

Reactive compatibilization of blends of nylon 6 and ABS materials

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Blends of nylon 6 with various ABS materials including its styrene/acrylonitrile, SAN, matrix component were examined for rheological behaviour, mechanical properties, and phase morphology. These mixtures have poor mechanical properties unless properly compatibilized. This was done here by adding to the SAN phase a polymer that is miscible with it but which contains functional groups that can react with the nylon 6 to form *in situ*, graft copolymers at the polymer-polymer interfaces. These compatibilizer molecules contained either anhydride or oxazoline units for reactivity. Evidence of reactions in the blends was seen in the rheological behaviour of the melt and in the morphology and mechanical behaviour of the solid. Some blends exhibited outstanding toughness. A more quantitative assessment of the extent of reaction was provided by a selective solvent extraction technique. Lap shear adhesion measurements for laminates of nylon 6 with materials containing reactive polymers provided a direct way to assess the effectiveness of the interfacial reaction.

(Keywords: nylon 6; ABS; SAN; blends; compatibilization)

INTRODUCTION

There is intense commercial interest in multiphase polymer blends, or alloys, because of the potential opportunities for combining the attractive features of each material into one or for improving deficient characteristics of a particular material¹⁻⁴. However, quite often immiscible blends have poor mechanical properties relative to their components and their phase morphology is strongly dependent on details of the processing history. The reason for this is the unfavourable interaction between molecular segments of the components, responsible for their immiscibility in the first place, that leads to a large interfacial tension in the melt, which makes it difficult to properly disperse the components during mixing and drives phase rearrangements during low stress or quiescent conditions. It also leads to poor interfacial adhesion in the solid state which causes premature mechanical failure via these weak defects between phases. Remediation of these problems, or compatibilization, can be effected by the addition of appropriate block or graft copolymers that act as interfacial agents as demonstrated repeatedly over the last two decades⁵⁻¹⁰. Grafting has been widely used with considerable success to incorporate a rubber phase into brittle polymers to effect toughening^{3,11}. With this exception, compatibilization by preformed block or graft copolymers has not been used as extensively as the potential utility might suggest. A primary reason for this is the lack of economically viable industrially practical routes for synthesis of such additives for systems of interest.

An attractive alternative is to form the block or graft copolymer *in situ* during blend preparation via inter-

facial reaction of added functionalized polymeric components^{5,12-30}. This approach has already been implemented in a number of commercial products and in many instances appears to be the method of choice for compatibilization. There are many important questions about how to most effectively design and implement a reactive compatibilization scheme which cannot be answered with available experience or theory. We have undertaken a broad based fundamental programme to address these questions. By necessity our programme includes many facets. These include selection of the chemistry to be used (types of functional groups), synthesis to incorporate functional groups, processing, rheology, blend analysis (chemical and morphological), interfacial adhesion, mechanical properties and fracture characteristics, to mention only the most obvious. This paper serves as an introduction applied to a specific system, nylon/ABS type blends.

The nylons are an attractive class of polymers for engineering applications, but they have a number of deficiencies for certain applications, for example, brittleness, high moisture sorption, poor dimensional stability and marginal heat deflection temperatures. Many of the deficiencies can be improved by blending with other plastics, like poly(phenylene oxide)^{17,18}, ABS^{16,31}, polyolefins²⁵, or polycarbonate³², or with rubber^{23,24,27-30}. A particularly attractive feature of the nylons for reactive coupling to other polymers is their inherent chemical functionality through the amine or carboxyl end groups that may be present, and potentially, the amide linkage itself. Thus, there is no need to functionalize this component by further reaction or by physical addition of a functional component. Use of ABS as the other phase was attractive to us, beyond the demonstrated importance of this system³¹, because of the numerous options

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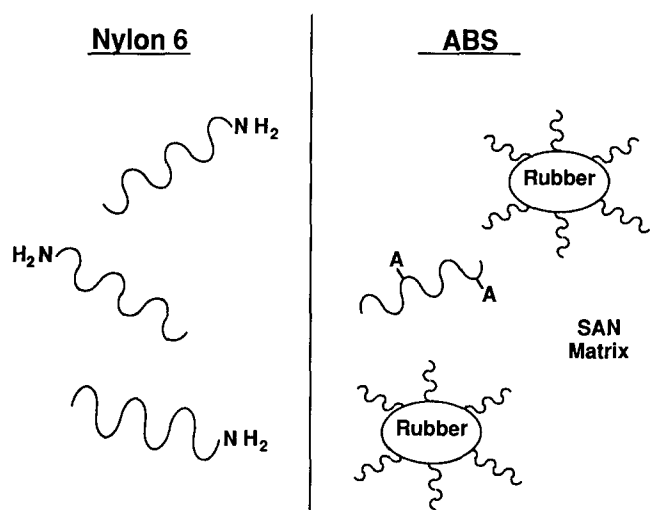


