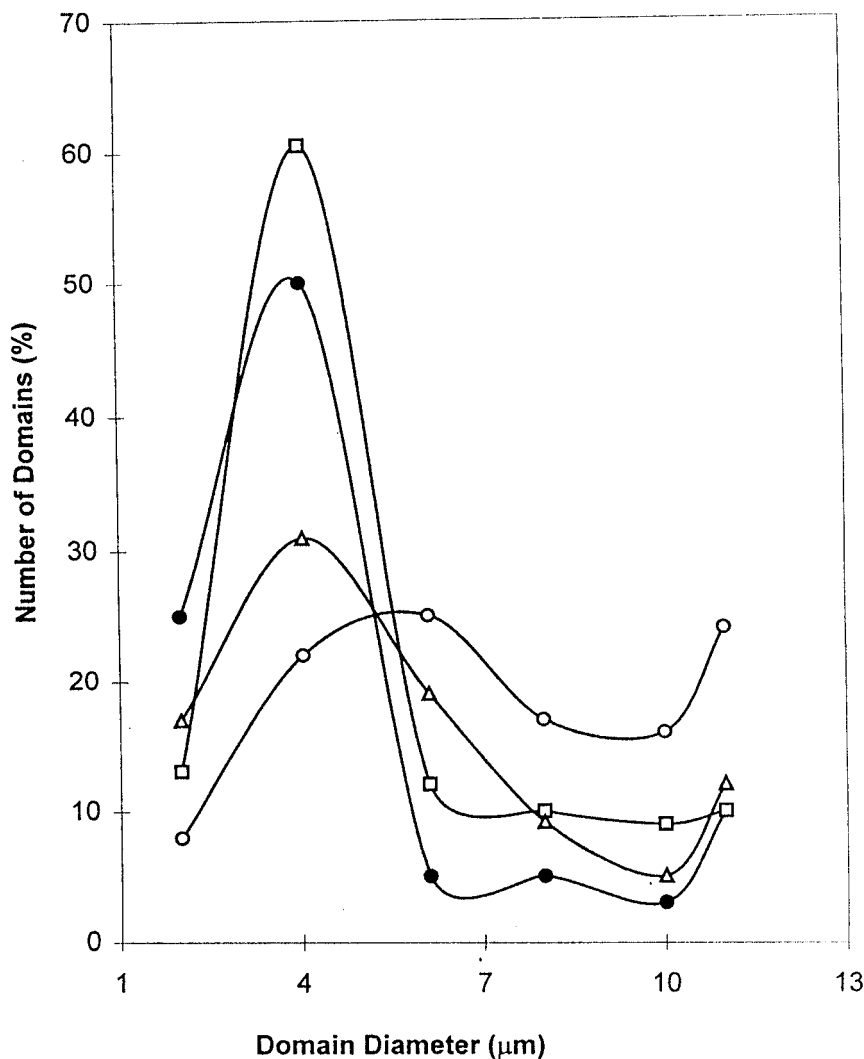| Blend Composition PP/ABS/Compatibilizer (w/w)	$\overline{D_n}$ (μm)	$\overline{D_w}$ (μm)	$\overline{D_{vs}}$ (μm)	PDI
90/10/0	7.50	8.33	11.0	1.24
75/25/0	6.9	8.12	10.12	1.31
90/10/2.5	5.62	7.07	10.05	1.13
90/10/5	5.43	6.74	9.69	1.11
90/10/7.5	6.15	7.96	10.15	1.14
75/25/2.5	6.44	7.23	10.3	1.14
75/25/5	6.30	7.46	10.3	1.15
75/25/7.5	6.80	8.67	10.3	1.27

Figure 3 Polydispersity of the dispersed phase in blends: PP/ABS 75/25/0 (○), PP/ABS 75/25/2.5 (●), PP/ABS 75/25/5 (□), and PP/ABS 75/25/7.5 (△).

dispersed particles, indicating that 5 wt % compatibilizer was sufficient to occupy the interface between PP and ABS [Fig. 2(a–d) and Table II]. As a result, an excess of compatibilizer remained in the bulk and did not contribute to the reduction of interfacial tension, which would cause further reduction in particle size.

