Mechanical properties and morphology of nylon-6/acrylonitrile–butadiene–styrene blends compatibilized with imidized acrylic polymers

B. Majumdar*, H. Keskkula and D. R. Paul†
Department of Chemical Engineering, and Center for Polymer Research, University of Texas at Austin, Austin, TX 78712, USA
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The mechanical properties and phase morphology of blends of nylon-6 with various acrylonitrile–butadiene–styrene (ABS) materials and compatibilizers are explored. The main focus was on nylon-6/ABS blends compatibilized with one particular imidized acrylic polymer that is miscible with the styrene–acrylonitrile (SAN) matrix of the ABS and has nearly optimal content of functional groups (anhydride and free acid) for reaction with nylon-6 to form graft copolymers *in situ* at the polymer–polymer interfaces. The effects of compatibilizer content, rubber concentration and the mixing protocol on the mechanical properties of these blends were extensively explored. In general, the most efficiently dispersed ABS domains in the nylon matrix led to the lowest ductile–brittle transition temperatures and the maximum tensile modulus for the super-tough nylon-6/ABS blends. The effects of varying the functionality and miscibility characteristics of imidized acrylic polymers on the mechanical properties and morphology of nylon-6/ABS blends were also investigated. Some other types of polymers with a high anhydride content were also tested as compatibilizers for this system. It appears that compatibilizers with high levels of reactive functinality are not very effective; hence, there is an optimal level of functionality.

(Keywords: nylon/ABS blend; imidized acrylic; morphology)

INTRODUCTION

There has been considerable interest in the development of multiphase polymer alloys in recent years, motivated by the potential opportunities for combining the attractive features of each material while reducing their deficient characteristics[1-4]. Block or graft copolymers have been used successfully over the last two decades[5-9] as interfacial agents to control the morphology and to strengthen the interfaces in blends of immiscible polymers. The applicability of this method, however, has been limited, owing to the lack of industrially viable routes for synthesis of such additives for various systems of interest. An attractive alternative is the formation of the block or graft copolymer *in situ* during blend preparation through interfacial reaction of added functionalized polymeric components[10-31]. Although this approach has become an increasingly popular route to achieve compatibilization in various immiscible systems, there are many important but unanswered questions related to the choice of the compatibilization scheme for specific systems. This paper addresses some key issues related to the design of an effective compatibilizer for blends of nylon-6 and acrylonitrile–butadiene–styrene (ABS).

Our interest in nylon-6/ABS blends has been stimulated by the numerous options that are available for reactively coupling these two immiscible polymers. A particularly appealing strategy is the addition of a polymer that is miscible with the styrene–acrylonitrile (SAN) phase and that can react with the amine end-groups of the nylon phase[24-30]. Examples of such compatibilizing additives that have been used previously include styrene–maleic anhydride (SMA) copolymers[28,29] and stryene–acrylonitrile–maleic anhydride (S/AN/MA) terpolymers[24]. An alternative route involving grafting of maleic anhydride to the ABS prior to blending with the polyamide has also been described[31].

In a recent paper[30], we described the effectiveness of a series of imidized acrylic polymers for controlling the morphology of nylon-6/SAN blends, which is a simplified model (no rubber phase) of the nylon-6/ABS system. These imidized acrylic polymers were synthesized via reactive extrusion of methylamines with poly(methyl methacrylate) and generally comprised at least four different types of chemical repeat units[32-35] as previously described[30]. In addition to generating methyl glutarimide units, this reaction also produces small amounts of methacrylic acid and glutaric anhydride entities, while some methyl methacrylate units remain unchanged.

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*Present address: 3M, St Paul, MN 55144-1000, USA
†To whom correspondence should be addressed

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These acid and anhydride groups provide the functionality for reaction with the polyamide. By controlling the amount of acid and anhydride groups in these polymers through a re-esterification process[33,35], it is possible to preserve their miscibility with SAN copolymers over a limited range of AN content in the SAN[30,36]. This paper demonstrates the relevance of that model study[30] to the more complex nylon-6/ABS systems. The main focus of the present work is on the relationship between the morphology and mechanical properties of nylon-6/ABS blends compatibilized with a particular imidized acrylic polymer that was found to be optimal for this purpose. This material is miscible with the SAN phase of the ABS material and readily reacts with nylon-6[30]. The consequences of varying the reactive functionality and the miscibility characteristics of the compatibilizer polymer on the morphology and mechanical properties of nylon-6/ABS blends are also examined using a wider range of reactive polymers.

A future report[59] will examine the effects of varying the rheological properties, the chemical functionality and the inherent ductility of the nylon matrix on the morphology and the mechanical properties of compatibilized nylon/ABS blends.

BACKGROUND

In the recent paper mentioned above[30], various factors influencing blend morphology in model nylon-6/SAN systems containing reactive imidized acrylic polymers were explored. Miscibility of the imidized acrylic polymer with the SAN phase and its reactivity with the polyamide phase were identified as key issues in controlling the morphology of these blends. While miscibility with the SAN phase can be preserved by limiting the imide and methacrylic acid content, the reactivity of these polymers with the nylon phase depends primarily on the anhydride concentration in these imidized acrylic polymers. Depending on the thermodynamic interaction of the compatibilizer with the SAN, three different locations were envisioned for the graft copolymer formed in these blends[30]. Among these, the most efficient for compatibilization is when the imidized acrylic polymer is miscible with the SAN phase and has adequate functionality for reaction with the amine end-groups of the polyamide. In this case, the imidized acrylic polymer should reside primarily in the SAN phase with its functional groups forming chemical linkages with the polyamide chains at the nylon-6/SAN interface. When the added compatibilizer is not miscible with the SAN phase but has moderate thermodynamic affinity for it, the graft copolymer formed is visualized to exist as a layer surrounding the SAN domains, i.e. it wets the SAN phase of the ABS but is chemically coupled to the nylon phase. When the compatibilizer has much less affinity for the SAN phase, the graft copolymer formed should form micellar aggregates away from the nylon-6/SAN interface. It was also suggested that in certain cases reaction of the compatibilizing polymer with the polyamide amine end-groups could influence its miscibility characteristics with SAN. For example, a compatibilizer that is initially miscible with the SAN phase could ultimately become immiscible after significant reaction with the polyamide chains and vice versa. This would, no doubt, affect where the graft copolymer formed would reside in such cases.

The size of the dispersed phase of SAN plus imidized acrylic polymer in blends when nylon-6 forms the continuous phase was found to be strongly dependent on the anhydride functionality level and concentration of the imidized acrylic polymer when this additive is miscible with the SAN phase. The most efficient size reduction in the dispersed phase was obtained when the miscible imidized acrylic polymer contained approximately 3–4% total acid (free acid plus anhydride) functionality. For the imidized acrylic polymers not miscible with the SAN phase, the dispersed-phase particle size was relatively insensitive to the total acid content. Although larger dispersed-phase particles are formed using immiscible imidized acrylics than the optimum miscible imidized acrylic polymers, these particles are significantly smaller than those obtained for the binary nylon-6/SAN blends containing no reactive compatibilizer[30].

Use of compatibilizing polymers (both imidized acrylic and other types) with high anhydride levels resulted in three distinct populations of dispersed-phase particles. These were classified as: (a) extremely small round particles less than 50 nm in size; (b) relatively large and elongated particles with a tendency towards co-continuity with the polyamide phase; and (c) intermediate-sized elliptical particles with effective diameters between 0.5 and 1.0 μm. It was proposed that this complex morphology is a consequence of partial segregation of the SAN and the compatibilizing polymer into separate domains. This phenomenon is believed to occur even in cases where the compatibilizing polymers are initially miscible with the SAN phase. As mentioned above, a high degree of reaction of such polymers with the polyamide phase could change the molecular structure to an extent that they are no longer miscible with the SAN. It was, thus, proposed that the extremely small spherical particles (~50 nm) seen in the TEM photomicrographs are actually highly grafted micellar structures of the compatibilizer containing little or no SAN, which reside away from the nylon-6/SAN interface. Other mechanisms can also lead to such micellar-type structures as mentioned previously[30]. In any case, these small grafted particles can lead to a large increase in the effective viscosity of the polyamide matrix, and this change in the relative rheological properties of the phases could cause the SAN domains to display some tendency towards co-continuity, similar to what has been observed[30,49,50].

EXPERIMENTAL

Table 1 summarizes pertinent information about the various materials used in this work. The nylon-6 is a commercially available material with $\bar{M}_n = 22\,000$ and 47.9 μeq g^{-1} of amine and 43.0 μeq g^{-1} of carboxyl end-groups. Before each processing step, all materials containing nylon-6 were dried for at least 12 h at 85°C in a vacuum oven to ensure removal of sorbed water.

The various ABS materials used in this work are also shown in *Table 1*. The one designated as BL-65 was used extensively and will be what we mean when the term ABS is used without other designation. The other ABS

Table 1 Polyamides and ABS used in this study

Polymer	Material/description	Composition	Molecular weight	Relative melt viscosity[a]	Source
Nylon-6	Capron 8207 F	End-group content: $NH_2 = 47.9\ \mu eq\ g^{-1}$ $COOH = 43.0\ \mu eq\ g^{-1}$	$\bar{M}_n = 22\,000$	1.0	Allied-Signal
ABS	SAN-grafted emulsion rubber (BL-65)	50% rubber 24% AN in SAN	$\bar{M}_n = 44\,000^b$ $\bar{M}_w = 167\,000$	4.0	Sumitomo Naugatuck Co.
ABS	SAN-grafted emulsion rubber (DP-611)	40% rubber 25% AN in SAN	n.a.[c]	3.3	Japan Synthetic Rubber
ABS	SAN-grafted emulsion rubber (DP-10)	25% rubber 26% AN in SAN	n.a.	2.1	Japan Synthetic Rubber
ABS	SAN-grafted emulsion rubber (Lustran 752)	34% rubber 30% AN in SAN	n.a.	n.t.[d]	Monsanto Chemical Co.
SAN 25	Styrene/acrylonitrile copolymer (Tyril 1000)	25% AN	$\bar{M}_n = 77\,000^b$ $\bar{M}_w = 152\,000$	1.0	Dow Chemical Co.