Figure 1 Schematic diagram showing the situation near the interface in nylon 6/ABS blends illustrating reactive groups on the polyamide (e.g. amine ends) and a miscible, functionalized polymeric additive (A groups are reactive) in the SAN phase of the ABS

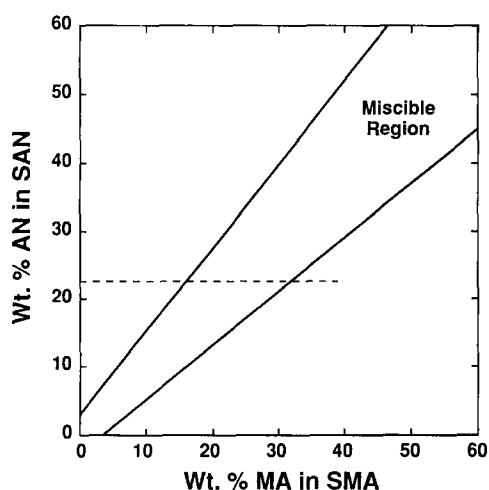


Figure 2 Miscibility map for blends of SAN-SMA copolymer. Horizontal dashed line shows composition of SAN phase in the material designated SAN-g

for adding to it a compatibilizing functional precursor that can react with nylon.

Our strategy for this system is to incorporate a polymer into the ABS which is miscible with its SAN phase and which can react with the nylon when the two meet at the nylon-SAN interface (see *Figure 1*). The compatibilizer precursor contains a certain number of functional groups, A, as shown in *Figure 1*. Some major molecular design choices include: the type of A groups, which determines the kinetics of reaction with the nylon; the number of A groups per chain; the manner in which these groups are incorporated (grafted, comonomer, or terminal groups); the molecular weight of the chain; and how to make this polymer miscible with SAN. One approach to the latter is to select a polymer that is miscible with the SAN, e.g. another SAN³³, PMMA³⁴, acrylic-glutarimide copolymers³⁵, and limit the extent of functionalization so that miscibility is preserved. Another approach is to take advantage of the fact that styrene/maleic anhydride, or SMA, copolymers are miscible with SAN copolymers³⁶⁻³⁹ within the composition ranges shown in *Figure 2*. Here, the MA is the functional group and is part of the cause for miscibility. In all of these approaches, the level of functionality and the conditions for miscibility are connected so the former cannot be varied independently over broad ranges. In this paper we examine several of these options in blends of nylon 6 with various ABS related materials.

EXPERIMENTAL

Table 1 summarizes pertinent information about the materials used in this work. The nylon 6 (N6) is a commercially available material with $\bar{M}_n = 25\,000$. It is believed to have one carboxyl and one amine group per chain or a total of 40 mmol kg^{-1} of each. Before every processing step, all materials containing any nylon 6 were dried for at least 12 h at 85°C in a vacuum oven to ensure removal of sorbed water.

An ABS typical of the plastics used in engineering applications (ABS 541) was used in selected blends with nylon 6. This material is a mass-made product which has

Table 1 Polymers used in this study

Designation	Material/description	Composition	Molecular weight	Source
N6	nylon 6 (Capron 8207)	—	$\bar{M}_n = 25\,000$	Allied-Signal
ABS	ABS 541	16% rubber 25% AN in SAN	$\bar{M}_n = 59\,000^a$ $\bar{M}_w = 140\,000$	Dow Chemical Co.
SAN-g	SAN grafted emulsion rubber (BL-65)	50% rubber 22.5% AN in SAN	$\bar{M}_n = 44\,000^a$ $\bar{M}_w = 167\,000$	Sumitomo Naugatuck Co.
SAN 25	styrene/acrylonitrile copolymer (Tyril 1000)	25% AN	$\bar{M}_n = 77\,000^a$ $\bar{M}_w = 152\,000$	Dow Chemical Co.
SMA 25	styrene/maleic anhydride copolymer ^b	25% MA	viscosity = 4.73^c	Monsanto Chemical Co.
SMA 14	styrene/maleic anhydride copolymer (Dylark 332)	14% MA	$\bar{M}_n = 90\,000^a$ $\bar{M}_w = 180\,000$ viscosity = 7.95^c	Arco Chemical Co.
Imide	methyl methacrylate/ <i>N</i> -methyl glutarimide copolymer	57 wt% imide 1.8% free acid 1.0% anhydride	$\sim 90\,000$	Rohm & Haas Co.
R-SAN	reactive SAN	30% AN 1% oxazoline	$\sim 135\,000$	Dow Chemical Co.

