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Compatibilized polymer blends of isotactic polypropylene and styrene–maleic anhydride copolymer

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Compatibilized polymer blends of isotactic polypropylene, styrene–maleic anhydride copolymer (SMA) and two amino functionalized polyolefins—a rubbery amino functional ethylene propylene copolymer and an amino functional isotactic polypropylene—have been formulated over a wide composition range. Blends containing approximately 25% SMA have a morphology that consists of a continuous polyolefin matrix with a dispersed phase of micrometre-sized SMA particles. The amino polyolefins are believed to form graft polymers with SMA by an amidation reaction with the maleic anhydride. The blends have bulk properties such as impact strength and solvent resistance similar to polypropylene; however, their surface reactivity (e.g. adhesion of paint and polar substrates) is similar to that of SMA. The rheology of these blends is complex but typical of immiscible polymer blend systems.

(Keywords: polymer blends; styrene–maleic anhydride; polypropylene)

INTRODUCTION

The field of polymer blends is developing rapidly, both in terms of scientific understanding and commercial utility. Existing polymers can be used in blends and alloys to provide materials[1–4] with a combination of properties unattainable in any single polymer. A blend morphology with 0.1–5 μm diameter dispersed particles is usually required to attain most of the benefits. Structures significantly outside these limits either show only an average of component polymer properties or, more frequently, severe degradation in important properties. Within this range of particle size the physical properties (mechanical, transport or optical) of these materials depend crucially on the degree of dispersion. Thus the synergistic benefits of blending derive from the formation and retention of the appropriate blend morphology. Control of morphology is therefore control of polymer blend properties.

The long chain nature of polymers leads to two competing factors, one thermodynamic and the other kinetic, which affect the formation and stability of these micrometre-sized structures. First, the entropy of mixing for macromolecules is very small, so that most pairs of polymers are immiscible or insoluble in each other. Second, their viscosity also makes the dynamics of phase ripening of these mixtures very slow, so that complete phase separation of a blend takes a very long time. The combination of these two factors means that most polymer blends, made by conventional mixing (e.g. extruders, Banbury mixers) of either bulk polymers or solutions of polymers, have a morphology of phase domains separated on the scale of 0.1–50 μm.

Polymer blends containing mixtures of isotactic polypropylene (PP) and engineering thermoplastics[5–9] (ETP; e.g. polyamides) or inorganic fillers are gradually gaining wide acceptance. These blends ideally combine the high use temperature of ETP resins with the economy, durability and the easy processability of polypropylene. Useful blends can be made over the entire composition range. Blends with a majority of isotactic polypropylene can have bulk and surface reactivity characteristic of an ETP while the processability, mechanical and thermal properties of the blends are similar to those of isotactic polypropylene. Blends with a majority of ETP present are expected to be an economical version of the ETP with undiminished chemical, thermal and mechanical properties.

A significant barrier to the development and use of these blends is the inherent lack of compatibility between the ETP and isotactic polypropylene. This is due to the non-polar nature of the polyolefin in contrast to the more polar ETP. Favourable dipolar interactions in the ETP are lost or weakened when the polypropylene is used to dilute the matrix. This absence of compatibility leads to blends which are both poorly dispersed with large domain sizes (typically 50–100 μm) and have very little adhesion between the polyolefin and the ETP phases. The combination of these factors leads to blends which have poor mechanical properties (low impact strength and tensile elongation) and inhomogeneous attributes (e.g. surface *versus* bulk polarity).

A way to control the morphology is through the use of

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Table 1 Polymer characteristics

Polymer	Wt% MA[a]	Amine content	Molecular weight $\times 10^3$ M_w	M_n	M_w/M_n	Density (g cm^{-3})	Viscosity[b] (Pa s $\times 10^4$) 200°C	250°C	Melt flow rate[c] (g/10 min) 180°C	230°C
SMA[d]	14	–	180[e]	90	2.0	1.06	–	–	0.16	21
Amine-EP[f]		0.3[g]	88	44	2.0	0.86	1.75	1.40	2.8	20
Amine-PP		0.4[h]		–	–	0.90	–	–	–	–
PP	–	–		–		0.90	–	–	–	0.40

[a] MA, maleic anhydride

[b] Measured at $10\,s^{-1}$

[c] Shear stress at die wall = 8.9 Pa, strain rate = $50\,s^{-1}$ at 20 MFR, 10 kg

[d] SMA resins from ARCO Chemical Co.

[e] Molecular weights of SMA resin obtained from ref. 28

[f] Ethylene content = 44 wt%; Mooney viscosity: M_L (1 + 4) 125° = 20

[g] Mol% (primary amine)

[h] Wt% (secondary amine: *N*-methyl 1,3-propanediamine)

'compatibilizers' which are block or graft polymers capable of acting as interfacial agents in polymer blends[2,10–12]. Usually, but not always, the blocks in the compatibilizer are identical with the blend components. These molecules are expected to be found at the interface of dissimilar polymers[2,11,13] because part of the compatibilizer molecule is miscible with one component[14], and part with the other. There are two effects of the presence of the compatibilizer at the interface: the adhesion between the phases increases[2,13,14] and the interfacial tension, γ, between them decreases[2,15]. At some level of compatibilizer incorporation, γ may drop to zero, so there is some finite, equilibrium size of the domains for a given amount of compatibilizer. Even when γ is nonzero, the fact that it is lowered means that a finer dispersion of the phases can be achieved during intensive mixing[16–19]. The presence of the compatibilizer at the surface of the particles of the blend may also reduce phase growth by a steric stabilization mechanism[20]. The smaller phase size plus the increased phase adhesion results in improved physical properties such as impact strength[11,21,22] and tensile strength[23]. The stress amplification for interfacial failure increases in direct proportion to the diameter of the particle.

The difficulty in the synthesis of compatibilizers for blends of polypropylene and engineering thermoplastics is in the different chemistry of polymerization for these polymers. Copolymerization of propylene with the monomers used for ETPs is difficult since polypropylene is made by a Ziegler polymerization procedure which is easily poisoned by the presence of the polar monomers used for the ETP. Alternative polymerization techniques for the synthesis of PP are currently unavailable. The synthesis of a block polymer by sequential polymerization of propylene followed by the ETP monomer has been more mythical than real. Grafting of an ETP to an isotactic polypropylene backbone has been inhibited by lack of a suitable reactive site on the PP backbone. A solution to this synthetic dilemma is the generation of reactive sites on the polypropylene backbone by grafting a suitable reactive moiety (e.g. maleic anhydride). This can then be used directly or chemically modified to yield a reactive site to react with the engineering thermoplastic of choice.

The synthetic target in this study was a graft copolymer of styrene–maleic anhydride (SMA) and isotactic PP which is made *in situ* by the reaction of amine-functionalized PP with the maleic anhydride functionality of SMA. The amine functional PP is made by first grafting a maleic anhydride group onto the PP in a free-radical process, followed by imidization with an excess of a diamine. This leads to a pendent amine functionality on the PP. In our studies we found that the mechanical properties (e.g. tensile elongation, impact strength) of the blends were significantly improved on addition of a third component, an ethylene propylene (EP) copolymer containing amine functionality. We are unable to explain clearly the role of the amine-functional EP polymer, except to note that this elastomer reacts with SMA and has a low interfacial tension with the PP matrix. It is possible that addition of a 'compatible' rubber to both of the thermoplastic phases leads to improvements in the mechanical properties indicated above.

EXPERIMENTAL

Polymer blend preparation

Table 1 shows the polymers used in this study. The functionalized ethylene propylene elastomer has a primary amine functionality incorporated by a synthetic procedure we have described earlier[24]. The functionalized polypropylene resin contains a secondary amine functionality introduced by reacting maleic anhydride (MA)-grafted PP (0.45 wt% MA by i.r.) with a 100% molar excess of an unsymmetrical diamine, *N*-methyl-1,3-propanediamine. This mixture is passed through a 30 mm Welding Engineers non-intermeshing twin-screw extruder at 185 ± 15°C where the primary amine preferentially reacts with the anhydride functionality leaving the secondary amine pendent from the polyolefin. Excess diamine is removed under vacuum through ports near the discharge of the extruder.