[a] Brabender torque at 240°C and 60 rev min^{-1} after 10 min relative to nylon-6
[b] From g.p.c. using polystyrene standards; for BL-65, the information shown is for soluble SAN
[c] n.a. = not available
[d] n.t. = not tested

Table 2 Compatibilizers used in this study

Designation[a]	T_g (°C)	Relative melt viscosity[b]	Methyl glutarimide (MGI) (wt%)	Total acid content (MAA+GA) (wt%)	Methacrylic acid (MAA) (wt%)	Glutaric anhydride (GA) (wt%)	Methyl methacrylate (MMA) (wt%)	Miscibility with SAN 25[c]
IA-250-A	130	1.8	55.7	2.24	1.50	0.74	42.1	Yes
IA-250-B	130	2.0	55.7	2.98	1.94	1.04	41.3	Yes
IA-250-C	131	1.6	55.7	3.26	2.18	1.08	41.0	Yes
IA-250-D	134	1.7	55.7	4.05	2.80	1.25	40.3	Yes
IA-250-E	137	2.1	55.7	7.04	4.64	2.40	37.3	No
IA-245	143	2.1	74.5	0.53	0.08	0.45	25.0	Yes
IA-268	147	n.t.[d]	75.7	4.42	3.13	1.29	19.9	No[e]
IA-269	165	3.1	89.5	6.50	5.40	1.10	4.0	No
GA-92[f]	110	n.t.	0	9.20	0.60	8.60	90.8	Yes
Delpet 980N[g]	130	1.7	0	9.00	0	9.00[h]	73.0	Yes
SMA 25[i]	149	1.6	0	25.0	0	25.0[h]	0	Yes

[a] For the IA polymers, $\bar{M}_w = 95\,000$
[b] Brabender torque divided by that of nylon-6 (all at 240°C and 60 rev min^{-1} after 10 min)
[c] Tested primarily at 50/50 composition
[d] n.t. = not tested
[e] Tested also at SAN 25/IA-268 compositions of 95/5, 90/10, 80/20 and 20/80
[f] Methyl methacrylate/glutaric anhydride/methacrylic acid (90.8/8.6/0.6) terpolymer; $\bar{M}_w = 125\,000$
[g] Methyl methacrylate/styrene/maleic anhydride (73/18/9) terpolymer: $\bar{M}_n = 61\,800$
[h] Denotes maleic anhydride concentration
[i] Styrene-maleic anhydride (75/25) copolymer; viscosity = 4.73 mPa s (of 10% solution in methyl ethyl ketone, at 25°C)

materials will be identified by their commercial designations shown in *Table 1*. As described in earlier work[28,37,38], BL-65 consists of SAN copolymer grafted to a butadiene-based latex rubber. The rubber phase comprises 50% of the mass and has a broad distribution of particle sizes; typical particle diameters lie in the 0.2 μm range. The SAN contains 24% AN by weight, with 40% of the SAN mass chemically grafted to the rubber. Other emulsion-made ABS materials have lower rubber contents, and other details of their composition are provided in *Table 1*. The styrene–acrylonitrile copolymer, SAN 25, was used for diluting the rubber content of the BL-65 material in one series of blends.

Table 2 shows the imidized acrylic polymers selected for this work. In the IA-250 series, the imide content is held constant at 55.7%. while the free acid and anhydride functionality vary. Other imidized acrylic polymers with higher imide contents were also used. The ninth entry in *Table 2*, GA-92, is a terpolymer of methyl methacrylate, methacrylic acid and glutaric anhydride (MMA/MAA/GA). It is quite similar in structure to the other imidized acrylic polymers shown in *Table 2* except that it does not have any imide units. *Table 2* also lists two other polymers that were used as compatibilizers, SMA 25 and Delpet 980N. SMA 25 is the styrene–maleic anhydride polymer containing 25% maleic anhydride units that has been used extensively in our previous work on nylon/SAN blends. Delpet 980N is a terpolymer of methyl methacrylate, styrene and maleic anhydride (MMA/St/MA) that is miscible with SAN 25 and capable of reacting with the nylon.

For rheological characterization, the various polymers were tested in a Brabender Plasticorder with a 50 ml mixing head and standard rotors by recording the torque at 240°C and 60 rev $\min^{-1}$. A Capirograph 1B capillary rheometer (manufactured by Toyo Seiki Seisaku-Sho Ltd, Japan) with $L/D=20$ (diameter = 1 mm) was also used to obtain the melt viscosity over a range of shear rates (10–1000 s^{-1}) at 240°C for some key materials used in this study. The ternary blends were prepared by simultaneous extrusion of all components (except where mentioned otherwise) in a Killion single-screw extruder ($L/D=30$, 2.54 cm diameter) at 240°C using a screw speed of 30 rev $\min^{-1}$. The extruded pellets were injection moulded into standard tensile (ASTM D638 type I) and Izod (ASTM D256) bars (thickness = 0.3175 cm) using an Arburg screw injection moulding machine. Mechanical properties were determined for samples in the dry as-moulded state.

Transmission electron microscopy (TEM) was used to determine blend morphology from ultra-thin sections cryogenically microtomed from Izod bars perpendicular to the flow direction. The dispersion of the butadiene rubber phase in the ABS was examined via an osmium tetroxide staining technique, which involved exposing the ultra-thin microtomed samples to vapour from a 2% aqueous solution of OsO_4 for at least 8 h. Phosphotungstic acid (PTA) was also used to stain the polyamide phase selectively[39–43] and provides very effective contrast between the major phases. This procedure involved floating the samples in a 2% aqueous solution of phosphotungstic acid for 30 min. Occasionally, the two staining techniques were used in conjunction with each other. This was accomplished by first staining the samples with PTA and then exposing them to OsO_4 vapour for at least 8–10 h.

RHEOLOGY

From Brabender torque rheometry (see *Tables 1* and *2*) it is clear that nylon-6 has the lowest melt viscosity of the various blend components. This is also seen in *Figure 1*, where melt viscosity obtained via capillary viscometry is shown as a function of shear rate for the components at 240°C. Within the range of shear rates shown, the ABS material exhibits a strong shear-thinning behaviour while the nylon-6 is more nearly Newtonian. As expected, the uncompatibilized 50/50 blend of nylon-6 and ABS shows a viscosity dependence on shear rate that is intermediate between the two components. The imidized acrylic compatibilizer shows viscosity behaviour that is intermediate between those of nylon-6 and ABS.

The rheological behaviour of the components is an important factor in determining blend morphology[44–52]. In the absence of a compatibilizer, it is expected that over a broader range of compositions this nylon-6 will tend to form the continuous phase while the ABS will tend to form dispersed domains[49–52].

NYLON-6/ACRYLONITRILE-BUTADIENE-STYRENE BLENDS COMPATIBILIZED WITH AN IMIDIZED ACRYLIC POLYMER

In this section, we examine the effects of varying the nylon-6/ABS ratio, compatibilizer concentration, rubber content and mixing protocol on the mechanical properties and morphology of blends compatibilized by a particular imidized acrylic polymer, IA-250-C. This particular compatibilizer was selected since it is miscible with the SAN phase and shows significant reaction with the nylon-6[30].

Uncompabilized nylon-6/ABS blend

From the mechanical properties listed in *Table 3* it is clear that the imidized acrylic polymer, IA-250-C, is a very brittle material. The other compatibilizers used also have similar mechanical properties. *Table 3* shows that a 50/50 nylon-6/ABS blend without any compatibilizer is not very tough and has lower elongation at break than either nylon-6 or the ABS. The modulus and yield strength of this blend show essentially additive contributions of each component.

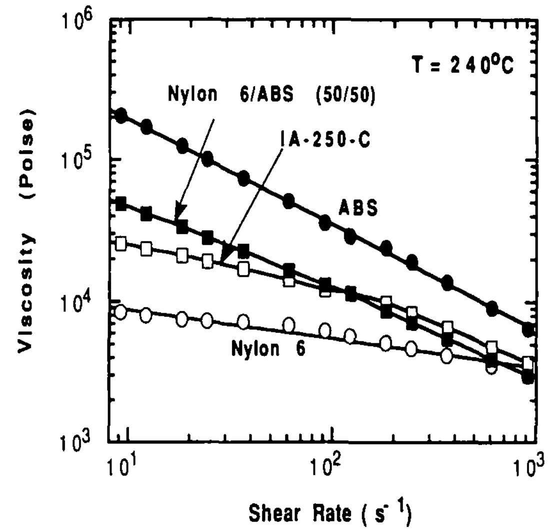

Figure 1 Melt viscosity *versus* shear rate for nylon-6, ABS (BL-65), nylon-6/BL-65 (50/50) and IA-250-C

Table 3 Mechanical properties of some key materials

Polymer	Izod impact (J m^{-1})	Modulus (GPa)	Yield stress (MPa)	Elongation at break (%)
Nylon-6	40	2.8	69.6	233
BL-65	300	0.8	17.0	98
IA-250-C	20	3.5	89.1	5
SAN 25	18	3.3	67.6	3
Nylon-6/BL-65 (50/50)	105	1.5	34.0	50

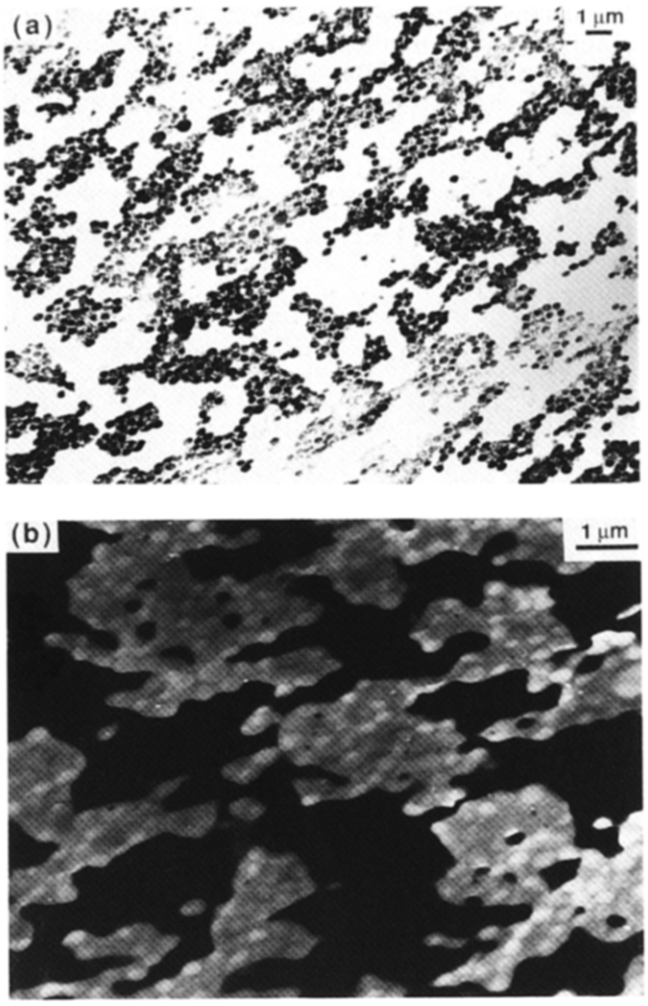

Figure 2 TEM photomicrographs of binary blend of nylon-6/ABS (50/50) in which (a) the butadiene rubber particles have been stained with OsO_4 and (b) the nylon phase has been stained with phosphotungstic acid (PTA)

Figure 2a shows a TEM photomicrograph of the binary nylon-6/ABS (50/50) blend where OsO_4 has been used to stain the butadiene-based rubber particles in the ABS phase. Nylon-6 clearly forms a continuous phase while the ABS forms large domains with some tendency for interconnectivity. *Figure 2b* shows a higher magnification of the same blend where the nylon-6 phase has been stained with phosphotungstic acid. The butadiene rubber particles can still be distinguished within the SAN matrix using this staining technique. The tendency towards a co-continuous morphology is also clearly evident in this photomicrograph.