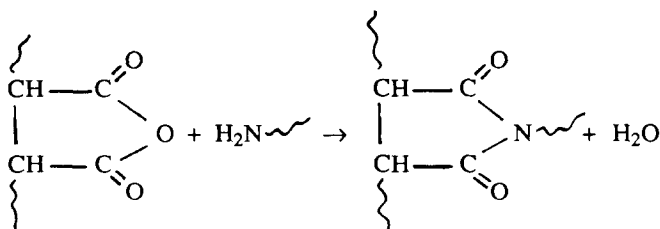
^aFrom g.p.c. using polystyrene standards. For ABS materials, the information shown is for soluble SAN

^bContains a small amount of a third monomer

^cViscosity at 25°C , in mPa s, of 10% solution in methyl ethyl ketone

a high rubber content (16% by weight) in the form of 0.5 to 1 μm particles. Its SAN phase contains about 25% AN. Most of the work reported here employed an ABS-type material having a much higher rubber content (50% by weight). As described in earlier work^{40,41}, this product consists of SAN copolymer grafted to a butadiene-based latex rubber which has a broad distribution of particle sizes but typical particle sizes are in the range of 0.2 μm in diameter. The SAN contains 22.5% AN by weight and only 40% of it is chemically grafted to the rubber. This grafted rubber concentrate is designated here as SAN-g to avoid confusion with the previous ABS or other typical materials of this family of plastics. Because all materials of this category have an SAN matrix phase, some experiments were done using a typical commercial copolymer, SAN 25, to observe responses in the absence of a rubber phase.

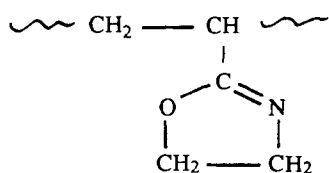
A number of functional polymers which can potentially react with nylon 6 were considered. However, the most extensive investigation was done with a single material, a styrenic copolymer containing 25% by weight of MA, SMA 25. As can be seen in Figure 2, SMA 25 is well within the region of miscibility with an SAN containing 22.5% AN (dotted line in Figure 2 corresponds to SAN-g) or with SAN 25. This material has more than ample functional groups for reacting with nylon 6 chain ends by the route suggested below.



In some regards, this molecule may be over functional, but it will be used in limited quantities. As suggested by the dashed line in Figure 2, there is a limit to how low the MA content can be reduced while maintaining miscibility with the matrix phase of SAN-g. A few experiments were done with SMA 14, which lies just outside the miscibility zone in order to gain insight into the requirement for miscibility.

As reported previously³⁵, certain methyl glutarimide/methyl methacrylate copolymers are miscible with SAN copolymers of the type of interest here. One of these which has some chemical functionality (free acid = 1.8%, anhydride = 1.0%) and 57% by weight glutarimide units was selected for limited studies. This material was shown⁴² to be miscible with SAN 25 and SAN 20. Therefore, it should be miscible with the matrix phase of SAN-g. Evidence is presented later that this material, designated here as Imide, does react with nylon 6.

The final material to be mentioned is the reactive SAN which has oxazoline functionality.



This material contains 30% AN by weight and should

be miscible with SAN 25 but probably would not be miscible with an SAN 22.5 based on the work of Molau³³. It has 1% oxazoline containing monomer that is said to react with carboxyl, anhydride, phenolic hydroxyls, amine and other groups⁴³. Thus, it should be able to react with nylon 6.

For rheological purposes, various materials and blends were mixed in a Brabender Plasticorder which has a 50 cm^3 mix-head while the torque (at 60 rev min^{-1}) was recorded. Except as noted, these tests were all carried out at 240°C.

To prepare samples for mechanical testing, blends were mixed in a Killion single screw extruder (diameter = 2.54 cm, $L/D = 30$). A single strand (≈ 0.3 cm in diameter) was extruded, cooled in a water bath, and pelletized. Temperatures were set as necessary. In every case, the reactive component was first mixed with the SAN based material, and this blend was then mixed with nylon 6. Except where noted, each extrusion step was repeated twice to ensure good mixing. In subsequent discussions, compositions of the reactive component will be expressed as a percentage of the premix with the SAN-based material. 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. The detailed processing conditions used are reported elsewhere⁴².

Test specimens were visually inspected for air bubbles, and those with defects were discarded. Immediately following moulding, the samples were introduced into a sealed plastic bag or a desiccator to avoid moisture sorption. These samples were tested dry as moulded. Tensile testing was done on an Instron in accordance with ASTM D638 using a crosshead speed of 0.50 cm min^{-1} . An extensometer was used to obtain modulus and yield strain. Separate tests were made on ductile samples to obtain the elongation at break. Izod bars were notched and tested in accordance with ASTM D256 method A.

For lap shear adhesion measurements, void-free plaques (20 cm \times 20 cm \times 0.318 cm) of nylon 6 were prepared by compression moulding using a frame mould. All other materials were pressed, without using a frame, into films of 0.5 ± 0.1 mm thick. A sandwich of two nylon 6 outer layers with the film in between were laminated in a frame mould at 240°C under a pressure of 250 psi for 10 min followed by cooling to room temperature by circulating water in the platens of the mould. These were cut and notched to form specimens conforming to ASTM D3165 with dimensions shown in Figure 3. Samples with any visible defect were not tested. The specimens were pulled with an Instron at 0.50 cm min^{-1} to failure, and the results reported are failure load divided by the lap area.