Polymer blends of PP, SMA and amino polyolefins were prepared by reacting the individual components in a 300 cm^3 Brabender Plasticorder internal mixer for 4 min at temperatures less than 220°C. The order of adding the component polymers influenced the morphology. Equivalent results were obtained when the blending was performed in a 'B' Banbury internal mixer. Component addition effects are discussed below. About 0.3 wt% of Irganox 1076, an antioxidant, was added to the blend prior to mixing to minimize oxidative degradation. These polymer blends were injection moulded into test bars (3 mm thick) on a 20 ton Boy injection machine. A nozzle temperature of 210 °C and a total cycle time of 28 s (injection time = 8 s and cooling time = 20 s) was used for the moulding operation. The mould was not water chilled and its temperature was equilibrated at 30–45°C.

FT*i.r. analysis*

Evidence of chemical reaction between the components was obtained through Fourier transform infra-red analysis (*FT*i.r.). Films for *FT*i.r. analysis were prepared by compression moulding polymer samples for 10 min at a temperature of 200°C and pressure of 4.8 MPa. The thickness of the films ranged from 0.17 to 0.35 mm. Surface composition of the polymer blend was determined from injection-moulded test specimens using attenuated total reflectance (ATR) *FT*i.r. spectra.

Thermal analysis

Thermal properties of the PP/SMA polymer blend and the component polymers were measured with a Polymer Laboratories Dynamic Mechanical Thermal Analysis (DMTA) instrument. Test data were collected from −100°C to 150°C using a scanning rate of $2°C\,min^{-1}$ and a frequency of 3 Hz. Samples were run in a dual cantilever bending mode arrangement. The tangent δ and storage modulus were measured.

Microscopy

Morphology of the samples was examined with a transmission electron microscope (TEM; Hitachi 500). The specimens were cryomicrotomed at −100°C after staining for 16 h with ruthenium tetroxide (RuO_4) vapour from 0.5 wt% aqueous solution. Such staining leads to deposition of ruthenium in all of the amorphous, non-glassy regions of the blend with particularly heavy stain at the boundaries of the crystalline lamellae of polyolefins, and at all polymer–polymer interfaces.

Mechanical property measurements

The test bars of the polymer blends were evaluated in the following ASTM tests: (1) Izod impact strength—ASTM D 256, Method A; (2) flexural modulus—ASTM D 790, Method 1; (3) tensile strength and elongation—ASTM D 638; and (4) heat distortion temperature at 1.82 MPa—ASTM D 1637. Results reported here are the average values of at least five test samples. The notched Izod impact test at subambient temperatures was performed on samples cooled in an isopropanol bath, chilled with dry ice. The chilled test samples were rapidly mounted and tested in the impact tester before any significant warming of the specimen could occur. The heat distortion temperature (HDT) measurement unit was calibrated against standard polycarbonate specimens of known HDT values. Temperature control of this unit was ±3°C.

Lap shear adhesion experiments

The adhesion of PP/SMA polymer blend to other polar substrates (e.g. acrylonitrile–butadiene–styrene (ABS)) was evaluated with a lap shear test. The lap shear deformation tests the interface of two materials in a composite formed by laminating a portion of the two materials. *Figure 1* shows a schematic representation of this technique. Our specimen was prepared by offset compression moulding a bar-shaped PP/SMA blend specimen measuring $100 \times 12 \times 3\,mm^3$ over a similarly shaped ABS sample. The overlap of the two specimens was 25 mm. The laminates were pressed at 230°C in a compression mould at 1.4 MPa for 10 min. This laminated assembly was extended to failure in tension on an Instron tensile tester, and the failure tensile stress and the location and nature of the failure was recorded.

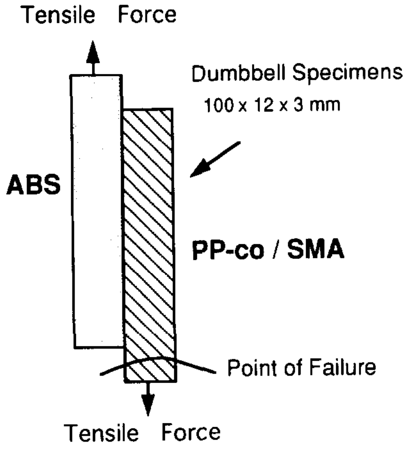


Figure 1 Schematic representation of sample arrangement for lap shear adhesion test

Paint adhesion experiments

The paint retention of PP/SMA compositions was evaluated using a paint peel test. Injection-moulded plaques ($100 \times 38 \times 3\,mm^3$) were wiped clean with isopropanol. They were coated with Morton International 89025-W7E paint and dried at 21°C for 144 h prior to testing. Experiments were also conducted using a primer (Morton International P-46). Paint adhesion on the dried plaques was measured with a peel test conforming to GM 4350 Class CO Interior Initial Adhesion test. The test procedure involved scratching a letter X on the surface of the painted plaque and attempting to remove paint from the boundaries of the scratch with adhesive tape. Failure is indicated by a significant amount of paint lifting off the surface and adhering to the tape.

Rheology

Rheological properties of the PP/SMA systems varying in PP/SMA ratio were measured at 250°C from dynamic oscillations in a Rheometrics Mechanical Spectrometer, System IV at constant strain amplitude of 10% using a parallel plate geometry. Melt flow rate was measured using standard equipment (Ceast) at several temperatures.

RESULTS AND DISCUSSION

Compatibilization

Two amino functional polyolefins are used—(a) amine functionalized poly(*co*(ethylene propylene)) elastomer (amine-EP) and (b) amine-*g*-isotactic polypropylene (amine-PP). The amine-EP is made by the incorporation of 5-norbornene-2-methyl amine into the EP backbone. This leaves a pendent primary amine functionality on the