To determine the particle size of the dispersed phase, approximately 100 particles were selected for each sample. The number-average diameter (D_n), weight-average diameter (D_w), and surface-area-average diameter (D_{vs}) were calculated and used for the determination of the polydispersity index (PDI). The results are given in Table II. The polydispersity curves of the blends containing 75% PP and different concentrations of compatibilizer are given in Figure 3. The uncompatibi-

lized binary blends showed the broader particle size distribution of ABS into PP. With the incorporation of the compatibilizer, the particle size distribution became narrow, and the size of the dispersed ABS particles also decreased up to 5 wt % compatibilizer. Further increases in compatibilizer concentration did not contribute to the interface phenomenon, as its critical concentration can occupy the interface, and excess concentration may form micellar aggregations in the bulk. Similar observations were reported by Asaletha et al.[25] and Thomas and Praud 'Homme[26] for PP–nitrile rubber blends.

Mechanical Properties

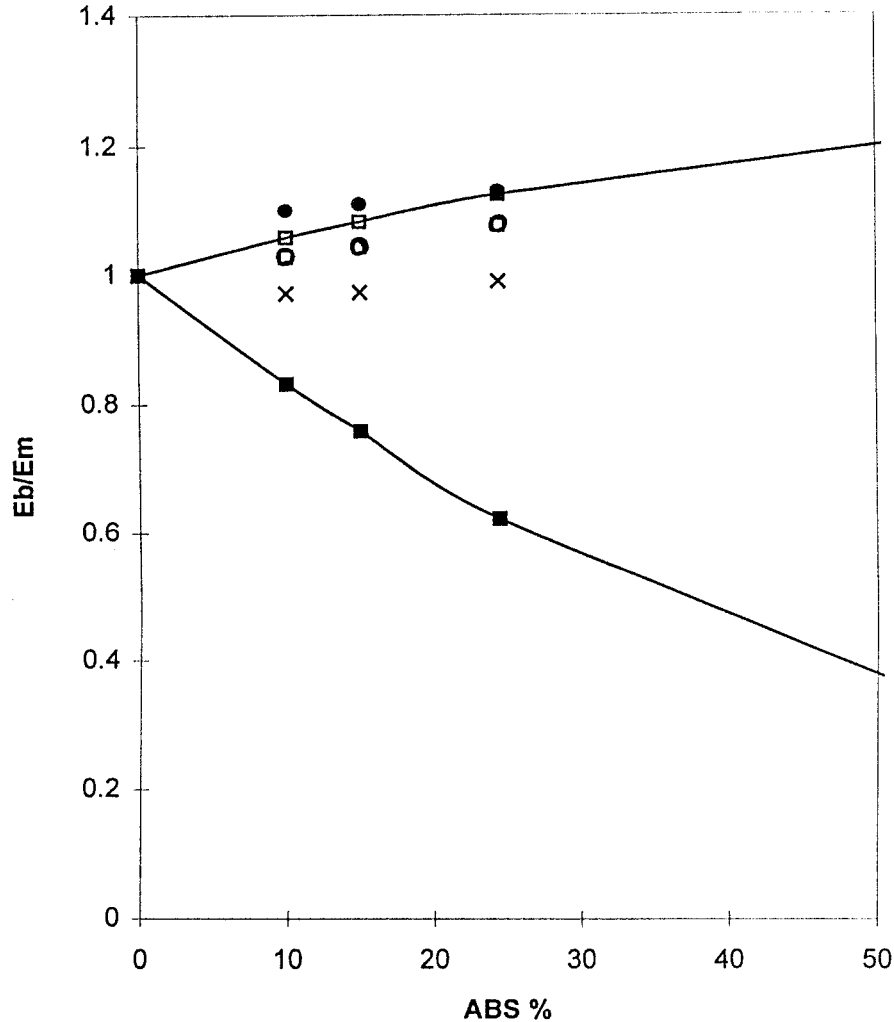Many theories have been put forward for the prediction of the elastic modulus of heterogeneous