For all mechanical tests, at least seven specimens (and usually more) were tested and the results reported are averages. Generally, the standard deviations were typical for these types of measurements and are, therefore, not reported here for the sake of brevity. One special case is described in detail in what follows.

RHEOLOGY

Rheology has an important influence on the morphological structure formed during blend processing and can

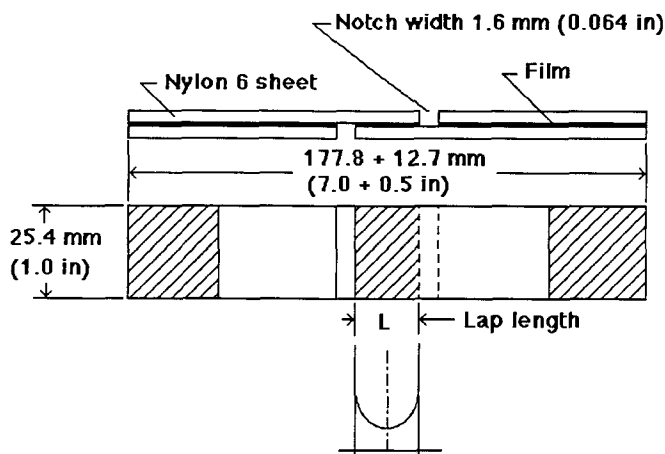


Figure 3 Description of lap shear specimens for adhesion measurements ($L = 1.27$ cm used here)

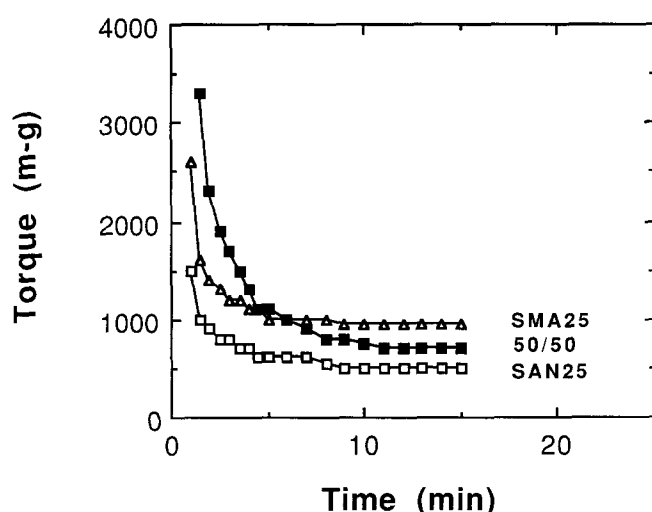


Figure 4 Brabender torque response for SAN 25, SMA 25 and their 50/50 blend at 240°C and 60 rev min^{-1}

be used to a certain extent to judge whether a reaction is occurring in functionalized systems^{15,22,26}. For non-reactive systems, melt viscosity (or torque in the Brabender experiment) is, to a first approximation, an additive property for blends. Compatibilizing reactions between phases of interest here are expected to lead to an increase in viscosity relative to this additive level and, with respect to processing time, depending on the rate of the reaction.

Figure 4 shows a Brabender torque experiment for the SMA 25/SAN 25 pair which form a miscible mixture but do not react. In the first 5 min or so, the torque response is dominated by fluxing of the cold pellets introduced into the heated chamber, but thereafter the torque levels off with the blend at a level intermediate to that of the pure components. Similar results are seen for SAN and nylon 6. However, the addition of small amounts of SMA 25 to SAN 25 raises the steady state torque for blends with nylon 6 to levels higher than any of the components as seen in Figure 5. This is a result of reaction of the MA units with the amine groups of nylon 6. One might expect the torque to continue to rise with mixing time, but evidently the anhydride-amine reaction is very fast and any increase with time is masked by the fluxing process. In fact, at higher SMA 25 levels

higher SMA 25 levels there is evidence for a decrease in torque with time that probably reflects mastication of the graft material formed⁴². This is also illustrated in Figure 6 where torque is plotted versus amount of SMA 25 with time in the Brabender as a parameter. Here nylon 6 is being mixed with a blend of SAN-g and SMA 25 prepared by extrusion. Similar indications of reaction can be seen during extrusion by monitoring the power used by the extruder motor (given by the current). Figure 7 shows examples for SMA 25 and SMA 14 blends with SAN-g during compounding with nylon 6. The response for SMA 25 is similar to that in Figure 6 at the short times like the extruder residence time. The increase in current for SMA 14 is considerably less than that when SMA 25 is used. The difference seems to be greater than the difference in levels of functionality of the two SMA copolymers.