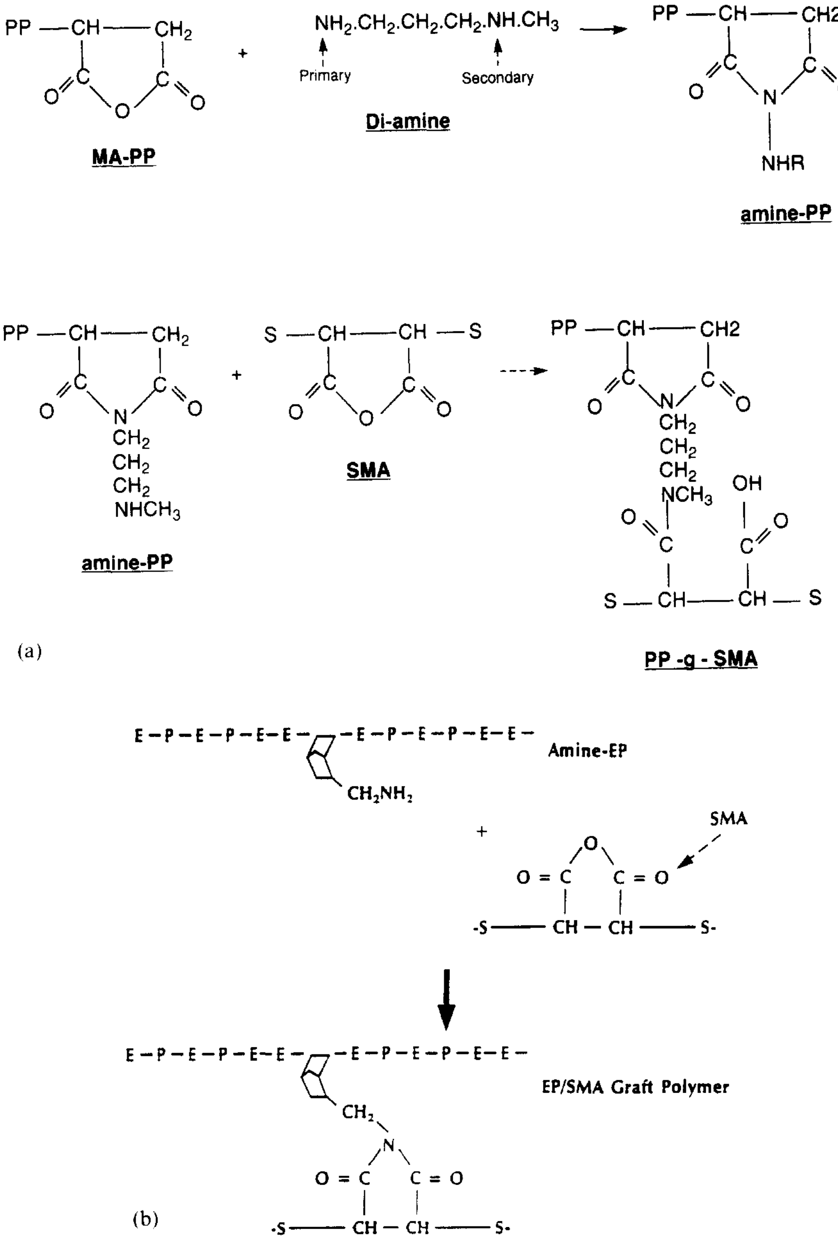


Figure 2 Reaction scheme illustrating formation of compatibilizers: (a) PP-*g*-SMA; (b) EP-*g*-SMA

EP polymer. The amine-PP is formed in a two-step synthesis. In the first step maleic anhydride (MA) is grafted to polypropylene at 170–190°C using a peroxide free-radical initiator. One would expect the radical sites to be randomly located along the polypropylene molecule[25]; however, there is evidence (molecular weight decrease) for chain scission at the grafting site and this should lead to terminal anhydride functionalization for much of the polypropylene. We expect that most of the polypropylene has only a single MA graft per polymer molecule. The interchain compositional distribution of the anhydride groups is not uniform since a significant amount of highly functionalized oligomeric fraction is present. The maleic anhydride-grafted PP polymer is reacted subsequently with a nonsymmetrical diamine, *N*-methyl-1,3-propanediamine, as shown in *Figure 2a*. In the presence of excess amine (typically 100% stoichiometric excess), the primary amine group in the diamine molecule preferentially reacts with the succinic anhydride grafted on PP to form an imide, leaving the secondary amine as a pendent functionality. Since the unsaturation in the maleic anhydride is lost upon grafting it is referred to as succinic anhydride, and it has the chemical reactivity of the saturated acid.

Two graft polymers are responsible for the compatibilization of dissimilar polymers in the blend. These are PP-*g*-SMA and EP-*g*-SMA; they are formed by the reaction of the amine functionality on the polyolefins with the anhydride functionality on the SMA. *Figure 2a* illustrates the formation of PP-*g*-SMA graft polymer. The secondary amine functionality in amine-PP reacts with MA groups in SMA to form an amide linkage. The formation of the EP-*g*-SMA graft polymer is shown in *Figure 2b*. In this case the primary amine moiety in amine-EP reacts with SMA to form an imide.

The amidation/imidation reactions are conveniently

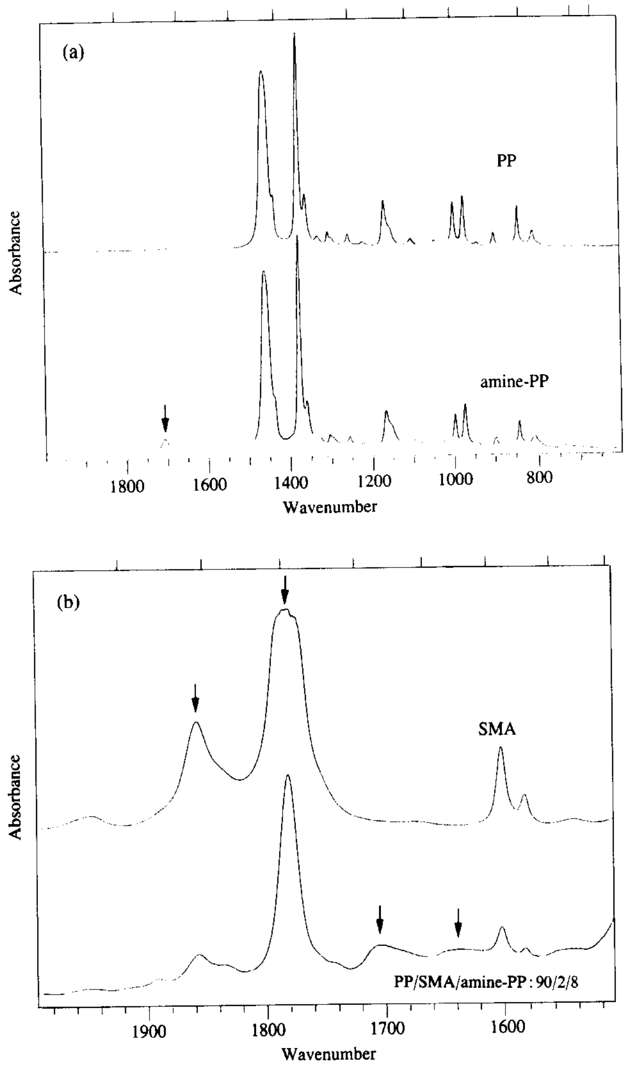


Figure 3 *FT*i.r. spectra of: (a) PP and amine-PP polymers; (b) SMA resin and PP/SMA/amine-PP polymer blend

monitored using i.r. in the carbonyl region. For the composition and blend ratios of SMA and amine functionalized polyolefins that we have used, reaction of only 2–5% of the maleic anhydride consumes all the amine groups in the polyolefins. The diminution of the maleic anhydride band at 1782 cm^{-1} is too small to be observed. However, the reaction does lead to the formation of the imide/amide group linking SMA to the amine-EP/amine-PP respectively, which can be observed in the i.r.

The interpretation of the i.r. spectra is complicated for the PP-*g*-SMA since it contains additional carbonyl resonances from the grafting of maleic anhydride and the initial reaction with the diamine. *Figure 3a* shows the *FT*i.r. spectra for PP and the amine-PP graft polymer. The grafting of maleic anhydride to PP introduces carbonyl resonances at 1782 and 1856 cm^{-1}. These absorption bands are characteristic of maleic anhydride and can be seen more clearly in the spectrum of SMA shown in *Figure 3b*. The reaction of maleic anhydride-grafted PP with a primary amine tip of the diamine leads to the formation of a new carbonyl absorption band at 1705 cm^{-1} (*Figure 3a*) which is characteristic of imides[26]. This transformation is also accompanied by the complete loss of absorption bands at 1782 and 1857 cm^{-1} (precursor PP-*g*-MA not shown) in the amine-PP spectrum. This indicates that all the succinic anhydride groups have been reacted and converted to maleimide while the terminal secondary amine functionality on the diamine is available for reaction with the SMA. *Figure 3b* also shows the *FT*i.r. spectra for the PP/SMA/amine-PP ternary blend. The spectrum of a PP/SMA blend shows all the characteristic absorption bands corresponding to its principal components—PP (1378 cm^{-1}), amine-PP (imide: 1708 cm^{-1}) and SMA (anhydride: 1782 and 1857 cm^{-1}). In addition, a new band at 1638 cm^{-1} appears: this is due to amide groups[27] formed during the condensation reaction of anhydride in SMA and the secondary amine in amine-PP. The anticipated free carboxylic acid formed from this amidation is not observed: we presume it is obscured under the bands due to SMA.