Figure 4 Theoretical models for the tensile modulus: Kerner's model for perfectly bound inclusions ($\square$), Kerner's model for loosely bound inclusions ($\blacksquare$), Nielsen's model for rubber dispersed in rigid matrix (at $\phi_{\max} = 0.56$) ($\bigcirc$), PP/ABS blend experimental values ($\times$), and PP/ABS /2.5%PP-*g*-acrylic acid blend experimental values ($\bullet$).

blends.[27] There are three principal groups of models that can predict the modulus-composition dependence of blends:

1. Mechanical coupling model.
2. Self-consistent model.
3. Bounds on modulus model.

Among these, the self-consistent model, which is widely used for various blends, is based on three assumptions:

1. Perfect adhesion exists between the matrix and the inclusions.
2. Interinclusion interactions are negligible.
3. The inclusions are spherical.

On the basis of these assumptions, Kerner[28] proposed the following model for the systems having similar Poisson ratios and perfect adhesion at the boundary for the calculation of the tensile modulus (E) as

$$E_b = E_m \frac{[\varnothing_d E_d/(\{7 - 5v_m\}E_m + \{8 - 10v_m\}E_d + \varnothing_m 15(1 - v_m)]}{[\varnothing_d E_m/(\{7 - 5v_m\}E_m + \{8 - 10v_m\}E_d + \varnothing_m 15(1 - v_m)]} \quad (1)$$

where E is the tensile modulus, $\varnothing$ is the volume fraction, and v is the Poisson ratio. Subscripts b, m, and d refer to the blend, matrix, and dispersed phases, respectively.
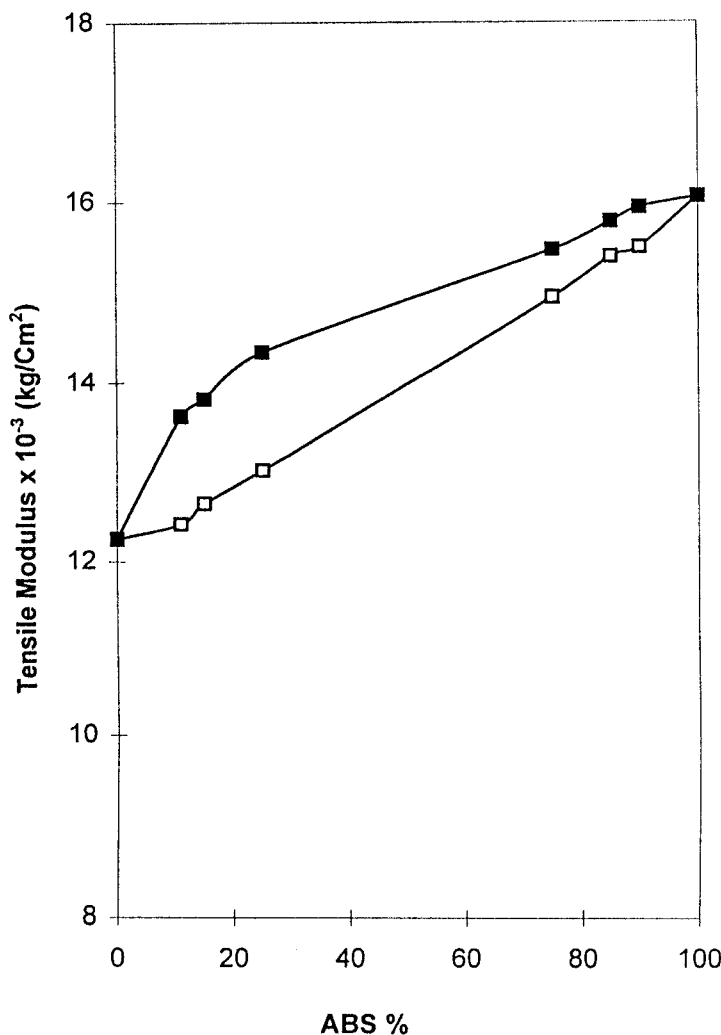
Figure 5 Tensile modulus of PP/ABS blends: PP/ABS (□) and PP/ABS/2.5% PP-*g*-acrylic acid (■).