Figure 8 shows a torque-time plot for a blend of nylon 6 with the functional methyl glutarimide/methyl methacrylate material (referred to as Imide). At all times

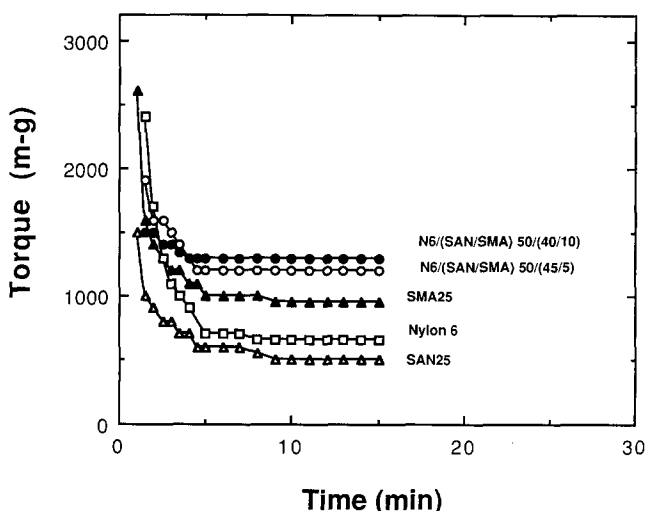


Figure 5 Brabender torque response for nylon 6 and blends with SAN 25 containing SMA 25 at 240°C and 60 rev min^{-1}

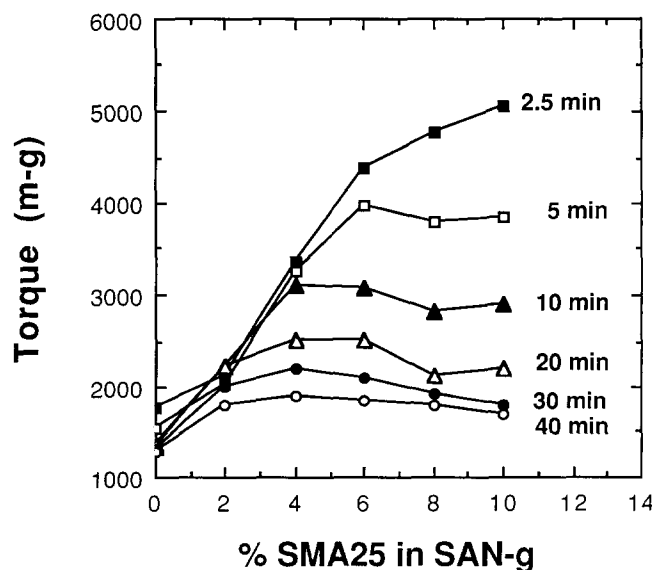


Figure 6 Brabender torque versus the amount of SMA 25 in SAN-g for 60/40 blends of nylon 6/(SAN-g/SMA 25) with mixing time as a parameter at 240°C and 60 rev min^{-1}

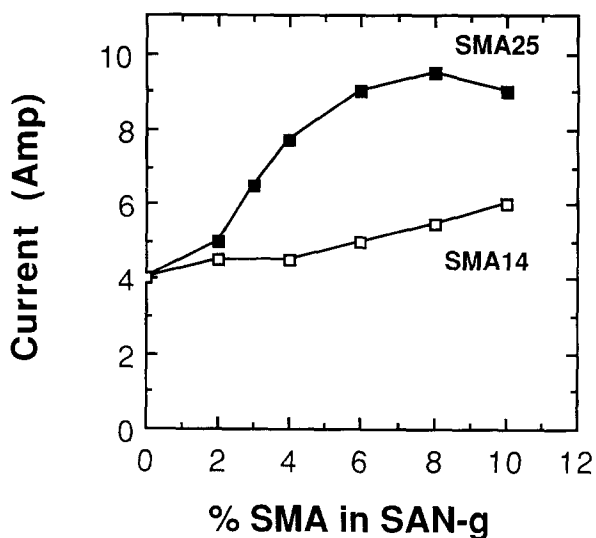


Figure 7 Extruder motor current for fixed screw rev min⁻¹ as a function of SMA content in SAN-g for 60/40 nylon 6/(SAN-g/SMA) blends during final extrusion