Effect of nylon-6/ABS ratio in compatibilized blends

Figure 3 shows the Izod impact properties of nylon-6/ABS blends containing 5% of the imidized acrylic polymer, IA-250-C. It is evident that super-tough materials can be achieved over a broad range of compositions. The ductile–brittle transition temperatures of these blends are also shown as a function of the polyamide/ABS ratio. The ductile–brittle transition temperature has been defined as the mid-point of the sharp drop in notched Izod impact strength as the testing temperature is reduced[54,55]. Low-temperature toughness is favoured the more ABS there is in the blend. *Figure 4* shows that the tensile modulus and the yield stress for these compatibilized blends vary almost linearly with their nylon-6 content. There is a precipitous drop in the impact strength as the nylon-6 content goes from 70 to 80% (*Figure 3*). This corresponds to the ductile–brittle transition temperature rising above room temperature. Evidently, this reflects a critical rubber content for toughening at room temperature. At less than 30% nylon-6, these blends have very low moduli.

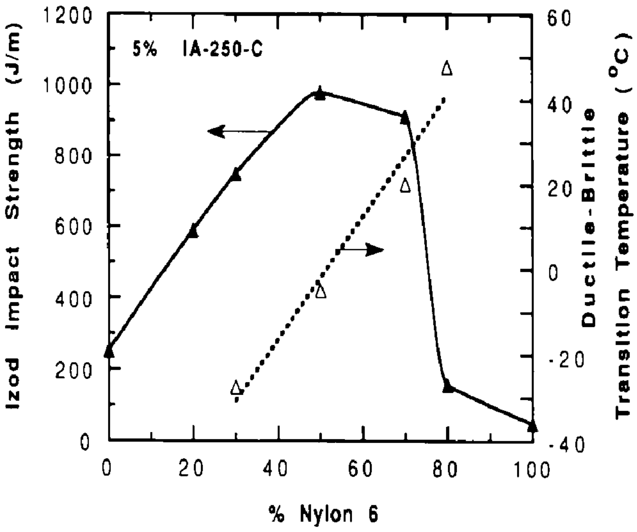

Figure 3 Izod impact strength and ductile–brittle transition temperature *versus* composition for nylon-6/ABS blends containing 5% IA-250-C

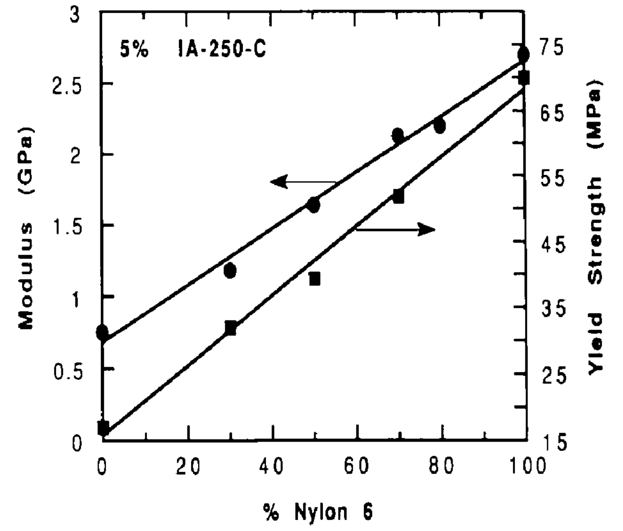

Figure 4 Tensile modulus and yield strength *versus* composition for nylon-6/ABS blends containing 5% IA-250-C

Figure 5 shows the morphology of a 50/50 nylon-6/ABS blend containing 5% of the imidized acrylic polymer, IA-250-C. This composition corresponds to the maximum in Izod impact strength shown in *Figure 3*. The two methods of staining described earlier reveal different features of the phase morphology of this blend. As seen in *Figure 5a*, where the rubber particles have been stained with OsO_4, the rubber particles are much more uniformly distributed than in the uncompatibilized blend (*Figure 2*). Staining of the polyamide phase with

PTA (*Figure 5b*) more clearly shows that there are SAN linkages between the different butadiene rubber particles.

Figure 6 shows TEM photomicrographs, PTA stained, for two other blend compositions in the super-tough range seen in *Figure 3*. At the 70/30 nylon-6/ABS ratio, the polyamide clearly forms the continuous phase surrounding ABS domains that are well dispersed (*Figure 6a*). At the 30/70 nylon-6/ABS ratio (*Figure 6b*), the ABS phase assumes a more continuous character. However, the nylon-6, in spite of its much lower concentration, retains some degree of phase continuity. This may be attributed to its much lower melt viscosity[49–52].

Effect of compatibilizer content

Figure 7 shows how the ductile–brittle transition temperature and the modulus vary, at fixed ABS content, with the amount of IA-250-C compatibilizer used. All blends in this series have impact strengths in the super-tough range ($>850\,\mathrm{J\,m^{-1}}$). The ABS content in these blends corresponds to constant rubber content of 22.5%. As the compatibilizer concentration is increased, the ductile–brittle transition temperature drops to −15 C and remains at this level over a broad range of compositions (5–15%), and then increases. The tensile modulus of these blends shows a slight maximum at 10% compatibilizer and is lowest for the blend containing only 2% compatibilizer. The soft ABS tends to form a continuous phase in the uncompatibilized blends, which lowers the modulus of the blend. Adding compatibilizer breaks up the ABS phase continuity, which stiffens the

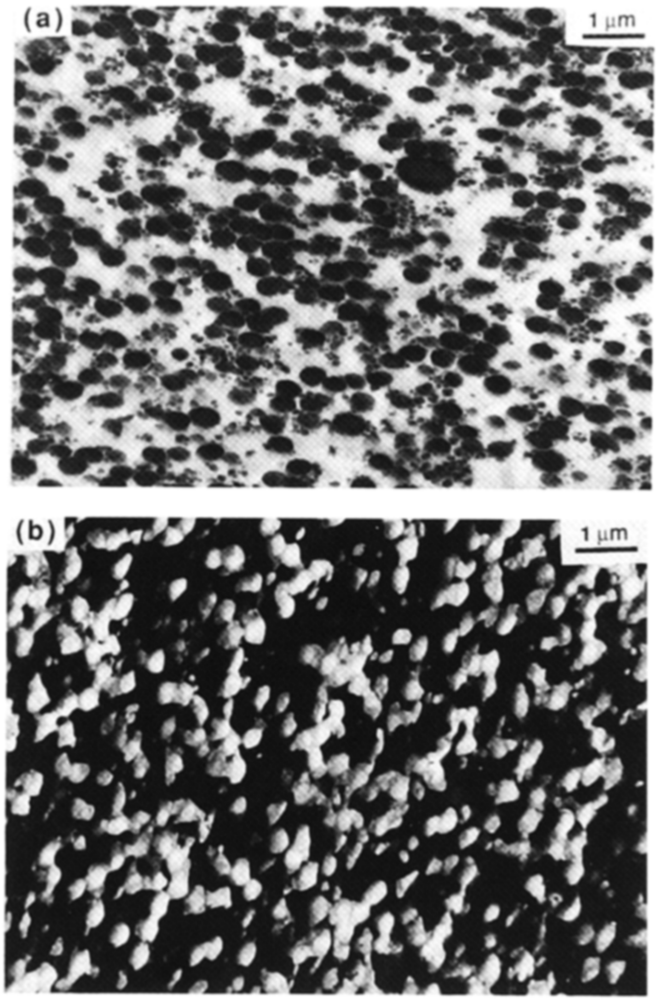

Figure 5 TEM photomicrographs for nylon-6/ABS (47.5/47.5) blends compatibilized with 5% IA-250-C stained with (a) OsO_4 and (b) PTA

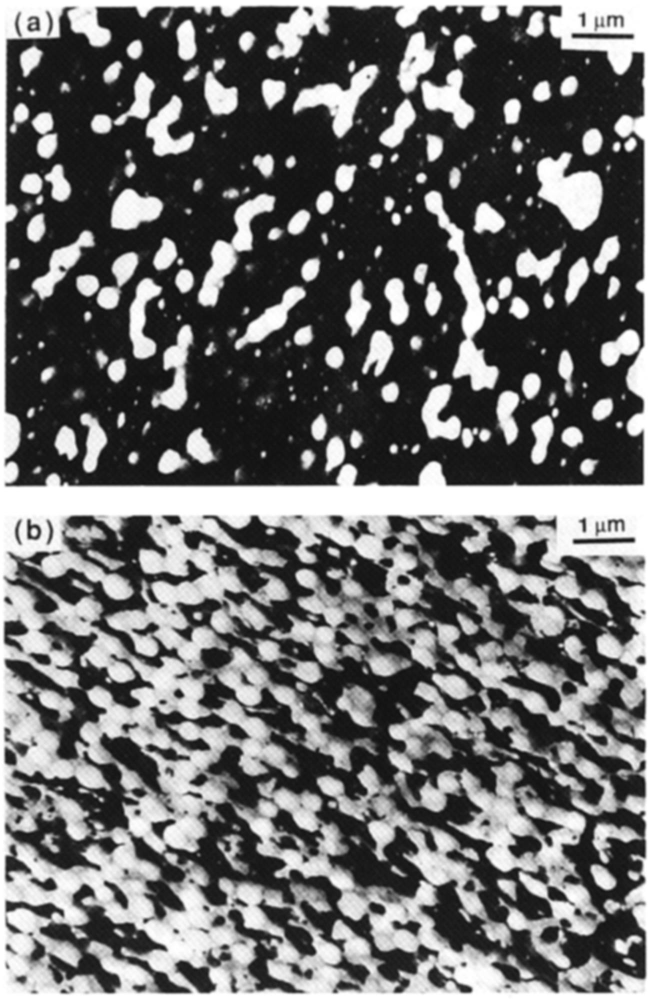

Figure 6 TEM photomicrographs for nylon-6/ABS blends at (a) 70/30 and (b) 30/70 ratios containing 5% IA-250-C. The polyamide phase was stained with PTA