For the blends in which inclusions are loosely bound, they contribute little to the overall modulus of blends (E_b). Hence, the observed modulus of blends is mainly due to the matrix, and the contribution of E_d is negligible ($E_d \cong 0$). As a result, eq. (1) is reduced to

$$\frac{1}{E_b} = \frac{1}{E_m} \left[1 + \frac{\varnothing_d 15(1 - \upsilon_m)}{(7 - 5\upsilon_m)\varnothing_m} \right] \qquad (2)$$

In Kerner's model, only particle–matrix interaction was considered, but no particle–particle interaction was considered. Therefore, Kerner's model was modified by Nielsen[29] to consider particle–particle interaction in the blend. According to Nielsen, for a rigid polymer dispersed in a rubbery matrix,

$$\frac{E_b}{E_m} = \frac{1 + AB\varnothing_d}{1 - B\psi\varnothing_d} \qquad (3)$$

where $B = (E_d/E_m - 1)/(E_d/E_m + A)$ and $\psi = 1 + (1 - \varnothing_{max}/\varnothing^2_{max})\varnothing_d$; for a rubbery polymer dispersed in a rigid matrix,

$$\frac{E_m}{E_b} = \frac{1 + AB_i\varnothing_d}{1 - B_i\psi\varnothing_d} \qquad (4)$$

where $B_i = (E_m/E_d - 1)/(E_m/E_d + A)$, and $\psi = 1 + (1 - \varnothing_{max}/\varnothing^2_{max})\varnothing_d$.

The constant $A = (7 - 5\nu_m)/(8 - 10\nu_m)$ for eq. (3) and $(8 - 10\nu_m)/(7 - 5\nu_m)$ for eq. (4); $\varnothing_{max}$ is the maximum packing volume and can be considered a scale of interaction between two phases. A
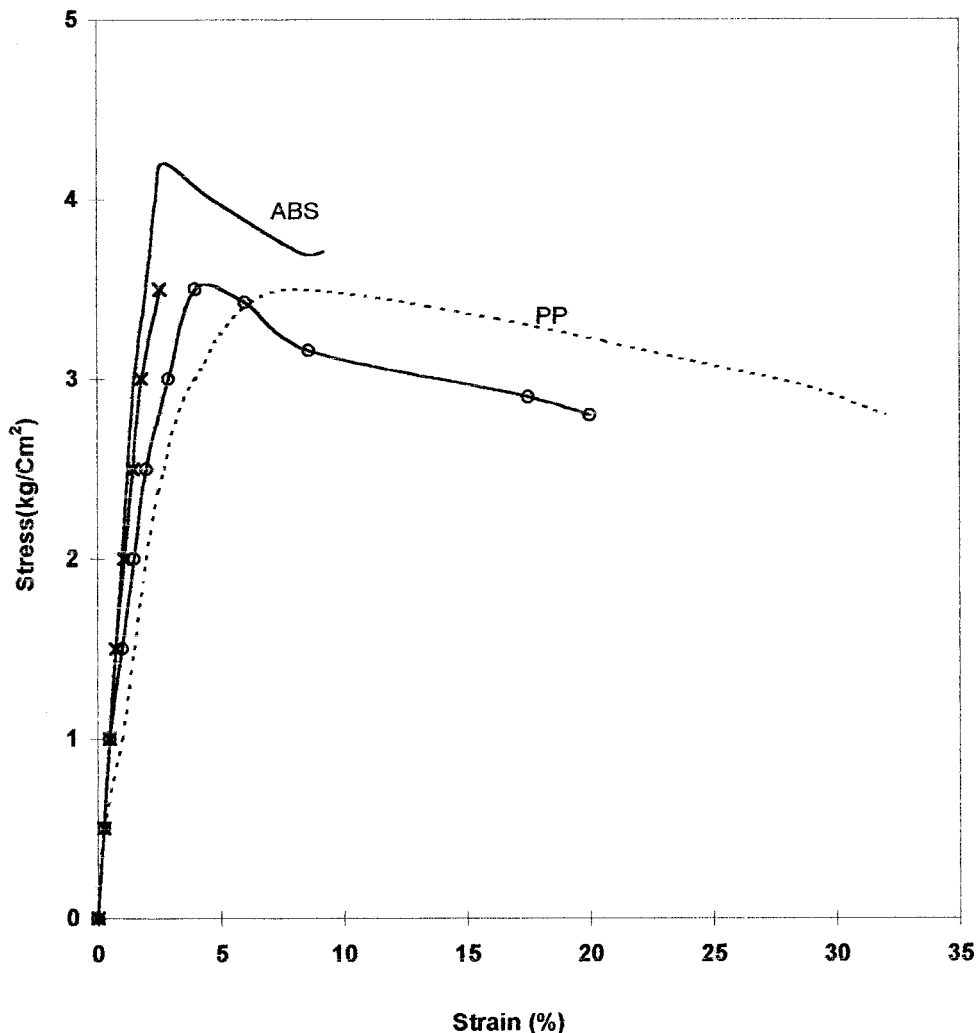
Figure 6 Stress–strain curves of PP/ABS blends: ABS (—), PP (· · ·), 90/10/2.5% PP-*g*-acrylic acid (○), and 75/25/2.5% PP-*g*-acrylic acid (×).