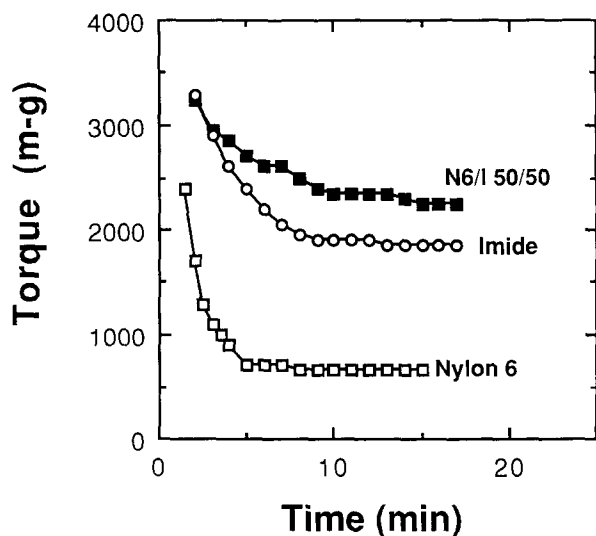


Figure 8 Brabender torque response for methyl methacrylate/methyl glutarimide copolymer and its blend with nylon 6 at 240°C and 60 rev min⁻¹

its torque is higher than that of either pure component, which is good evidence that a reaction between the two does occur in the melt and that this reaction is rapid. Figure 9 shows torque data for nylon 6 blends with R-SAN and with SAN 25 as a control after 15 min of mixing. The torques for the nylon 6/R-SAN blends are just barely, if at all, above the line connecting the pure components. Note, however, that the non-reactive nylon 6/SAN 25 control seems to fall below the additive line. Thus, one might argue that some reaction is needed to bring the blend torque up to additive. In any case, the rheological evidence for reaction is not as dramatic as that for all the previously described functional materials. Of course, the level of functionality of the SMA copolymers is much higher than the 1% of oxazoline units contained in R-SAN, so the SMA copolymers are expected to be much more reactive. However, the level of functionality of R-SAN is essentially the same as that for the Imide material. This suggests that oxazoline functionality may be less effective than anhydrides.

The rheological properties, or viscosity in the simplest

of cases, of each component are important factors in the blending process and the resulting morphology. Because most of the work reported later deals with blends of nylon 6 with SAN-g, we show in Figure 10 an indicator of their viscosities as a function of temperature. The high rubber ABS material is substantially more viscous than nylon 6 at all temperatures.

MECHANICAL PROPERTIES

Mechanical properties were determined for blends of nylon 6 with the materials designated in Table 1 as SAN 25, ABS, and SAN-g that were prepared by various extrusion procedures followed by injection moulding. The reactive compatibilizers, when present, were blended with the SAN-based materials in a prior extrusion step. The results presented first were obtained in an early exploratory phase of this work and helped lead to the more intense investigation of the nylon 6/(SAN-g/SMA 25) blends presented last.

Table 2 shows tensile properties of blends containing 75% nylon 6, with the remainder being SAN 25 plus

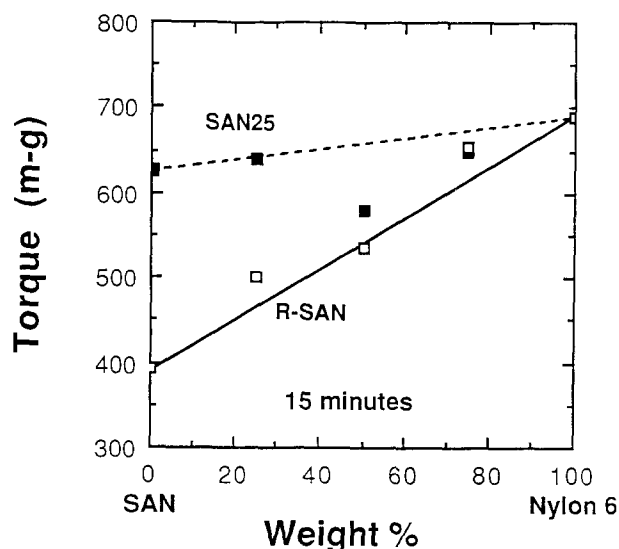


Figure 9 Torque for blend for nylon 6 with SAN 25 and R-SAN after 15 min in Brabender at 260°C and 60 rev min⁻¹

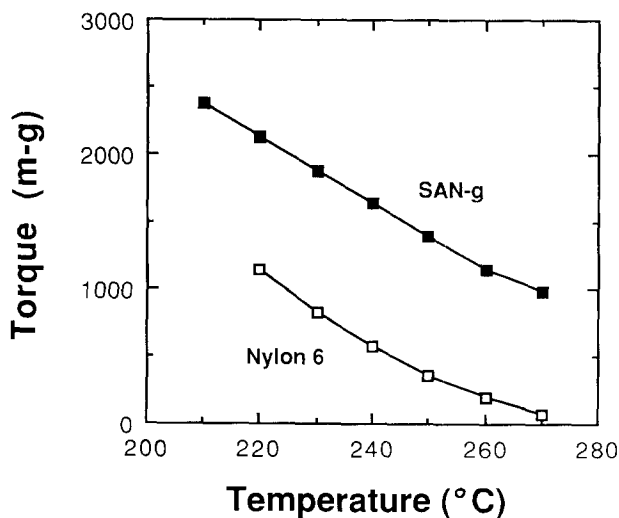


Figure 10 Brabender torque at 60 rev min⁻¹ for nylon 6 and SAN-g as a function of temperature