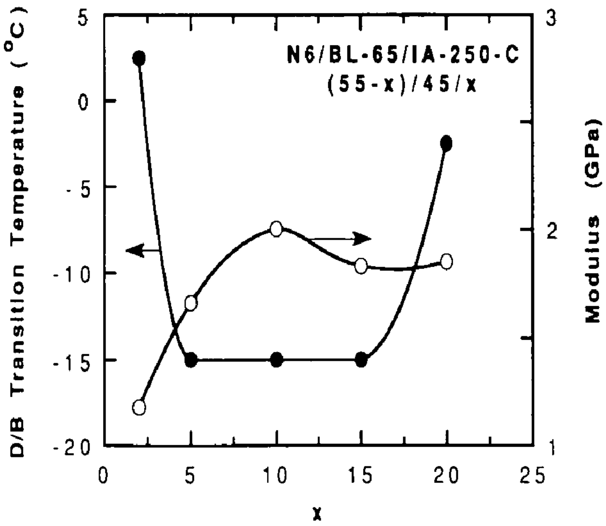

Figure 7 Variation in ductile-brittle transition temperature and tensile modulus for nylon-6/ABS/IA-250-C ($(55-x)/45/x$) blends with IA-250-C content x at constant ABS concentration

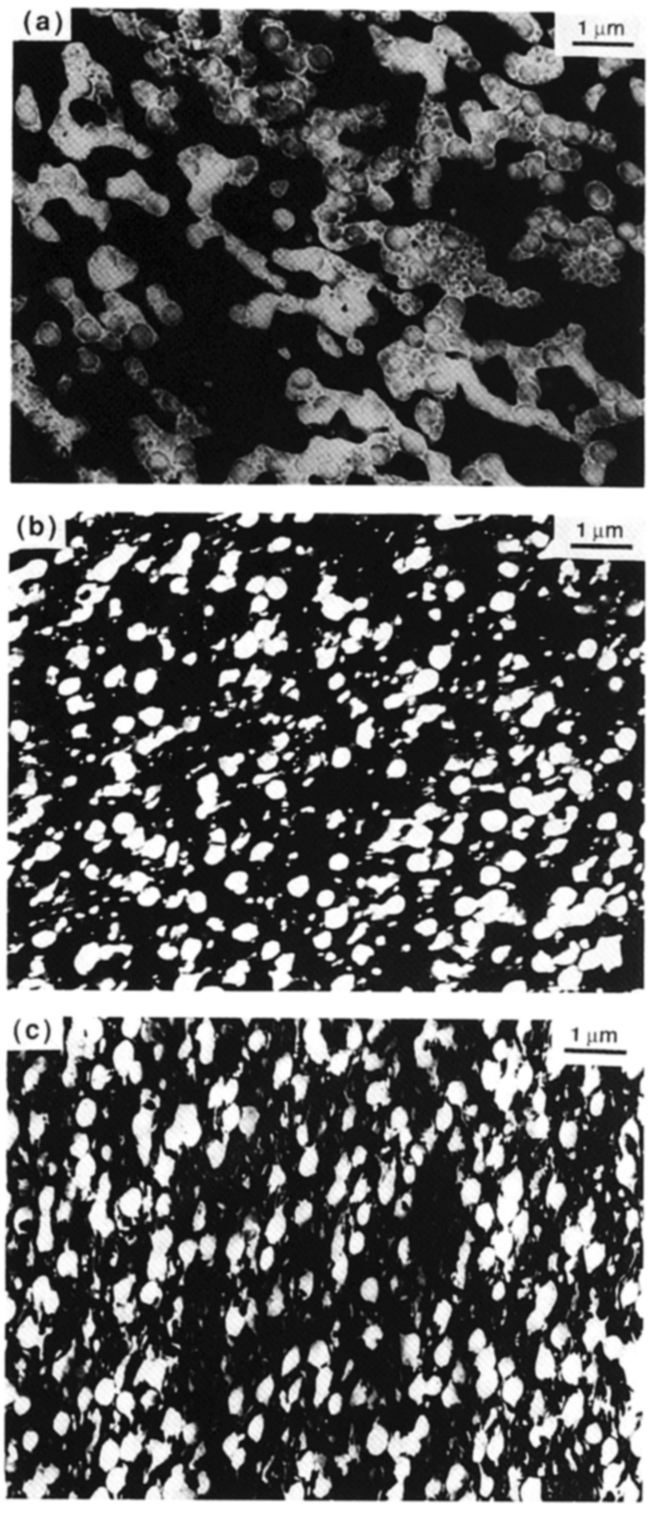

Figure 8 TEM photomicrographs of nylon-6/ABS/IA-250-C ((55 − *x*)/45/*x*) blends containing (a) 2% IA-250-C (dual stained with PTA and OsO_4), (b) 10% IA-250-C (stained with PTA) and (c) 20% IA-250-C (stained with PTA). Note that all blends have the same ABS concentration (45%)

blends. Beyond 10% concentration, the tensile modulus does not appear to change significantly. An attractive feature of toughened blends containing a high concentration of the imidized acrylic polymer, IA-250-C, would be an improved heat distortion temperature[53].

Figure 8 shows how the morphology changes within the series of blends described in *Figure 7*. With only 2% compatibilizer, there is still significant clustering of the ABS domains as revealed by the dual staining technique employed here. The polyamide matrix is stained dark with PTA while the butadiene rubber particles are stained by OsO_4. In spite of the relatively poor dispersion of the ABS domains observed in *Figure 8a*, this blend is super-tough at room temperature. As the amount of compatibilizer is increased, the ABS domains become more efficiently dispersed, as shown in *Figures 8b* and *8c*. It is interesting to note that the blend with 2% IA-250-C, where the ABS dispersion is relatively poor, has the highest ductile–brittle transition temperature and the lowest modulus, while the blend with 10% IA-250-C (excellent dispersion of the ABS) exhibits the lowest ductile–brittle transition temperature as well as the maximum tensile modulus in this series. Although increasing the compatibilizer concentration from 10% to 20% leads to no significant change in the dispersion level of the ABS domains, the butadiene rubber particles appear to be connected to each other in some cases by fine stringy structures. It is possible that such a morphology stems from a portion of the compatibilizer being forced from the nylon-6/ABS interface to form strongly grafted micellar aggregates in the polyamide matrix. It is expected that such a situation would lead to an increased effective viscosity of the polyamide matrix with the SAN phase tending to form co-continuous structures as mentioned earlier[30]. The stringy SAN structures tending to connect the butadiene rubber particles observed in *Figure 8c* possibly reflect this phenomenon. The presence of hard brittle micellar aggregates of the IA-250-C material in the polyamide matrix could also contribute to the sharp increase in the ductile–brittle transition temperature for the blend containing 20% IA-250-C (see *Figure 7*).

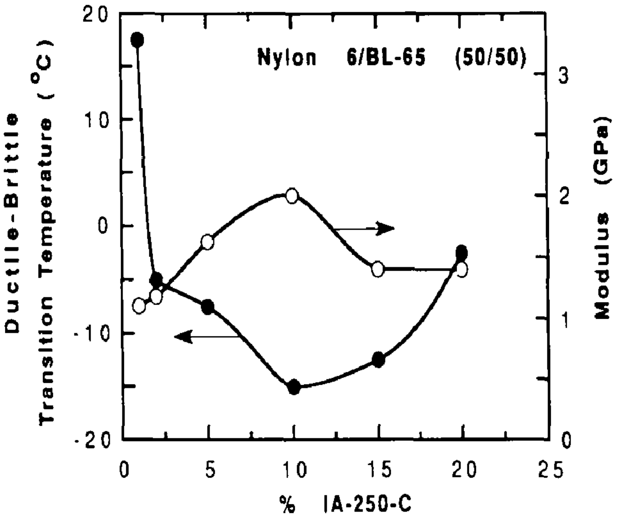

Figure 9 Ductile–brittle transition temperature and tensile modulus for blends containing 50/50 nylon-6/ABS ratio as a function of IA-250-C content

The effect of the compatibilizer concentration was also examined by holding the nylon-6/ABS ratio at 50/50. *Figure 9* shows how the ductile–brittle transition temperature and the tensile modulus vary with imidized acrylic content in this series. The blend containing only 1% compatibilizer is super-tough at room temperature but becomes brittle on cooling to 18°C. Increasing the