smaller value of $\varnothing_{max}$ represents a larger interface, and a large value of $\varnothing_{max}$ represents a smaller interface. The tensile modulus of the blends under study was calculated with these models and with the Poisson ratio v for PP and ABS as 0.35 and 0.39, respectively. The calculated tensile modulus values were compared with those obtained experimentally (Fig. 4).

It was observed that Kerner's model for loosely bound dispersion shows considerable deviation from the experimental values for binary and ternary blends. Hence, it can be assumed that some sort of adhesion/interaction exits even in binary blends. Because of the higher coefficient of thermal expansion of PP compared with that of ABS (1.7×10^{-4} k^{-1} and 0.8×10^{-4} k^{-1}, respectively, for PP and ABS), PP contracts more than ABS on

cooling. Thus, in PP-rich blends the ABS phase is tightly embedded in the PP matrix, imparting an increased tensile modulus even in binary blends. The application of Kerner's perfect adhesion model to the blends under study showed better agreement with the experimental data. The observed trend in ternary blends indicates better adhesion between phases in comparison with binary blends.

Because of the stiffening effect of ABS, the incorporation of ABS into PP increased the tensile modulus (Fig. 5). From the results, it can be observed that the tensile modulus of ternary blends was higher than that of binary blends.

Representative stress–strain curves for PP, ABS, binary PP/ABS, and ternary PP/ABS/PP-*g*-acrylic acid blends are given in Figure 6. With the
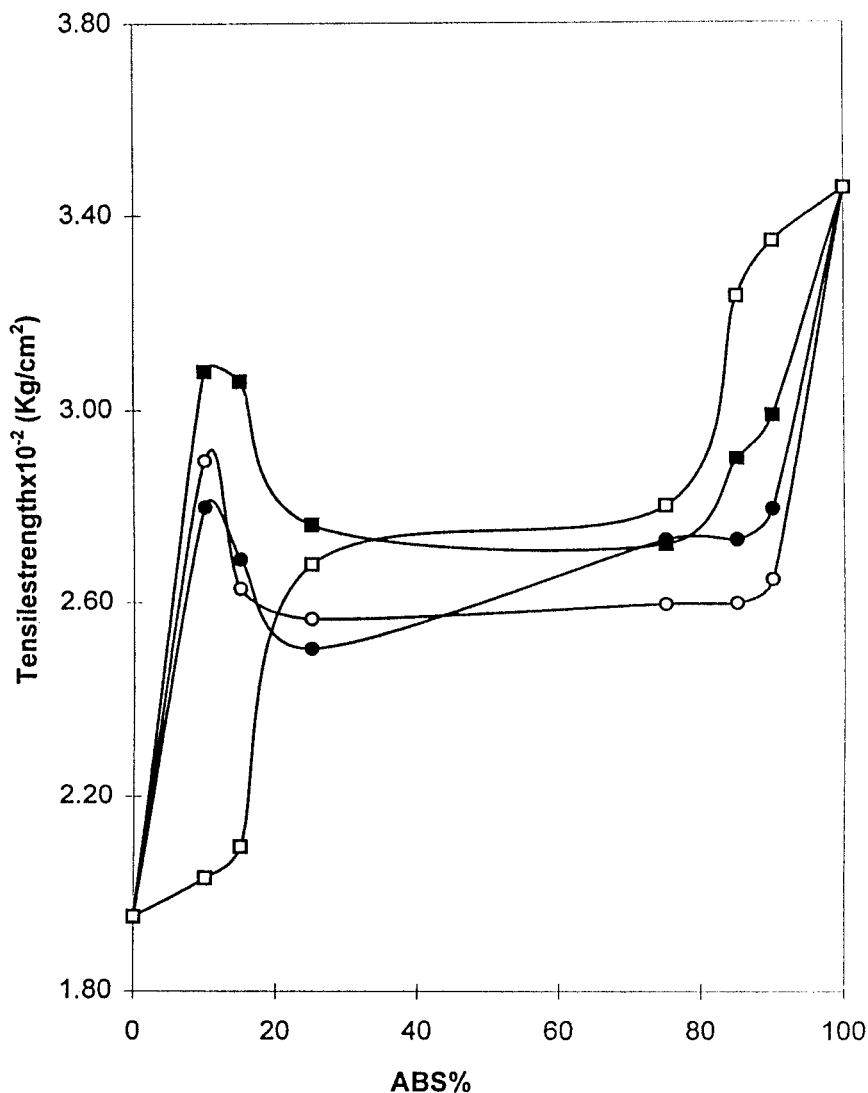
Figure 7 Tensile strength of PP/ABS blends: PP/ABS (□), PP/ABS/2.5% PP-*g*-acrylic acid (■), PP/ABS/5% PP-*g*-acrylic acid (○), and PP/ABS/7.5% PP-*g*-acrylic acid (●).

addition of ABS, the ductility of blends decreased even in ternary blends. The fracture of blends containing 10–15% ABS was ductile (Fig. 6), whereas brittle fracture was observed when the concentration of ABS was more than 20% in the blends.

Improvement in tensile strength with the addition of compatibilizer was observed only in the blends rich in PP (Fig. 7). Maximum tensile strength was observed for the blends containing 2.5% compatibilizer. However, in ABS-rich blends, the incorporation of PP decreased the tensile strength of the binary and ternary blends, and so the use of PP-*g*-acrylic acid in ABS-rich blends is not recommended.

Figure 8 illustrates the effect of ABS concentration on the impact strength of PP/ABS blends. In PP-rich binary blends, the incorporation of ABS did not improve the impact strength of blends.