Table 2 Mechanical properties of nylon 6/(SAN 25/SMA 25) blends

Composition	% SMA 25 in SAN 25	Yield stress (MPa)	Modulus (MPa)	Break strain (%)
Nylon 6	–	69.6	2800	233
SAN 25	–	67.6	3280	2.8
N6/SAN 25 75/25	0	74.5	3120	3.2
N6/(SAN 25/SMA 25) 75/25	2	80.7	3150	4
N6/(SAN 25/SMA 25) 75/25	5	59.3	2760	2.4

Table 3 Mechanical properties of nylon 6 blends with SAN 25 and R-SAN as a function of number of extrusion steps

Composition	Runs in extruder	Yield stress (MPa)	Modulus (MPa)	Break strain (%)	Notched Izod impact ($J m^{-1}$)
Nylon 6	0	69.6	2800	233	40
SAN 25	0	67.6	3280	3	–
R-SAN	0	68.3	3660	2.8	–
N6/SAN ^a	1	65.5	2900	3	23
N6/R-SAN ^a	1	69.0	2790	12.5	20
N6/SAN ^a	2	67.6	3200	2.9	17
N6/R-SAN ^a	2	72.4	2900	170	20
N6/SAN ^a	3	70.3	3300	2.8	18
N6/R-SAN ^a	3	71.7	2890	75	30

^aNylon 6 content of each blend is 75% by weight

varying amounts of SMA 25. Data for pure nylon 6 and SAN 25 are also shown for comparison. The simple binary blend has poor ductility similar to SAN 25 even though nylon 6 is the major component. Addition of SMA 25 produces essentially no improvement in mechanical properties. This is in sharp contrast to the improved toughness reported by Inoue *et al.*¹⁹ using very similar materials. We believe that the origin of this difference may lie in the methods of sample preparation. The previous workers used a miniature moulding system that produces rather oriented materials which can be more ductile than unoriented blends⁴⁴, e.g. their 70/30 nylon 6/SAN 25 blend had an elongation at break > 135%. Such ductile, oriented materials may respond more to interfacial coupling than a blend having a rigid and brittle phase that is dispersed more or less like spherical inclusions. However, the experiments with the reactive SAN described next confounds this argument.

Table 3 shows mechanical properties of 75/25 blends of nylon 6 with R-SAN and with SAN 25 along with the appropriate controls. The latter were formed into test specimens directly by injection moulding while the blends were prepared by one, two or three passes through the extruder. Blends with SAN 25 show the same poor ductility regardless of the number of passes through the extruder. None of the specimens of this composition ever displayed a yield point during tensile testing. On the other hand, blends based on R-SAN showed yielding behaviour (see Figure 11) even after one pass through the extruder. A second pass through the extruder increased the elongation at break substantially but a third pass resulted in a reduction relative to two passes (see Table 3). Multiple extruder passes may allow more time for reaction, more shear for dispersion, and more opportunity for break down of graft structure formed, so an optimum number of passes is not altogether

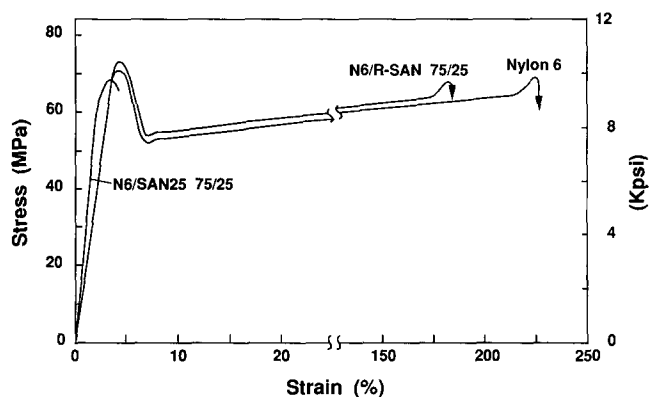


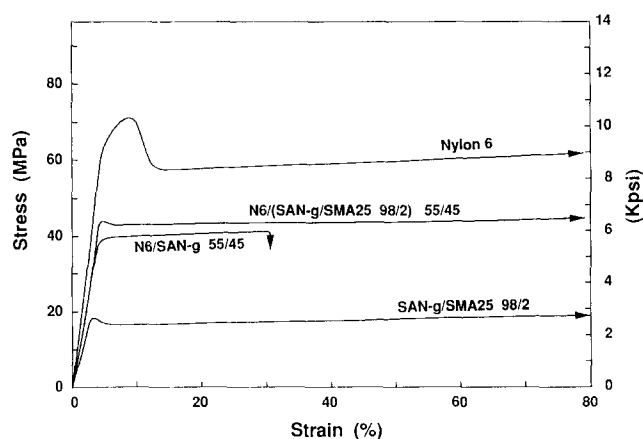
Figure 11 Stress-strain diagrams for nylon 6, nylon 6/SAN 25 and nylon 6/R-SAN blends at 5.08 mm min^{-1}