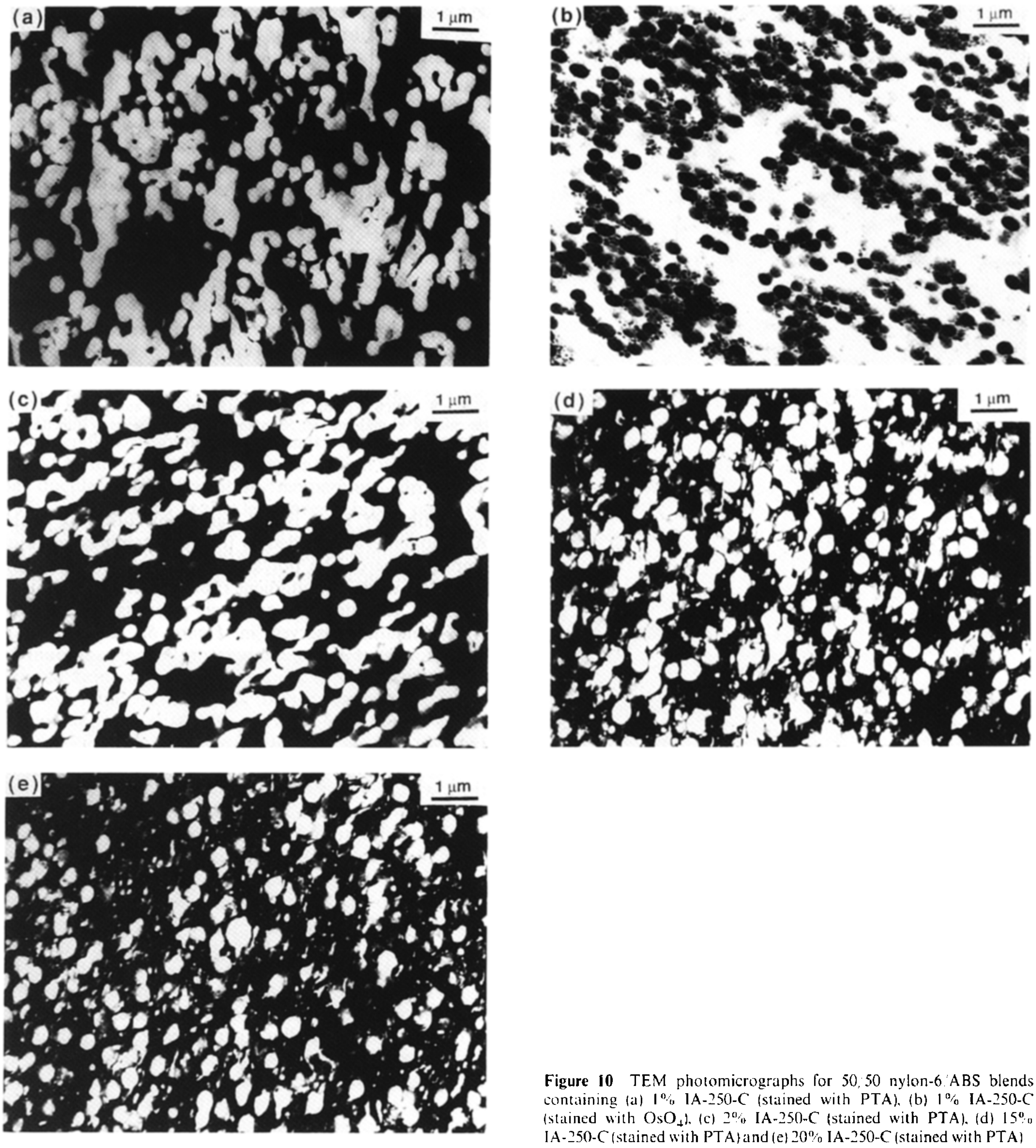

Figure 10 TEM photomicrographs for 50/50 nylon-6/ABS blends containing (a) 1% IA-250-C (stained with PTA), (b) 1% IA-250-C (stained with OsO_4), (c) 2% IA-250-C (stained with PTA), (d) 15% IA-250-C (stained with PTA) and (e) 20% IA-250-C (stained with PTA)

compatibilizer concentration to 2% results in a reduction in the ductile–brittle transition temperature to −5°C. The lowest ductile–brittle transition temperature in this series was obtained when the compatibilizer concentration was 10%. Increasing the compatibilizer level beyond 10% increases the ductile–brittle transition temperature. The tensile modulus shows a maximum value within this series at 10% compabilitizer concentration. *Figure 10* shows TEM photomicrographs for selected blends in this series. The two different staining techniques for the blend containing 1% IA-250-C (*Figures 10a* and *10b*) clearly show significant clustering of the ABS domains. The dispersion of the ABS domains improves significantly as the amount of the imidized acrylic polymer is increased. Stringy ligaments of SAN appear to connect some adjacent butadiene rubber particles in the ABS in blends with high IA-250-C concentrations (*Figures 10d* and *10e*).

Both series of blends in which the compatibilizer level was varied clearly indicate that there is an optimum concentration of the compatibilizer necessary for generating the best possible combination of impact and tensile properties. In general, low concentrations (1–2%) of the compatibilizer lead to poor dispersion of the ABS domains and a combination of low impact and tensile properties, while increasing the compatibilizer concentration beyond the optimum level (~ 10%) leads to a marked increase in the ductile–brittle transition temperature with some deterioration in the tensile properties as well.

Effect of rubber content

This section explores the minimum rubber concentration necessary for achieving a super-tough compatibilized blend. For this purpose, the polyamide and the imidized acrylic compatibilizer concentrations will be held constant while the rubber content is varied. Two different approaches are used. The first strategy involves preblending the BL-65 ABS material with SAN 25 before extruding with nylon-6 and IA-250-C. This allows precise control of the rubber concentration in the final blend at any desired level. The second strategy employs several different commercially available ABS materials with varying rubber contents.

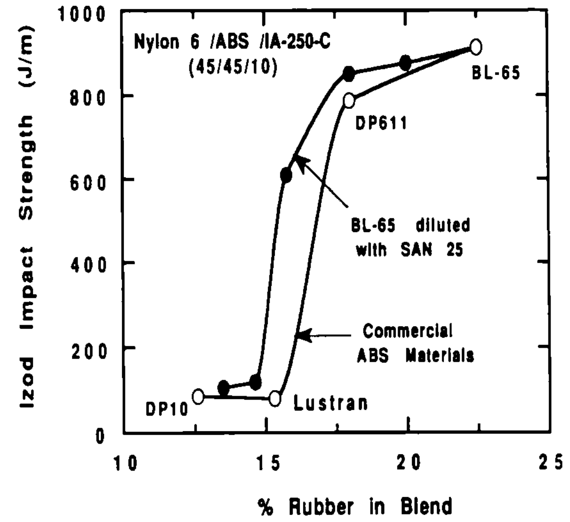

Figure 11 Impact strength *versus* rubber concentration in nylon-6/ABS blends containing 10% IA-250-C

Figure 11 shows the impact strength as a function of the total rubber concentration for both series where the contents of nylon-6, ABS (including BL-65+SAN 25) and compatibilizer are fixed. For the series where BL-65 was diluted with SAN 25, a dramatic drop in the impact strength is observed at ~15% rubber in the final blend. For the blend series based on various commercially available ABS materials, a similar transition is observed at a slightly higher rubber concentration. In the latter case, it is quite remarkable that the rubber concentration still emerges as a critical parameter in determining the transition in the impact strength in spite of the widely different chemical and physical properties of the commercial ABS materials used here.

Effect of mixing protocol

The sensitivity of the mechanical properties of compatibilized nylon/ABS blends to the sequence of mixing the various ingredients was examined. The nylon-6 and the IA-250-C contents were held constant at 45% and 10%, respectively. The ABS in this case consists of mixtures of the BL-65 material with SAN 25. *Table 4* summarizes the results for three different mixing protocols at selected rubber concentrations. Protocol (a) is similar to that used in *Figure 11* where SAN 25 was pre-blended with BL-65 in a first extrusion step and the product was subsequently mixed with both nylon-6 and IA-250-C in a second extrusion step. Protocol (b) involved mixing the BL-65, SAN 25 and IA-250-C in one extrusion step and then blending that extrudate with nylon-6 in a second. Protocol (c) consisted of first blending SAN 25 with BL-65, which was then blended

Table 4 Effect of mixing protocol on blend mechanical properties

Blend no.	Mixing protocol[a]	Rubber phase concentration in blend	BL-65/SAN 25 ratio	Notched Izod impact (J m^{-1})	Ductile–brittle transition temperature (°C)	Modulus (GPa)	Yield stress (MPa)	Elongation at break (%)
1	(a)	0.15	65/35	118	30	2.3	51	84
2	(b)	0.15	65/35	170	28	2.1	49	62
3	(c)	0.15	65/35	126	33	2.2	54	11
4	(a)	0.16	70/30	430	13	2.3	52	13
5	(b)	0.16	70/30	526	18	2.0	47	41
6	(c)	0.16	70/30	475	15	2.1	52	12
7	(a)	0.18	80/20	700	0	2.1	49	35
8	(b)	0.18	80/20	776	4	1.9	48	38
9	(c)	0.18	80/20	730	5	2.1	49	43
10	(a)	0.20	90/10	905	−5	1.8	46	61
11	(b)	0.20	90/10	920	−6	1.9	46	109
12	(c)	0.20	90/10	925	−5	2.0	45	146
13	(a)	0.23	100/0	980	−15	2.0	40	145
14	(b)	0.23	100/0	975	−13	1.8	41	137

[a] See text for details; in summary:
(a) (BL-65/SAN 25)/nylon-6/IA-250-C
(b) (BL-65/SAN 25/IA-250-C)+nylon-6
(c) (BL-65/SAN 25)+IA-250-C+nylon-6

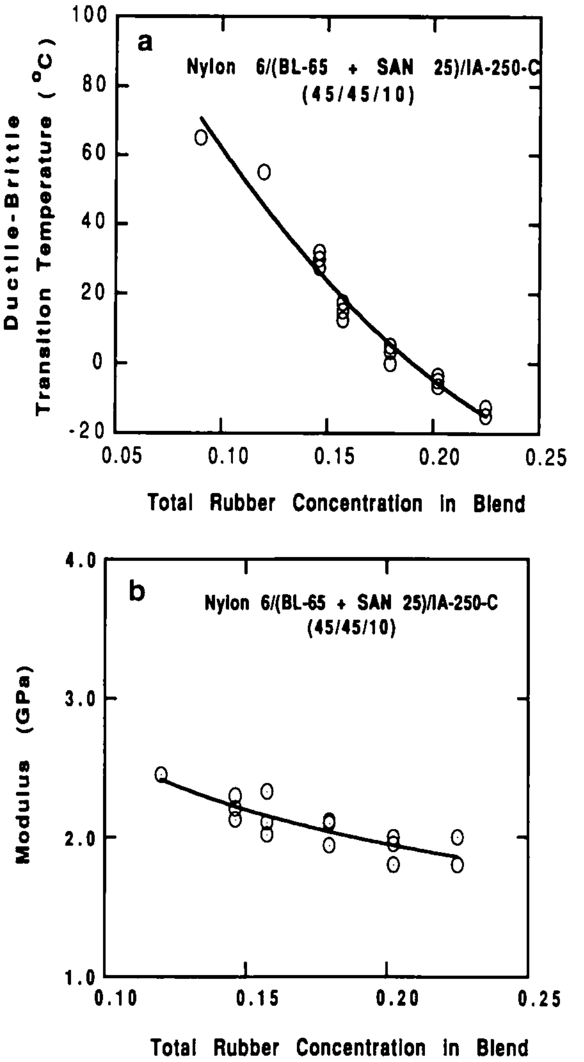

Figure 12 Effect of mixing protocol on (a) ductile–brittle transition temperature and (b) tensile modulus as a function of rubber concentration in the blend. Owing to the relative insensitivity of the mechanical properties to mixing protocol, the individual protocols have not been identified with different symbols

with the IA-250-C polymer in a second step. In a third step the extrudate from the second extrusion was blended with nylon-6.

The mechanical properties shown in *Table 4* appear to be relatively insensitive to the mixing protocol used. This is further illustrated in *Figure 12*, which shows the ductile–brittle transition temperatures and the tensile modulus of these blends as a function of the rubber concentration. Here the multiple points at a fixed rubber concentration represent the different mixing protocols employed to prepare these blends. Examination of the morphology of these blends prepared at each of these rubber concentrations using different mixing protocols did not reveal any major differences.

EFFECT OF COMPATIBILIZER MOLECULAR STRUCTURE

The results presented up to this point have been for blends based on a single compatibilizer, IA-250-C. In this section, the effects of varying the molecular structure of the compatibilizer (see the series of polymers listed in *Table 2*) on the mechanical properties and morphology of nylon-6/ABS blends are investigated. In addition to the series of imidized acrylic polymers, three different types of compatibilizers with high anhydride levels (GA-92, Delpet 980N and SMA 25) are also examined.