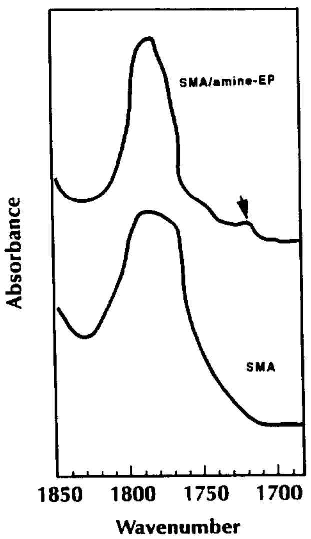


Figure 4 *FT*i.r. spectra of SMA resin and SMA/amine-EP polymer blend

The *FT*i.r. spectrum for the SMA/amine-EP blend is much less complicated since the only new carbonyl resonances are those formed by the formation of the imide at 1710 cm^{-1}, as shown in *Figure 4*. Differential solvent extraction experiments of the SMA/amine-EP blends that confirm and quantify the graft polymer in the blend have been reported earlier[28]. Similar extraction experiments were repeated in this study on a 50/50 mixture of SMA and PP or amine-PP. About 5 g of the compounded polymer sample was ground into fine pellets (1 mm diameter) and extracted with 500 ml of refluxing xylene at 120°C. After 10 h of extraction, the experiment was terminated, and the xylene solution was allowed to cool for 12 h at room temperature (21°C) to precipitate the PP fraction in the blend. This fraction is insoluble in xylene at 21°C. The precipitate was removed from the solvent through vacuum filtration, dried for 12 h at 85°C in a vacuum oven and pressed into a thin film (0.05 mm) for *FT*i.r. analysis. Absorption bands identifiable with PP (1371 cm^{-1}) and SMA (1782 cm^{-1}) were used in the analysis. Our experiments show that the non-reactive blend of SMA/PP dissolved completely in refluxing xylene with no insoluble gel. Analysis of the xylene precipitate from this blend showed a composition of 95% PP and 5% SMA. This compositional distribution is different in the reactive blend of SMA and amine-PP. The reactive mixture contained 13% insoluble gel. This loose gel formed either during the extraction experiment or compounding is fragile enough not to prevent flow of the polymer blend during processing. It is probably not a part of the continuous PP phase. Examination of the xylene-insoluble fraction showed a composition of 83% PP and 17% SMA. The increased SMA concentration in the xylene precipitate is a consequence of the extent of grafting reaction between the amine-PP and SMA segments. The data on SMA/PP together with our previous results of SMA/EP[28] illustrate that the amount of graft polymer formed in these systems is relatively small, and typically less than 10% of either polymer phase is involved in the grafting reaction.

In compatibilized blends the PP and SMA are immiscible. This can be verified by differential mechanical thermal analysis (d.m.t.a.) measurements. The variation of tangent δ with temperature is obtained from d.m.t.a. This is shown in *Figure 5* for the compatibilized PP/SMA blends. From the d.m.t.a. results we observe that the blends possess the individual glass transition temperatures (T_g) of the component polymers, as expected of an immiscible polymer blend system. There is no significant shift in the EP or PP component T_g after addition of the compatibilizers. The T_g of the SMA component could not be recorded in the instrument since the specimen softened significantly at higher temperatures making the modulus too low to be measured with the sample geometry chosen. Previous d.s.c. studies[28] indicate that the T_g of SMA polymer is 125°C, and in the blend its glass transition temperature remains unchanged from the pure polymer value.

Morphology

The TEM images of the PP/SMA polymer blend specimens showing the effect of compatibilizer on the blend morphology are provided in *Figures 6a* to *e*. The specimens were stained with RuO_4 on a smooth cut (−100°C) surface before thin sections were microtomed for TEM. This brings out much better contrast than staining microtomed slices. The slices are approximately 50–100 μm thick.

Figure 6a shows the morphology of the PP/SMA (70/30 weight ratio) blend without compatiblizers. The dispersion of SMA in the PP matrix is poor, with large, uneven zones of SMA. The dispersed SMA particles are elliptically oriented, and the particle size is typically greater than 10 μm in length. The addition of amine-PP (6 wt%) to the PP/SMA blend of *Figure 6a* leads to a much better dispersion of the SMA phase (*Figure 6b*). The SMA particles are almost spherical and their size is reduced to the range 0.5–1.5 μm. Smaller particles of less than 0.2 μm are also observed. It is tempting to postulate that the dark areas at the particle interface represent the PP/SMA graft polymer. However, interfaces in general appear to pick up RuO_4 stain better than a homogeneous polymer phase. For instance, in *Figure 6a*, where no graft polymer is formed the PP/SMA interface is also stained dark. A similar result was observed in a previous study while examining the morphology of a binary blend of SMA and high-density polyethylene without compatibilizer[29]. *Figure 6c* shows the morphology of the PP/SMA/amine-EP (65/19/16 weight ratio) three-component blend. The compatibilizer resides predominantly in the PP matrix but tends to cluster around SMA. The morphology of SMA in this blend is similar to the binary PP/SMA system of *Figure 6a*, but the particle size is smaller. The particles are elliptical and oriented and are approximately 5 μm in their longitudinal dimension. A few smaller particles of 0.5 μm dimension are also observed, and they are engulfed by amine-EP.

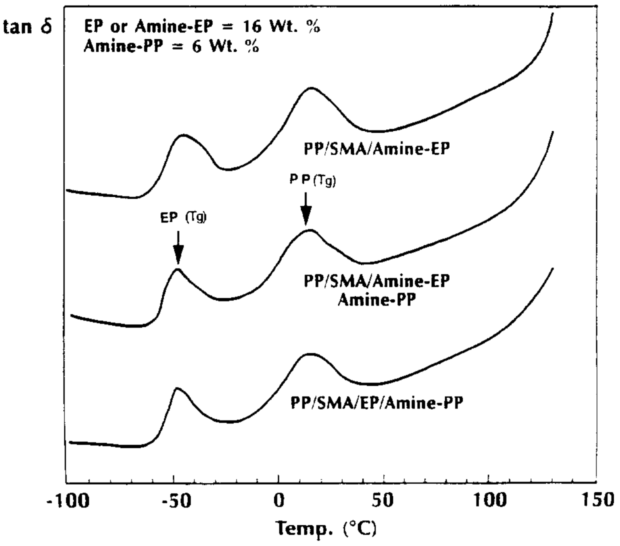


Figure 5 D.m.t.a. traces of PP/SMA/polyolefin blends

Figure 6d shows the morphology of the four-component PP/SMA/amine-EP/amine-PP (56/24/15/5 weight ratio) compound prepared in a single-step compounding where all four components are blended together. This is similar to *Figure 6c* since there is very little sub-inclusion of the polyolefin phase in SMA. The compatibilizer (amine-EP + amine-PP) is located mostly at the SMA/PP interface. The SMA particles are smaller than in *Figure 6c*, and range in domain size from 0.5 to 3 μm. Very small particles of less than 0.2 μm also appear which are surrounded by the compatibilizer. *Figure 6e* shows the morphology of the four-component PP/SMA composition of *Figure 6d*, but prepared using two-step compounding. SMA and amine-EP were blended initially. To this mixture PP and amine-PP were added in a second mixing step. The final blend composition was identical to the composition prepared in the one-step process. The morphology of this blend is significantly different from the one-step mix of *Figure 6d*. The SMA phase contains sub-inclusions of polyolefin particles. We postulate that this sub-inclusion is amine-EP, based on our experience of the morphology of the ternary blends. It is difficult to distinguish between amine-EP and amine-PP in these blends since there are no known available differential staining methods. The particle size of the dispersed phase ranges from 0.5 to 4 μm. This sub-inclusion of compatibilizer in SMA appears to increase the SMA particle size.