The introduction of PP-*g*-acrylic acid as a compatibilizer in PP/ABS blends resulted in a considerable improvement in the impact strength of PP-rich blends. Only 5 wt % compatibilizer was needed for the improvement in these properties. A further increase in compatibilizer (7.5 wt %) gave lower impact strength. This may be attributed to the smaller particle size observed in blends containing 5 wt % compatibilizer [Fig. 2(c)], whereas dispersed particles were of a larger
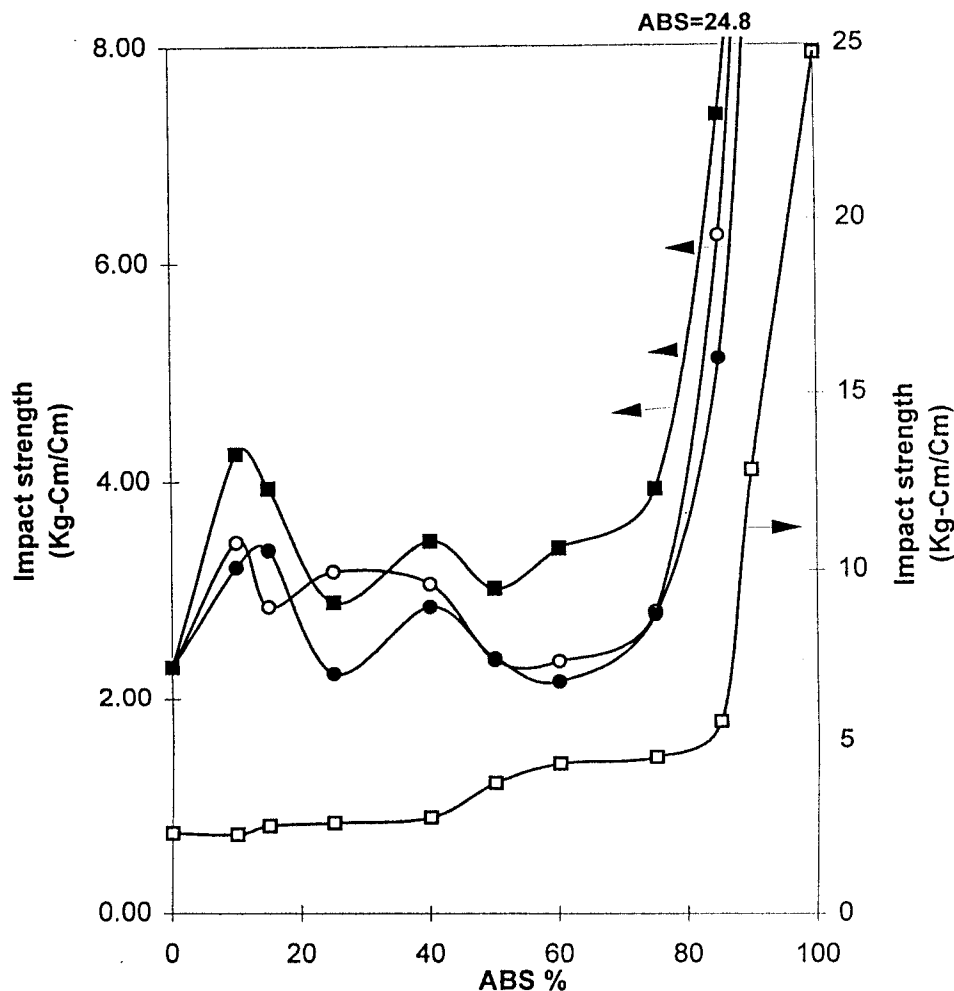
Figure 8   Impact strength of PP/ABS blends: PP/ABS (□), PP/ABS/2.5% PP-*g*-acrylic acid (○), PP/ABS/5% PP-*g*-acrylic acid (■), and PP/ABS/7.5% PP-*g*-acrylic acid PP/ABS (●).

size in the blends containing 7.5 wt % compatibilizer. A high thermal expansion coefficient of PP is also responsible for the improvement of impact strength in PP-rich region.

CONCLUSIONS

The use of PP-*g*-acrylic acid resulted in an improvement in Izod impact strength, tensile strength, and tensile modulus properties of PP/ABS blends. A 5% compatibilizer concentration was optimum for the improvement in these properties. Kerner's model for perfect adhesion was observed to be applicable only for PP-rich blends, whereas Nielsen's model was observed to be applicable to PP-rich and ABS-rich blends. The com-

patibilization of blends resulted in a smaller size dispersed phase (ABS) in PP-rich blends.

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