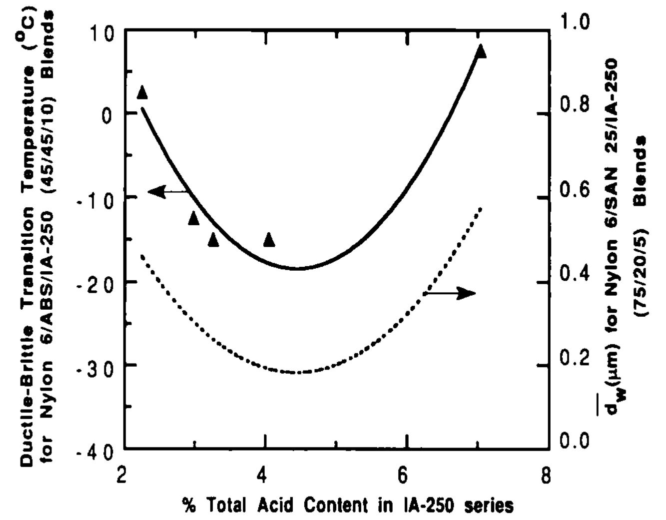

Figure 13 Ductile–brittle transition temperature of nylon-6/ABS/IA-250 blends as a function of total acid content in the IA-250 imidized acrylic polymers. The dotted curve shows the dispersed-phase domain size in nylon-6/SAN 25 blends compatibilized with IA-250 polymers with different total acid contents (ref. 30)

Effect of imidized acrylic functionality

The imidized acrylic polymers in the IA-250 series shown in *Table 2* have a constant imide content of 55.7% but varying levels of reactive functionality (acid and anhydride groups). All of these imidized acrylics are miscible with the SAN phase of the ABS with the exception of IA-250-E, which has the highest total acid content. Blends containing 45/45 nylon-6/ABS and 10% of each of the imidized acrylic polymers from this series proved to be super-tough at room temperature. However, the ductile–brittle transition temperatures of these blends vary with the total acid content (anhydride plus free acid) of the compatibilizer as shown in *Figure 13*. The imidized acrylic polymers with total acid functionality in the 3–4% range produce the best low-temperature toughness. The shape of this plot remains the same if the abscissa is changed to anhydride content rather than total acid since the two types of functionality are highly correlated as discussed previously[30]. The dotted curve in *Figure 13* shows the dispersed-phase particle size in ternary nylon-6/SAN 25/IA-250 blends reported previously[30]. Interestingly, the ductile–brittle transition temperatures closely parallel the trend in particle size[30].

Figure 14 shows the morphology of selected blends in this series. The ABS domains are relatively large and appear to be co-continuous with the polyamide phase for the blend compatibilized with the imidized acrylic containing the lowest degree of acid functionality, IA-250-A (*Figure 14a*). On the other hand, the ABS domains appear much better dispersed in the blend compatibilized with IA-250-D, which has an intermediate amount of acid functionality (*Figure 14b*). When the imidized acrylic IA-250-E is used as compatibilizer, the ABS domains appear to be somewhat elongated and less

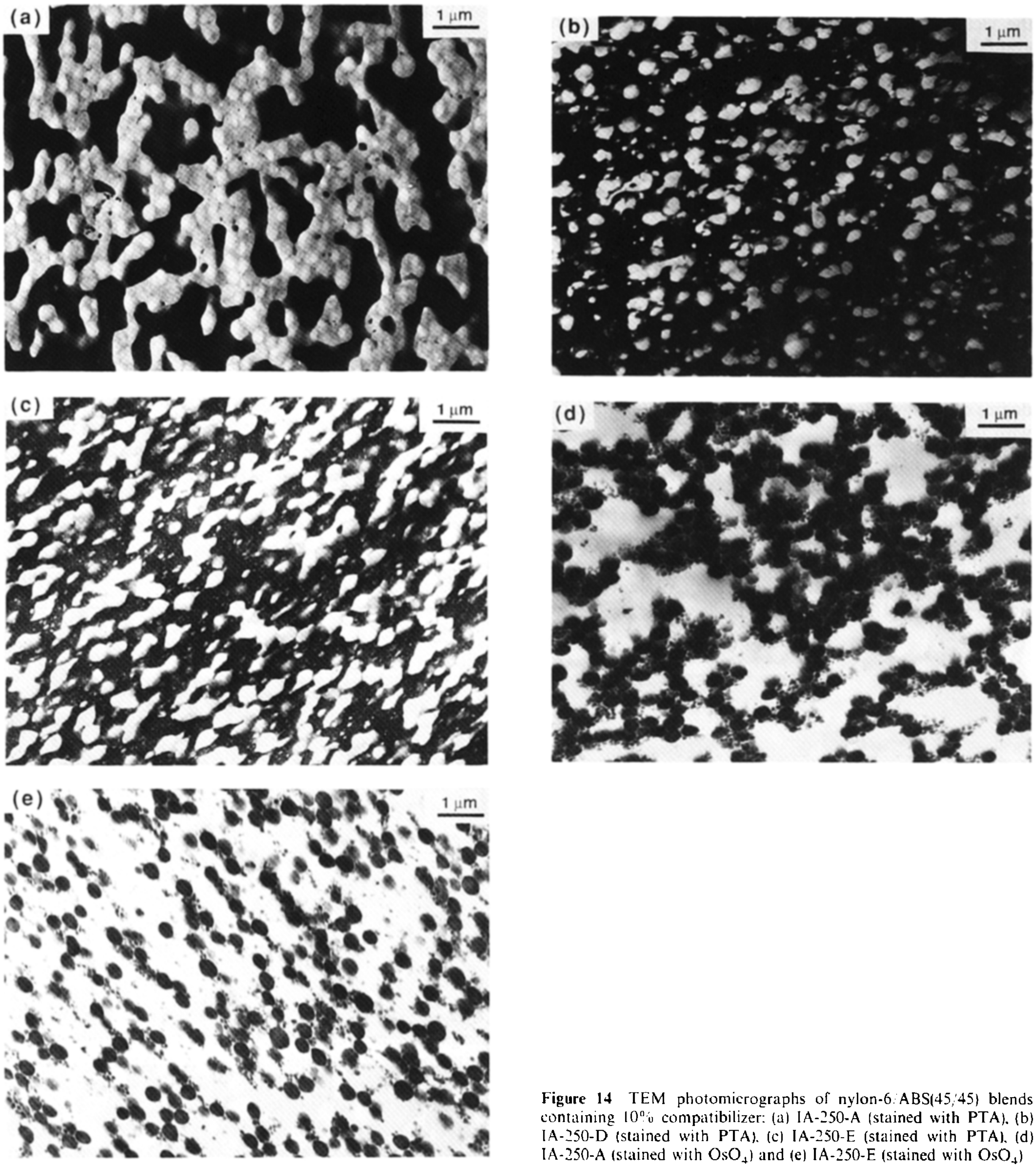

Figure 14 TEM photomicrographs of nylon-6/ABS(45/45) blends containing 10% compatibilizer: (a) IA-250-A (stained with PTA), (b) IA-250-D (stained with PTA), (c) IA-250-E (stained with PTA), (d) IA-250-A (stained with OsO_4) and (e) IA-250-E (stained with OsO_4)

efficiently dispersed. *Figures 14d* and *14e* show photomicrographs for the blends compatibilized with IA-250-A and IA-250-E, respectively, in which the butadiene rubber particles in the ABS are stained with OsO_4. The ductile–brittle transition temperatures observed here (*Figure 13*) seem to relate quite well to the degree of dispersion in this series of blends. For the blend compatibilized with the imidized acrylic with the lowest acid functionality, IA-250-A, both staining techniques reveal large interconnected clusters, which are probably responsible for the high ductile–brittle transition temperature in this case (*Figures 14a* and *14d*). Increasing the total acid functionality to 4.05% (IA-250-D) significantly improves the dispersion of the ABS domains (*Figure 14b*) and also leads to the lowest ductile–brittle transition temperature observed in this series. The imidized acrylic polymer with the maximum acid functionality in this series, IA-250-E, leads to less dispersed elongated domains (*Figures 14c* and *14e*). This may well be a consequence of the fact that IA-250-E is not miscible with the SAN phase and some portion of it, when grafted with nylon-6 chains, may not reside in the vicinity of the nylon/SAN interface but may form grafted micellar aggregates in the polyamide matrix. As discussed previously, this could tend to drive the dispersed phase (in this case, ABS) to become co-continuous owing to an increased effective viscosity of the polyamide matrix. Also, the existence of any hard, brittle micellar aggregates in the polyamide matrix could contribute to deterioration in the low-temperature impact properties of this blend.

Effect of varying imide content and reactive functionality

Table 5 summarizes key mechanical properties for nylon-6/ABS blends containing the remaining compatibilizers listed in *Table 2*. The blends containing 5% of the imidized acrylic polymer IA-245, which has the lowest amount of acid functionality, were brittle at room temperature. For the IA-269 polymer, which has a high degree of methacrylic acid functionality and is immiscible with the SAN matrix of the ABS (see *Table 2*), there is a distinct improvement in the impact strength when its concentration is raised from 5% to 10%. However, even at 10% concentration, the impact properties are significantly inferior to that achieved with IA-250-C (see *Figure 3*). In spite of the apparent immiscibility of IA-268 with the SAN phase in the ABS, this material leads to mechanical properties that are comparable to those atained using IA-250-C polymer (see *Table 5* and *Figure 3*).

The morphologies of selected blends from *Table 5* are shown in *Figure 15*. For the case of 5% IA-245, large domains (3–5 μm) of ABS are formed as a consequence of the low reactive functionality of this polymer (*Figure 15a*). *Figures 15b* and *15c* show photomicrographs using

Table 5 Nylon-6/ABS blends compatibilized with different polymers

Composition	Notched Izod impact (J m^{-1})	Tensile modulus (GPa)	Ductile–brittle transition temperature (°C)
Nylon-6/BL-65/IA-245 (47.5/47.5/5.0)	60	1.5	n.t.[a]
Nylon-6/BL-65/IA-269 (47.5/47.5/5.0)	245	1.6	n.t.
Nylon-6/BL-65/IA-269 (45/45/10)	535	1.7	20
Nylon-6/BL-65/IA-268 (45/45/10)	979	1.8	−13
Nylon-6/BL-65/GA-92 (45/45/10)	800	1.7	5
Nylon-6/BL-65/Delpet 980N (45/45/10)	955	1.7	13
Nylon-6/BL-65/SMA 25 (45/45/10)	200	1.6	n.t.