The morphology of the four-component PP/SMA composition produced in one-step mixing is without sub-inclusions of polyolefin inside SMA. In a two-step mixing process, we produce in the first step a 'locked in' morphology of the amine-EP compatibilizer in SMA through the formation of a EP-*g*-SMA graft polymer. The particle size of the amine-EP in SMA is reduced to the range 0.5–3 μm[29]. This morphology is stable and in subsequent compounding does not revert to the configuration shown in *Figure 6d.* Our results indicate that the mechanical properties measured at 21°C (notched Izod impact strength, tensile strength) of the four-component PP/SMA system is sensitive to the composition and the relative amounts of the four components, but is insensitive to the mixing protocol and hence the morphology of the blend. A possible explanation for this phenomenon could be attributed to the inherently high toughness of the polypropylene matrix (at 21°C) which dominates the blend properties in a compatibilized system, making the Izod impact behaviour insensitive to changes in morphology. Additional impact testing at 0°C (below the T_g of polypropylene) of the blends shown in *Figures 6d* and *e* shows that the 'locked-in' morphology with the compatibilizer forming a sub-inclusion in the SMA phase is the preferred architecture and results in enhanced impact strength. This complex morphology of an 'engulfed' polymer component in a dispersed polymer phase has been observed and discussed in other polymer blend systems by Hobbs *et al.*[30] (polycarbonate/polyethylene terephthalate blends) and also in our laboratory from studies on nylon/maleic anhydride-grafted EP compositions[31].

Mechanical properties

The variation of notched Izod impact strength (measured at 21°C) with SMA content in the PP/SMA blend is shown in *Figure 7a.* A high-impact PP copolymer resin with a notched Izod impact strength of 875 J m^{-1} was used as the polypropylene component. The SMA resin used in this study has a notched Izod impact strength of 16 J m^{-1}. Uncompatibilized blends of PP and SMA have poor impact properties ($<20\,\mathrm{J\,m^{-1}}$) over a wide range of SMA composition extending upward in content from 25 wt% SMA, and their impact performance falls well below the line of averages. The blends of PP and SMA formulated with a single compatibilizer (either amine-EP or amine-PP) also have low impact strengths ($<100\,\mathrm{J\,m^{-1}}$. When both amine-EP and amine-PP compatibilizers are used there is substantial improvement in the impact strength over the binary and ternary systems, and the performance of the four-component compositions are closer and in some cases better than the expected averages. The four-component PP/SMA polymer blend containing 25 wt% SMA has a notched Izod impact strength of 775 J m^{-1}: this is one of the toughest blends we have synthesized. *Figure 7b* shows the results of varying the relative levels of the amine-EP and amine-PP compatibilizers for best impact performance. The ratio of PP to SMA was kept constant at 70/30 in all the compositions and the total modifier (amine-EP + amine-PP) content was maintained at 20 wt%. Our results indicate that the maximum in the notched Izod impact strength (from measurements at 21°C and −20°C) occurs at a 3:1 ratio of amine-EP to amine-PP. The influence of varying modifier level on the impact strength of the PP/SMA (70/30) blend is shown in *Figure 7c.* The ratio of amine-EP/amine-PP was maintained at the optimal 3:1 level in all the compounds. Our data demonstrate that significant impact improvements occur when the total modifier contents exceeds 15 wt%; however, improvements in impact strength at higher levels of amine-polyolefins is relatively modest.

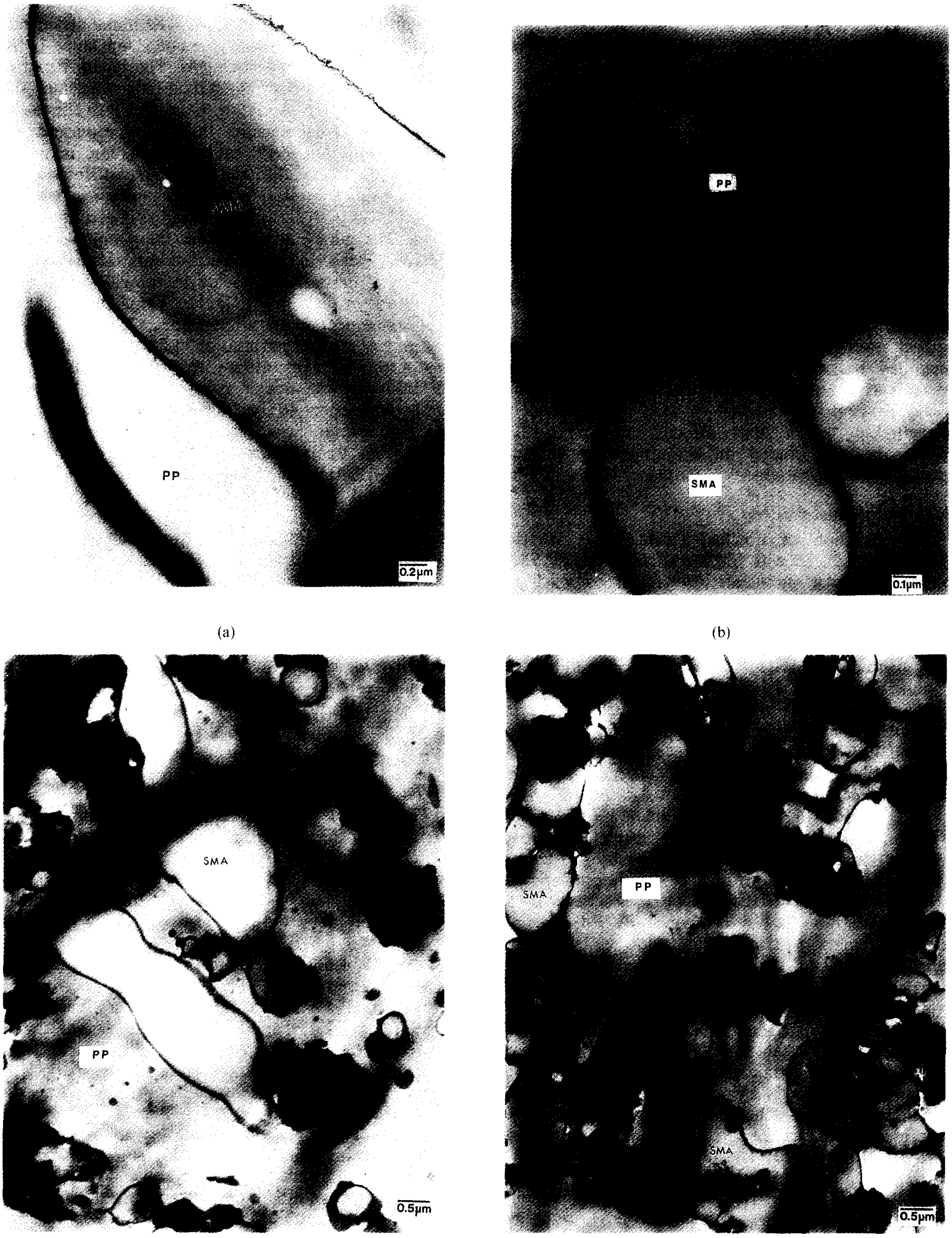
The most significant effect of compatibilization is in the stress–strain response of these blends. These data are shown in *Figure 8a* for the PP/SMA compounds having a constant PP/SMA (70/30) ratio. The initial strain rate was 0.02 s^{-1} at a cross-head speed of 51 mm min^{-1} in the room temperature measurements. The binary blend of PP and SMA has poor elongation (5% extension) and shows no yielding. Addition of amine-EP to this blend lowers the tensile strength through incorporation of rubber, while amine-PP causes an increase in tensile strength, probably through reducing particle size and thus stress intensity and by increasing interfacial tension. However, in both cases only marginal improvements in elongation can be achieved over the uncompatibilized PP/SMA blend. In the presence of both compatibilizers there is a substantial increase in the elongation with significant yielding prior to failure. The elongation of the four-component composition is 85%.