[a] n.t. = not tested

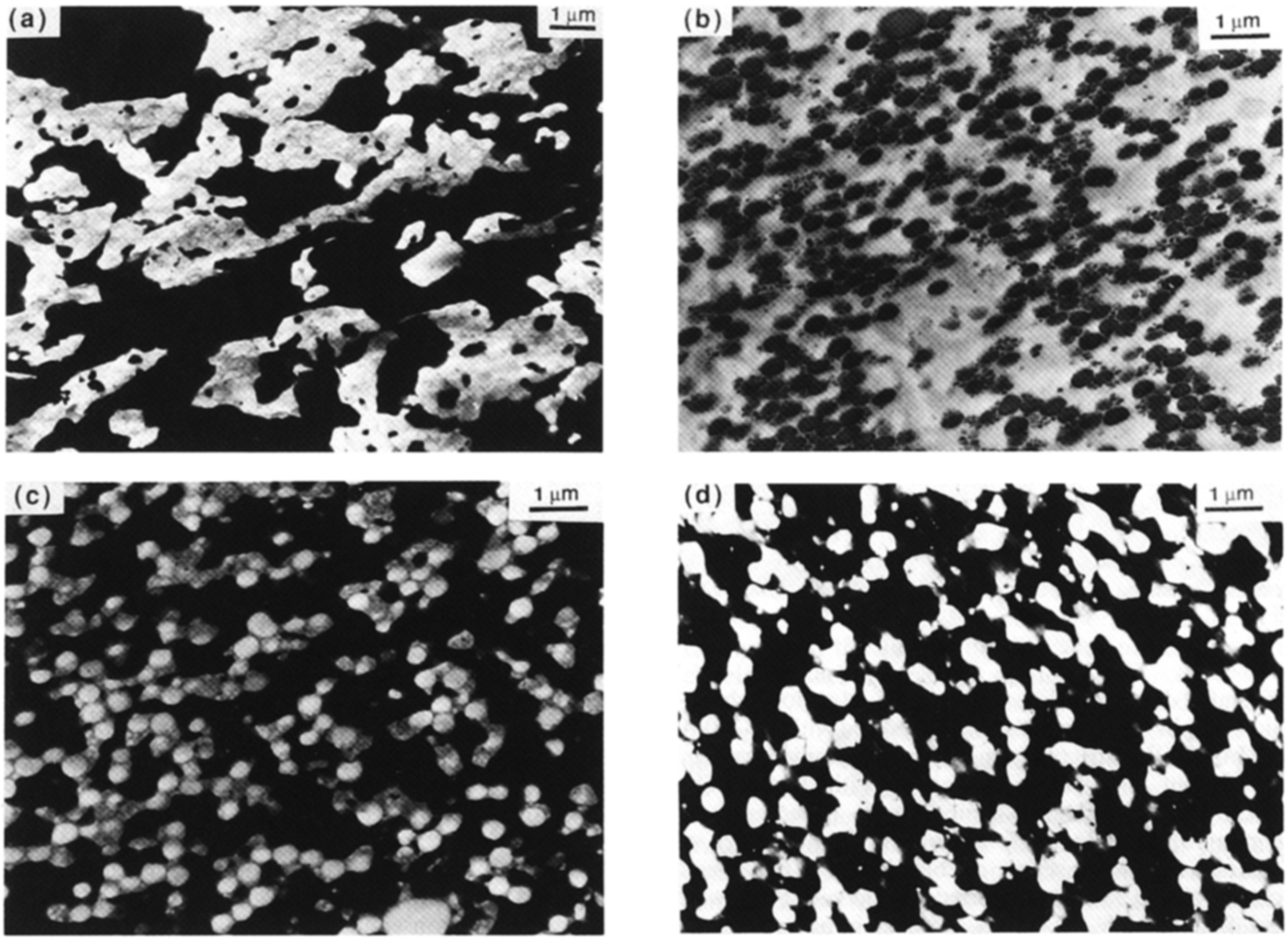

Figure 15 TEM photomicrographs of nylon-6/ABS (50/50 ratio) blends containing (a) 5% IA-245 (stained with PTA), (b) 5% IA-269 (stained with OsO_4), (c) 5% IA-269 (stained with PTA) and (d) 10% IA-268 (stained with PTA)

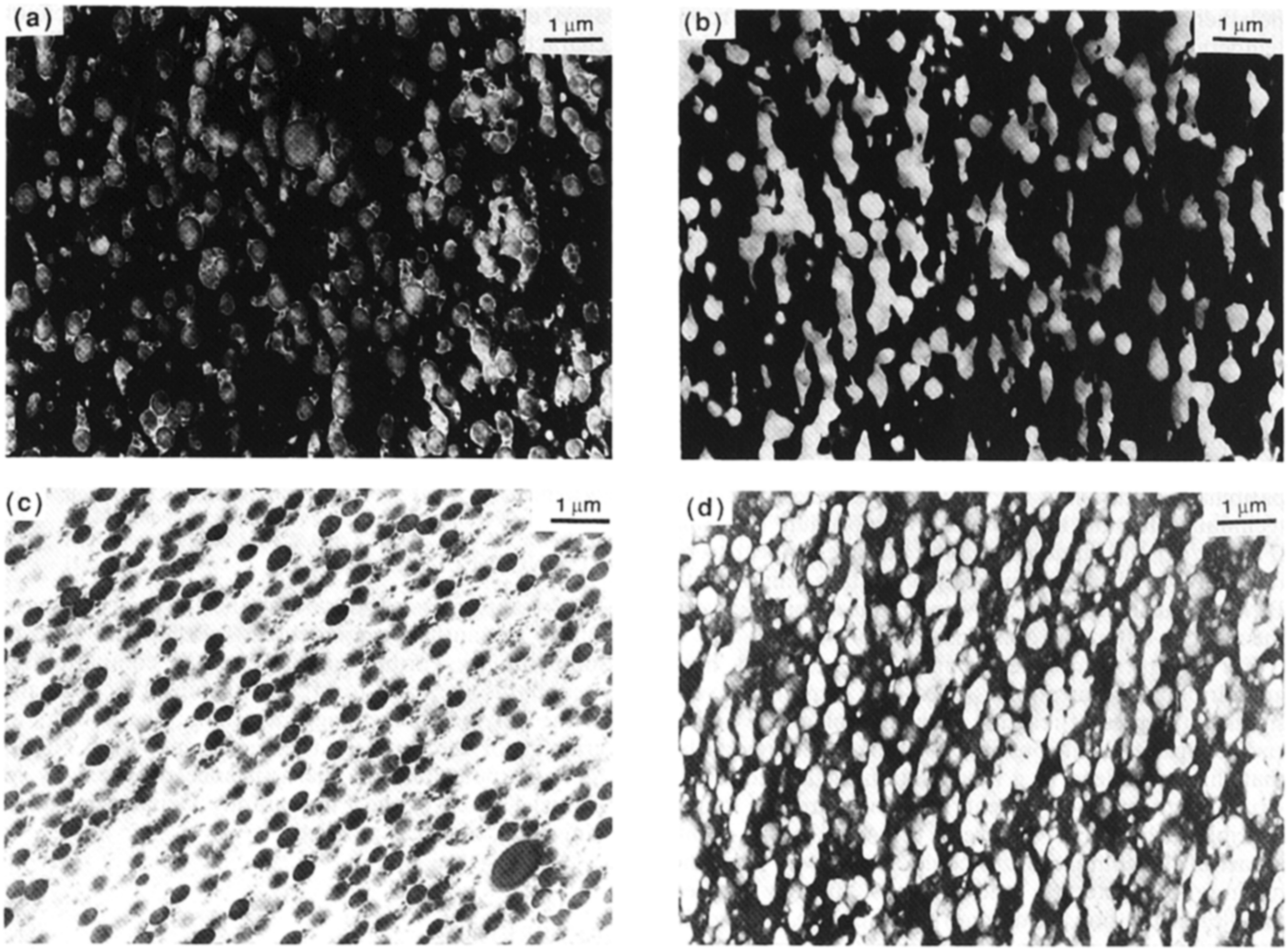

Figure 16 TEM photomicrographs of nylon-6/ABS (45/45) blends containing 10% comptibilizer: (a) GA-92 (dual stained with PTA and OsO_4), (b) Delpet 980N (stained with PTA), (c) SMA 25 (stained with OsO_4) and (d) SMA 25 (stained with PTA)

two different staining techniques for blends compatibilized with 5% IA-269 imidized acrylic. Staining with OsO_4 reveals some degree of clustering of the rubber particles (*Figure 15b*), while the PTA staining technique shows more clearly how the butadiene rubber particles are connected to each other by the SAN to form these clusters (*Figure 15c*). This imidized acrylic has a much higher concentration of free acid units, which are not as reactive with the polyamide as the anhydride units[54,55] and it is not miscible with the SAN phase in the ABS (*Table 2*). Both factors probably contribute to the large ABS domains and the relatively poor impact properties of this blend. Increasing the concentration of IA-269 to 10% results in more efficient dispersion of the rubber particles and improvement in the toughness (*Table 4*). *Figure 15d* shows a TEM photomicrograph for the blend compatibilized with 10% IA-268 where the polyamide has been stained with PTA. The ABS domains appear to be fairly well dispersed in this blend. In spite of the fact that IA-268 is not miscible with the SAN phase of the ABS material, this blend displays mechanical properties (both impact and tensile) comparable to the blend compatibilized with one of the most optimal compatibilizers used in this work, IA-250-C (see *Table 4* and *Figure 9*). Although this observation is somewhat unexpected, one might tentatively attribute this behaviour to a change in miscibility characteristics[56–58] after reacting with the nylon-6 during blend preparation. As discussed previously, during this process the compatibilizing polymer could actually develop more affinity for the SAN phase in the ABS and become a more efficient compatibilizer[30]. To explore this possibility in a definitive way would require techniques well beyond the scope of this work.

Highly functional compatibilizers

Table 5 also includes the mechanical properties of nylon-6/ABS blends using the compatibilizers GA-92, Delpet 980N and SMA 25, which are miscible with the SAN phase in the ABS but have significantly higher concentrations of anhydride groups than the imidized acrylic polymers described earlier. The terpolymer GA-92 is quite similar to the imidized acrylic polymers except that it does not have any imide repeat units. This compatibilizer leads to super-tough nylon-6/ABS blends under ambient conditions with a fairly low ductile–brittle transition temperature (see *Table 5*). Delpet 980N (a terpolymer of methyl methacrylate, styrene and maleic anhydride (73/18/9)), on the other hand, produces super-tough blends that become brittle slightly below room temperature. As described in a previous paper[28], a narrow range of compositions of nylon-6/ABS blends compatibilized with the styrene–maleic anhydride copolymer, SMA 25, leads to super-tough blends at room temperature that become brittle at temperatures just below this. This was largely attributed to the extremely high reactive functionality (25% MA) of this polymer. The particular composition shown in *Table 5* is not super-tough even at room temperature.