Figure 8b shows the variation in flexural modulus and heat distortion temperature with modifier content in the PP/SMA four-component composition. The properties of the component PP and SMA resins are also shown in the same figure for comparison. The flexural modulus of PP impact copolymer is 910 MPa and that of SMA resin is 3050 MPa. In the absence of compatibilizer the modulus of the binary PP/SMA (70/30) blend is 1450 MPa. The stiffer SMA blend component enhances the modulus. However, with the addition of compatibilizer the modulus decreases owing to the incorporation of the elastomeric amine-EP. The decrease in modulus is not severe enough to restrict the use of the compound for engineering applications. The heat distortion temperature (HDT) measured at 1.82 MPa (264 psi) load also shows a similar variation with modifier content. The HDT values for PP and SMA are 50°C and 103°C, respectively. The HDT of the uncompatibilized PP/SMA blend is 75°C and decreases to 58°C with 20 wt% modifier.

Surface properties

The presence of functional groups accessible to the surface is an important factor in the adhesion of these materials to paint and engineering plastics. This is promoted by the anhydride residues from SMA at the surface. The surface composition (more specifically composition near the surface to a depth of about 0.5 μm) was determined for injection-moulded compatibilized blends of PP and SMA by attenuated total reflectance techniques (ATR) on the *FT* i.r. spectrometer. This method is useful for this blend since PP and SMA have strong absorbances at different regions in the spectrum: the absorbance at 1378 cm^{-1} is used for PP while the SMA concentration was monitored by both the styrene absorbances at 700 cm^{-1} and maleic anhydride absorbances at 1790 cm^{-1} and 1840 cm^{-1}.

Data for analysis for several samples containing different ratios of PP and SMA are shown in *Figure 9* where the compositions of the bulk and surface are compared for both the maleic anhydride residues and the styrene residues of SMA to PP in the blend. These independent determinations show that there is not much difference in the composition of the bulk and the surface over a wide range of PP/SMA weight ratios. The tendency is for the surface 0.5 μm to be enriched in PP, but there are sufficient MA groups available near the



(a) (b)

(c) (d)

Figure 6 Transmission electron microscopy images of PP/SMA/amine polyolefin blends: (a) PP/SMA (70/30); (b) PP/SMA/amine-PP (73/21/6); (c) PP/SMA/amine-EP (65/19/16); (d) PP/SMA/amine-EP/amine-PP (56/24/15/5) compounded with simultaneous addition of all components; (e) PP/SMA/amine-EP/amine-PP (56/24/15/5) formulated from an SMA/amine-EP master batch

(e)

Figure 6 (continued)

surface for all useful compositions to provide adequate polar surface functionality for adhesion or painting. We also performed X-ray photoelectron spectroscopy (X.p.s.) to probe the surface of the PP/SMA composition to a shallower depth, e.g. 0–50 Å. These experiments did not provide conclusive results. Considerable silicone was detected owing to contamination during moulding. The surfaces were all enriched in polypropylene, and negligible concentration of carbonyl carbon associated with the MA moiety was detected at the 0–5 Å depth. In addition to olefin enhancement over the bulk concentration, the olefin itself segregates, with a tendency for the ethylene groups to be at the surface.

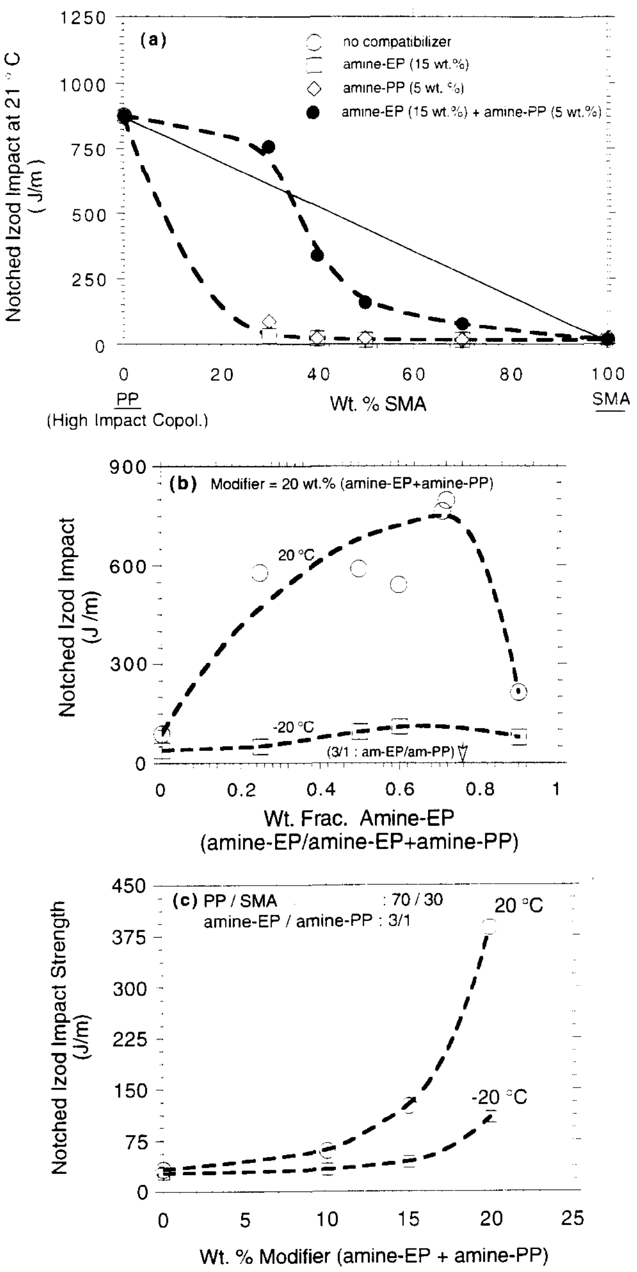


Figure 7 Variation of notched Izod impact properties in PP/SMA blends: (a) with SMA weight fraction; (b) at varying ratios of amine-EP to amine-PP; (c) with modifier levels

Adhesion characteristics

A limitation of non-polar polyolefin resins such as polypropylene has traditionally been the absence of adhesion to ETPs. Adhesion is particularly important in applications where polyolefins and polar materials are laminated together. The incorporation of SMA in PP facilitates adhesion to other substrates. We have evaluated the adhesion of PP/SMA compounds to ABS resins using the lap shear arrangement shown in *Figure 1*. These tests are a quantitative measure of the failure stress at the interface but a very qualitative measure of the inherent adhesion of the substrates that we intend to investigate here.

Figure 10 illustrates the failure stress measured from the lap shear test. Both PP/ABS and ABS/ABS laminates were used as control test samples. The non-polar PP impact copolymer shows no adhesion to ABS and delaminates upon removal from the mould. As expected, the ABS/ABS laminate had excellent adhesion properties. The PP/SMA sample shows good adhesion to the ABS substrate. Cohesive failure occurs in the PP/SMA specimen at the tensile strength of this material.

Paint adhesion properties of PP/SMA compositions

The adhesion of PP/SMA compounds to polar substrates extends to paints. Compositions containing varying SMA contents and modifier levels were assessed for paint adhesion in the absence of a primer or adhesion promoter. The compositions and the corresponding test results are provided in *Table 2*. The non-polar PP polymer will show no paint adhesion when painted without a primer, while the polar SMA resin can be painted with an adherent paint layer without using a primer. The four-component blends of PP/SMA (no. 3 in *Table 2*) containing 24 wt% SMA and 20 wt% modifier

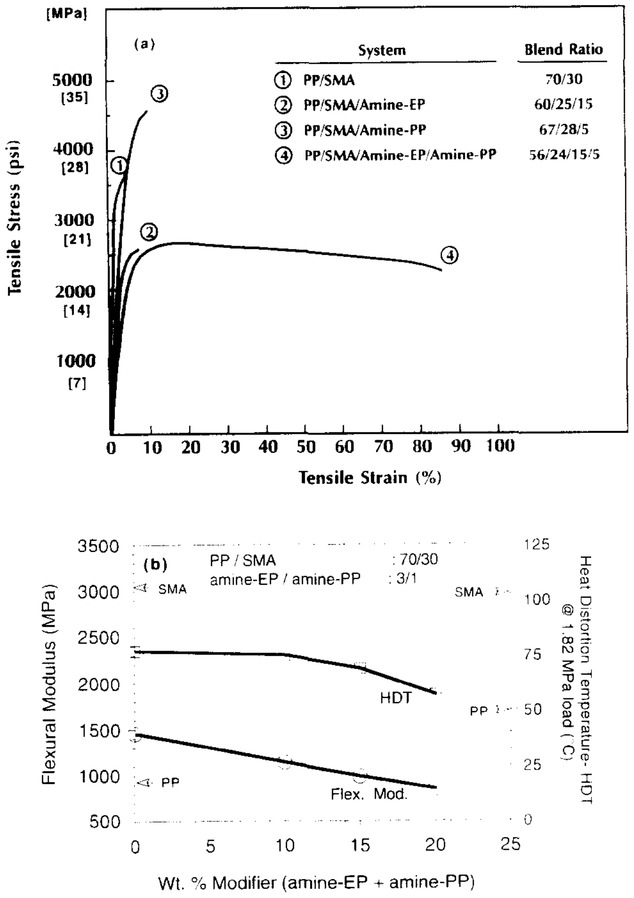


Figure 8 Mechanical properties of PP/SMA blends: (a) stress–strain response; (b) Variation of flexural modulus and heat distortion temperature at varying modifier levels

passed the paint adhesion test in the absence of a primer, with 99% of the surface area in the test specimen retaining the applied paint. The compositions with higher SMA contents (43 and 56 wt%: nos 4 and 5 in *Table 2*) also showed excellent paint adhesion (100% paint retention). However, lowering the modifier level and substituting the amine polyolefins with non-functional polymers had a detrimental effect on paint adhesion properties (nos 1 and 2 in *Table 2*). These formulations were not paintable without an adhesion promoter. Based on our data it appears that the threshold SMA concentration is about 25 wt% for paint retention.

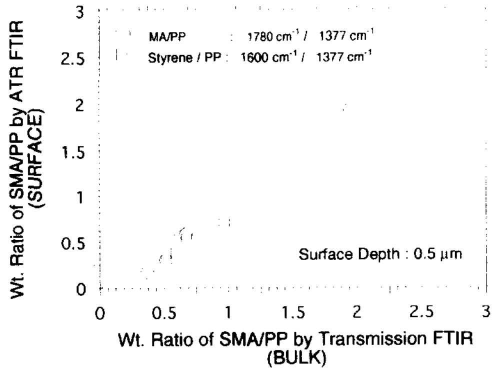


Figure 9 Correlation of surface composition with bulk composition in PP/SMA blends

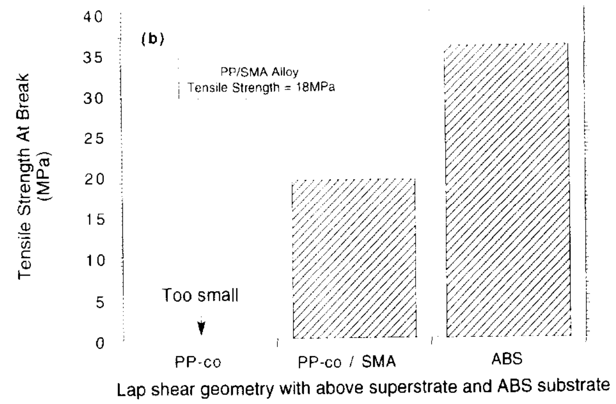


Figure 10 Adhesion evaluations of PP/SMA blend to various substrates using lap shear test

Blend rheology

Figure 11a shows the complex viscosity dependence on shear rate for SMA, PP and the PP/SMA polymer blends containing amine-EP (16 wt%) and amine-PP (6 wt%) compatibilizers. Both SMA and PP are non-Newtonian viscoelastic fluids, with the viscosity rising to a constant value at low shear rate. The compatibilized PP/SMA system shows an upturn in viscosity at low shear, which indicates the presence of a yield stress. This yield phenomenon observed in phase-separated multicomponent polymer blends can occur due to particle agglomeration of the dispersed blend component to form a network structure. This model was originally proposed by Munstedt[32] from rheological studies of ABS resins with varying butadiene contents. Yielding has been observed in other systems and well characterized by Utracki and Sammut in polystyrene/polyethylene[33] and polycarbonate/polyethylene[34] blends. *Figure 11b* shows the complex viscosity measured at two finite strain rates for the PP/SMA compositions of varying SMA contents but having a fixed (20 wt%) compatibilizer concentration. At low rates (10^{-2} s^{-1}) the blends deviate positively from the additive tie line, while at high shear (10^{2} s^{-1}) conditions this deviation is slightly negative. Negative deviations can occur because of slip at the component interface[3,34]. Our analysis shows that the rheological behaviour of the PP/SMA system is complex but typical of other immiscible polymer blends that do not contain a significant gel fraction.

The rheological properties of the blends can be described according to the Utracki[3,34] model from

Table 2 Paint adhesion evaluations of PP/SMA[a]

	Wt%				
No.	PP	SMA	EP/amine-EP/ amine-PP	Without primer	With primer[b]
1	63	27	4/2/4	Failed	Failed
2	60	26	7/4/3	Failed	Passed
3	56	24	0/15/5	Passed[c]	Passed
4	43	43	4/7/3	Passed	Passed
5	24	56	7/8/5	Passed	Passed

[a] Interior Initial Adhesion Test—GM 4350 Class CO
[b] Morton International P-46
[c] 99% retained on the surface

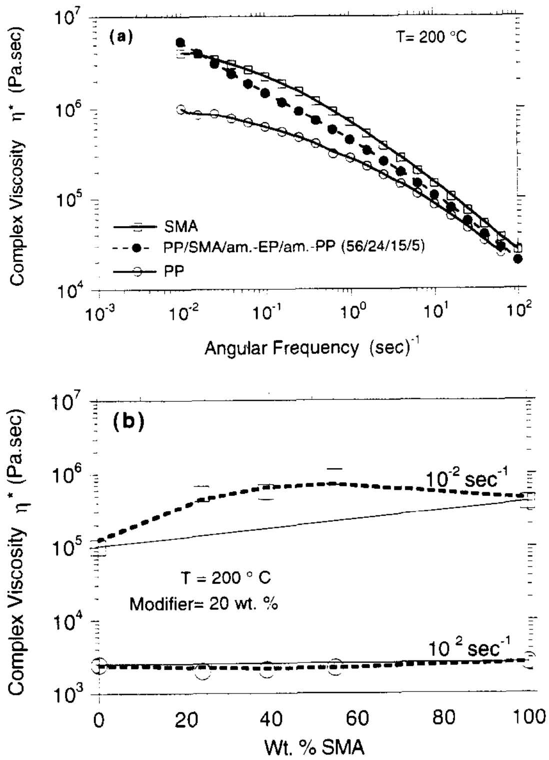


Figure 11 Rheological characteristics of PP/SMA blend and component polymers: (a) variation of viscosity with shear rate; (b) variation of viscosity with SMA weight fraction