Figure 16 shows TEM photomicrographs for the nylon-6/ABS blends, stained in the ways indicated, compatibilized with 10% of each of the above-mentioned additives. For the blend compatibilized with GA-92, the ABS domains appear to be fairly well dispersed in the polyamide matrix. For the blend compatibilized with Delpet 980N, relatively large ABS domains are observed (*Figure 16b*). Some of these domains are elongated in shape, which may indicate a tendency towards co-continuity in this blend. *Figures 16c* and *16d* show TEM photomicrographs for the nylon-6/ABS blend compatibilized with SMA 25 using two different staining techniques. For the blend stained with osmium tetroxide (*Figure 16c*), the butadiene rubber particles appear to be relatively well dispersed in the nylon matrix; staining with PTA reveals significant SAN interconnections between the various butadiene domains (*Figure 16d*).

For all three of these compatibilizers with high anhydride concentrations, one can expect a very signficant degree of reaction with the polyamide amine end-groups. It is quite possible, as pointed out previously, that this could lead to a modification of the molecular structure to such an extent that they are no longer miscible with the SAN phase in the ABS. In this event, a part of the compatibilizer could move away from the nylon-6/ABS interface and exist as strongly grafted micelles in the polyamide matrix. Of course, this could be the underlying cause for the poor low-temperature impact properties and the elongated ABS domains observed in these blends. Among these compatibilizers, SMA 25 has the maximum anhydride functionality, which we feel is the primary factor responsible for the fact that these blends are brittle even at room temperature. The conclusion that such high levels of functionality are undesirable for a compatibilizer stem entirely from empirical observations, and to date the specific mechanistic details that underlie this observation have not been proved, although various speculations have been offered.

CONCLUSIONS

An imidized acrylic polymer (IA-250-C) was successfully used for generating super-tough nylon-6/ABS blends over a wide range of component proportions. The mechanical properties of the blends can be optimized by controlling the nylon-6/ABS ratio and the concentration of this compatibilizer. Generally, an efficient dispersion of the ABS domains leads to a desirable combination of low-temperature toughness and high tensile modulus for these blends. A minimum rubber concentration was established for producing super-tough nylon-6/ABS blends. Varying the mixing protocol did not seem to affect the key mechanical properties in the blends or the critical rubber concentration for generating toughened blends.

The use of imidized acrylic polymers with varying molecular compositions clearly demonstrates the importance of optimizing the functionality and miscibility characteristics of additives intended to serve as effective compatibilizers for nylon-6/ABS blends. Imidized acrylic polymers that are miscible with SAN and have a total acid content in the 3–4% range lead to the lowest ductile–brittle transition temperatures. This range also corresponds to the most efficient dispersion of the ABS domains. Several other imidized acrylic polymers used in this work for compatibilizing nylon-6/ABS blends further illustrated the need for careful molecular design of the compatibilizing species. Besides the imidized acrylics, three different types of polymers with high anhydride content (which were miscible with the SAN phase of the ABS) were tested as compatibilizers for nylon-6/ABS blends. It was clear from these results that more than some optimal amount of anhydride in these polymers limits their use as compatibilizers for nylon/ABS systems.

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REFERENCES

1 Paul, D. R. and Newman, S. (Eds.) 'Polymer Blends', Academic Press, New York, 1978

2 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979

3 Paul, D. R., Barlow, J. W. and Keskkula, H. 'Polymer Blends' in 'Encyclopedia of Polymer Science and Engineering' (Eds. H. Mark, N. Bikales, C. G. Overberger and H. Menges), Wiley-Interscience, New York, 2nd Edn., 1988, Vol. 12, p. 399

4 Paul, D. R. in 'Functional Polymers' (Eds. D. E. Bergbreiter and C. E. Martin), Plenum Press, New York, 1989, p. 1

5 Paul, D. R. in 'Polymer Blends' (Eds. D. R. Paul and S. Newman), Academic Press, New York, 1978, Ch. 12

6 Teyssie, Ph. *Makromol. Chem., Macromol. Symp.* 1988, **22**, 83

7 Sjoerdsma, S. D., Bleijenberg, A. C. A. M. and Heikens, D. *Polymer* 1981, **22**, 619

8 Jerome, R., Fayt, R. and Teyssie, Ph. in 'Thermoplastic Elastomers: A Comprehensive Review' (Eds. N. R. Legge, H. Schroeder and G. Holden), Hanser, Munich, 1987, Ch. 12, Sect. 7

9 Paul, D. R. in 'Thermoplastic Elastomers: Research and Development' (Eds. N. R. Legge, H. Schroeder and G. Holden), Hanser, Munich, 1987, Ch. 12, Sect. 6

10 Xanthos, M. *Polym. Eng. Sci.* 1988, **28**, 1392

11 Baker, W. E. and Saleem, M. *Polymer* 1987, **28**, 2057

12 Wu, S. *Polymer* 1985, **26**, 1855

13 Hobbs, S. Y., Bopp, R. C. and Watkins, V. H. *Polym. Eng. Sci.* 1983, **23**, 380

14 Fowler, M. W. and Baker, W. E. *Polym. Eng. Sci.* 1988, **28**, 1427

15 Borggreve, R. J. M. and Gaymans, R. J. *Polymer* 1989, **30**, 63

16 Borggreve, R. J. M., Gaymans, R. J. and Schuijer, J. *Polymer* 1989, **30**, 71

17 Borggreve, R. J. M., Gaymans, R. J. and Luttmer, A. R. *Makromol. Chem., Macromol. Symp.* 1988, **16**, 195

18 Lavengood, R. E. and Silver, F. M. *SPE Tech. Papers* 1987, **33**, 1369

19 Lavengood, R. E., Padwa, A. R. and Harris, A. F. US Pat. 4713415, 1987 (assigned to Monsanto)

20 Lavengood, R. E., Patel, R. and Padwa, A. R. US Pat. 4777211, 1988 (assigned to Monsanto)
21 Howe, D. V. and Wolkowicz, M. D. *Polym. Eng. Sci.* 1987, **27**, 1582
22 Howe, D. V. and Wolkowicz, M. D. *SPE Tech. Papers* 1986, **32**, 324
23 Aoki, Y. and Watanabe, M. US Pat. 4987182, 1991 (assigned to Monsanto Kasei Co.)
24 Padwa, A. R. and Lavengood, R. E. *ACS Symp. Ser.* 1992, **33**, 600
25 Paul, D. R. in 'Advances in Polymer Blends and Alloys Technology' (Ed. K. Finlayson), Technomic, Lancaster, PA, 1993, Vol. 4, p. 80
26 Angola, J. C., Fujita, Y., Sakai, T. and Inoue, T. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 807
27 Aoki, Y. and Watanabe, M. *Polym. Eng. Sci.* 1992, **32**, 878
28 Triacca, V. J., Ziaee, S., Barlow, J. W., Keskkula, H. and Paul, D. R. *Polymer* 1991, **32**, 1401
29 Takeda, Y. and Paul, D. R. *J. Polym. Sci.* (*B*) *Polym. Phys.* 1992, **30**, 1273
30 Majumdar, B., Keskkula, H., Paul, D. R. and Harvey, N. G. *Polymer* 1994, **35**, 4263
31 Buskirk, B. and Akkapeddi, M. K. Proc. IUPAC 33rd Int. Symp. on Macmomolecules, Session 3.2.3, Montreal, 1990
32 Hallden-Abberton, M. US Pat. 4246374, 1989 (to Rohm and Haas)
33 Hallden-Abberton, M. *Polym. Mater. Sci. Eng.* 1991, **65**, 361
34 Hallden-Abberton, M., Cohen, L. and Wood, R. US Pat. 4874824, 1989 (to Rohm and Haas)
35 Hallden-Abberton, M., Bortnick, N., Cohen, L., Freed, W. and Fromuth, H. US Pat. 4727117, 1988 (to Rohm and Haas)
36 Fowler, M. E., Paul, D. R., Cohen, L. A. and Freed, W. T. *J. Appl. Polym. Sci.* 1989, **37**, 513
37 Kim, H., Keskkula, H. and Paul, D. R. *Polymer* 1990, **31**, 869
38 Kim, J. H., Keskkula, H. and Paul, D. R. *J. Appl. Polym. Sci.* 1990, **40**, 183
39 Martinez-Salazar, J. and Cannon, C. G. *J. Mater. Sci. Lett.* 1984, **3**, 693
40 Morel, D. E. and Grubb, D. T. *Polymer* 1984, **25**, 41
41 Boylston, E. K. and Rollins, M. L. *Microscope* 1971, **19**, 255
42 Spit, B. J. *Faserforsch. Textiltech.* 1967, **18**, 161
43 Rusnock, J. A. and Hansen, D. *J. Polym. Sci.* (*A*) 1965, **3**, 617
44 Wu, S. *Polymer* 1985, **26**, 1855
45 Min, K., White, J. L. and Fellers, J. F. *Polym. Eng. Sci.* 1984, **24**, 1327
46 Wu, S. *Polym. Eng. Sci.* 1987, **27**, 335
47 Serpe, G., Jarrin, J. and Dawans, F. *Polym. Eng. Sci.* 1990, **30**, 553
48 Favis, B. D. and Chalifoux, J. P. *Polym. Eng. Sci.* 1987, **27**, 1591
49 Work, J. L. *Polym. Eng. Sci.* 1973, **13**, 52
50 Avgeropoulos, G. N., Weissert, F. C., Biddison, P. H. and Bohm, G. G. A. *Rubber Chem. Technol.* 1975, **49**, 93
51 Paul, D. R. and Barlow, J. W. *J. Macromol. Sci.–Rev. Macromol. Chem.* (*C*) 1980, **18**, 109
52 Jordhamo, G. M., Manson, J. A. and Sperling, L. H. *Polym. Eng. Sci.* 1986, **26**, 517
53 Patterson, J. and Gruber, C. *SPE Tech. Papers* 1988, **34**, 643
54 Lu, M., Keskkula, H. and Paul, D. R. *Polymer* 1993, **34**, 1874
55 Lu, M., Keskkula, H. and Paul, D. R. *Polym. Eng. Sci.* 1994, **34**, 33
56 Paul, D. R. and Barlow, J. W. *Polymer* 1984, **25**, 487
57 ten Brinke, G., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1983, **16**, 1827
58 Kambour, R. P., Bendler, J. T. and Bopp, R. C. *Macromolecules* 1983, **16**, 753
59 Majumdar, B., Keskkula, H. and Paul, D. R. *Polymer* 1994, **35**, 5468