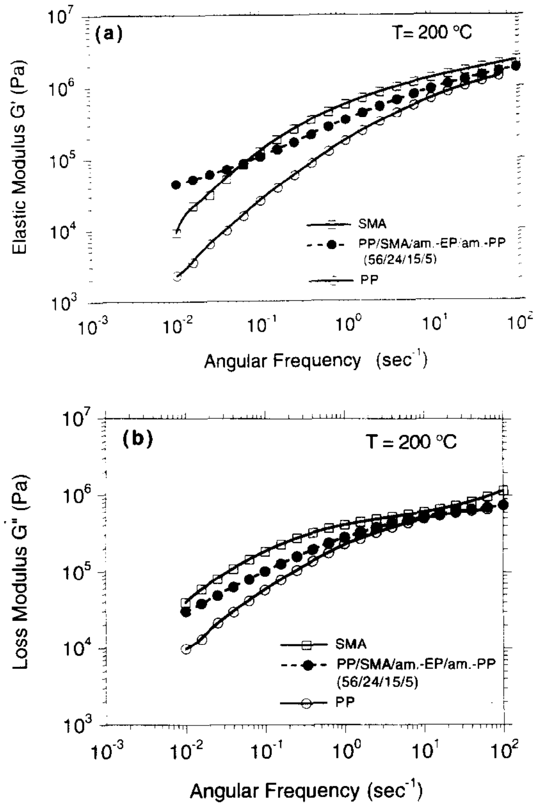


Figure 12 Variation of rheological parameters with angular frequency in PP/SMA blend and component polymers: (a) storage modulus; (b) loss modulus

dynamic mechanical measurements. *Figures 12a* and *b* show storage modulus (G') and loss modulus (G'') dependence on the angular frequency (ω) for SMA, PP and PP/SMA compound. In SMA and PP the elastic and loss moduli drop to zero with a ω^2 and ω dependence respectively. In the compatibilized PP/SMA composition this limiting low strain rate behaviour is not achieved. The PP phase is continuous and is not chemically crosslinked, consequently the dispersed phase comprising the SMA and compatibilizers must be interacting to produce the long relaxation times.

The method of analysis used by Utracki and colleagues requires determination of an apparent yield value for the blend. The moduli are modelled with phenomenologically derived functions of strain rate, zero strain rate viscosity and relaxation times. The magnitude of this yield stress can be calculated using a modified Casson equation[35,36] of the form

$$F^{1/2} = F_y^{1/2} + a^2 F_m^{1/2} \qquad (1)$$

where F represents a rheological parameter such as G' or G'' of the polymer blend, F_y the apparent yield, F_m the corresponding rheological function of the matrix polymer and a^2 is a parameter related to F. In the case where F is the shear stress, a^2 is a measure of the relative viscosity between blend and matrix. *Figure 13* illustrates a modified Casson plot construction for the PP/SMA four-component blend. G'' was used as the rheological function in this Casson plot. The dashed line in the figure confirms the linear relation expressed in equation (1). At shear rates exceeding 10 s^{-1} the data points start to deviate from the linear fit of equation (1). The yield parameter F_y was calculated by using only the data points that fall on the straight line. The yield stress parameters calculated using equation (1) for PP/SMA compositions with varying SMA content are summarized in *Table 3*. It is evident from *Table 3* that G'_y is always greater than G''_y. This trend has also been observed by Utracki and Sammut[33,34]. The magnitudes of both G'_y and G''_y depend on the SMA content in the blend.

In order to describe the rheological properties over a wide variation of shear rates, equation (1) should be combined with a suitable rheological function. As an illustration we have analytically represented the dynamic viscosity ($\eta' = G''/\omega$) variation with shear rate for the PP/SMA system. We first selected an equation that adequately describes η' *versus* ω dependence both at low and high shear rates. A suitable model that describes this

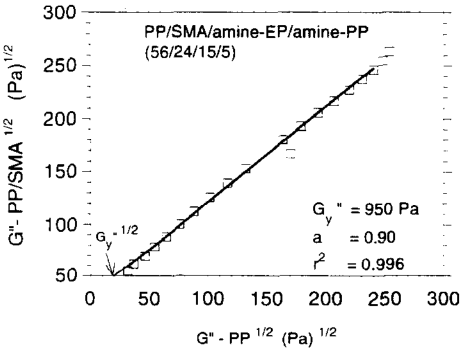


Figure 13 Modified Casson plot of G'' in PP/SMA blend for calculating yield parameter

Table 3 Summary of yield stress parameters in PP/SMA alloys containing amine-EP (15 wt%) and amine-PP (5 wt%) compatibilizers

PP/SMA ratio	Modulus	F_y (Pa)	a	r^2	Matrix
70/30	G'	2729	1.02	1.000	PP
	G''	659	0.97	1.000	PP
50/50	G'	2696	1.08	1.000	PP
	G''	875	0.98	1.000	PP
30/70	G'	3794	0.71	1.000	SMA
	G''	872	0.73	0.999	SMA

dependence is given below[3,4,33,34]

$$\eta' = \eta_0/[1+(\omega\tau)^{m_1}]^{m_2} \qquad (2)$$

where η' is the dynamic viscosity corrected for yield stress, η_0 is the zero-shear rate viscosity, τ is the characteristic relaxation time, and m_1 and m_2 are constants. At high shear rates ($>100\,\mathrm{s}^{-1}$) equation (2) will reduce to the familiar power law model ($n = 1 - m_1 m_2$). The experimentally measured dynamic viscosity ($\eta'_a = G''_a/w$) is actually an apparent viscosity and includes an yield stress component. η'_a can be written in the form:

$$\eta'_a = G''_a/\omega = (G'' + G''_y)/\omega = \eta' + G''_y/\omega \qquad (3)$$

Equation (3) was fitted to the measured η'_a *versus* ω data for the PP/SMA blend. *Figure 14* shows the comparison between the actual data points (open circles) and the model (dashed line). The model is obviously capable of fitting the experimental data. The value for the various parameters may be useful for comparison of these data with the work of others on PP/SMA systems.

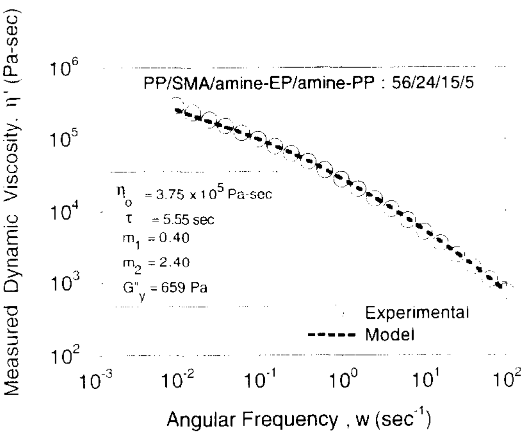


Figure 14 Comparison of experimentally determined dynamic viscosity with model predictions

CONCLUSIONS

We have demonstrated for the first time excellent properties in compatibilized blends of isotactic PP and SMA polymers over a range of SMA compositions using amine functionalized polyolefins as compatibilizers. Our results show that an amine-EP elastomer and an amine-PP thermoplastic resin are both required as compatibilizers for the PP/SMA blend to achieve optimal impact properties and significant extensibility before failure. In compositions that contain PP as the matrix phase, the incorporation of SMA in the blend expands the properties of unmodified polypropylene by providing special attributes such as paintability and adhesion to polar engineering thermoplastics. The morphology of the PP/SMA four-component polymer blend is complex and is influenced by the compounding protocol. For blends containing PP as the continuous matrix phase, the presence of both polyolefin compatibilizers creates a fine dispersion of the SMA particles, with SMA domain size ranging from 0.5 to 3 μm. When the PP/SMA blend is formulated using a single-step compounding procedure with simultaneous addition of all the ingredients, the compatibilizer which can be observed (amine-EP + amine-PP) is located near the PP/SMA interface. There are no sub-inclusions within the dispersed SMA phase. When the same composition is prepared from a preformed master batch of SMA and amine-EP the morphology is changed, and sub-inclusions of compatibilizer (presumably amine-EP) appear in the SMA phase. The Izod impact properties measured at 21°C of the blend produced by the master batch technique are independent of the changes in morphology. Rheological properties of the PP/SMA compositions are typical of other immiscible polymer blend systems. At low shear rates the compatibilized PP/SMA blend shows yielding, while the unmodified blend components of PP and SMA have finite zero shear viscosity.

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