surprising. Nylon 6 blends with (SAN 25 + SMA 25) may be more brittle than blends with R-SAN because the high functionality of SMA 25 leads to a more highly branched, comb-like graft at the interface than does the R-SAN with its much lower functionality. The improved elongation at break found for R-SAN blends, however, did not translate into improved impact strength as seen by the last column in Table 3. Obviously there are many unsettled questions about the mechanical behaviour of nylon 6 blends with SAN rigid phases. However, these were not pursued further; our main objective was to obtain toughened materials, which appears to require a rubber phase.

Table 4 shows results for blends, along with controls, made from the ABS material described in Table 1 to which varying amounts of SMA 25 were added prior to extrusion blending with nylon 6. All results are for a single extrusion pass. Note that addition of small amounts of SMA 25 to the ABS does not alter the

Table 4 Mechanical properties of nylon 6 blends with ABS containing varying amounts of SMA 25

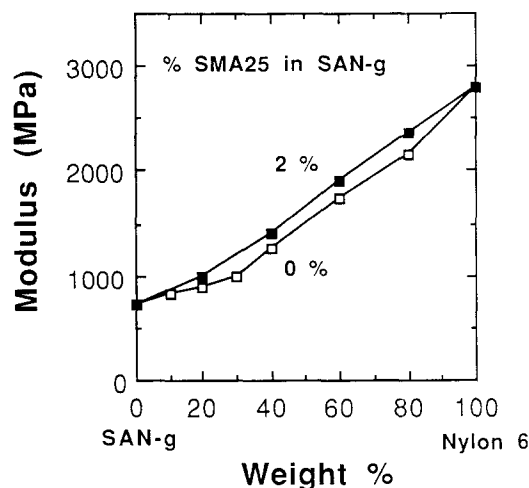
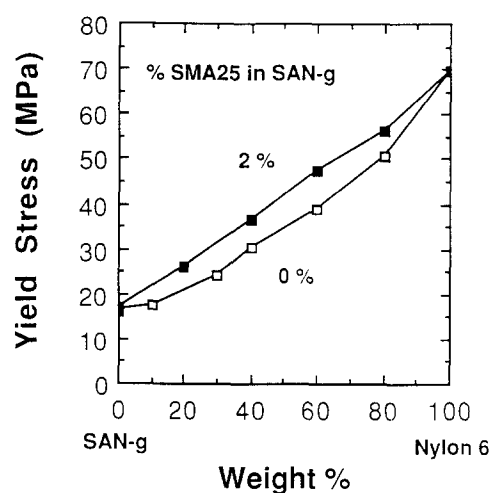
Composition	% SMA in ABS	Yield stress (MPa)	Modulus (MPa)	Break strain (%)	Notched Izod impact ($J m^{-1}$)
Nylon 6	—	69.6	2800	233	40
ABS	—	36.6	1980	16.6	235
ABS/SMA 25 98/2	—	35.9	1900	16.2	—
N6/ABS 75/25	0	64.1	2870	31.6	27
N6/(ABS/SMA 25) 75/25	0.5	67.6	3010	17.3	—
N6/(ABS/SMA 25) 75/25	2.0	64.1	2510	9.6	37
N6/(ABS/SMA 25) 75/25	5.0	60.7	—	7.2	—
N6/(ABS/SMA 25) 75/25	10	62.8	—	8.8	—
N6/ABS 50/50	0	52.4	2570	24.5	21
N6/(ABS/SMA 25 98/2) 75/25	2	40.0	2320	2.2	16

**Figure 12** Stress-strain diagrams for nylon 6 blends with SAN-g/SMA 25 mixtures

mechanical properties of the ABS significantly. As expected, nylon 6 blends with ABS are more ductile than corresponding blends with SAN. In fact, the nylon 6/ABS blends in *Table 4* have higher elongations at break than the pure ABS but the impact strength of the blends are lower. Addition of the SMA 25 resulted in lower elongations at break rather than improved ductility. At this point, one might question whether the strategy for coupling with added SMA 25 has any merits because it produces no beneficial results for nylon 6 blends with SAN 25 or with ABS. However, when SAN-g is used an entirely different picture emerges.

The ABS material designated as SAN-g was blended with the compatibilizer and then mixed with nylon 6 using two extruder passes for each mixing step because a preliminary study indicated this protocol gave optimum properties. These blends were then injection moulded into specimens for mechanical property determination. SMA 25 was found to be an effective compatibilizer for the SAN-g/nylon 6 system. *Figure 12* shows some typical stress-strain diagrams. It is important to note that SAN-g is considerably more ductile and less rigid than the commercial ABS mentioned earlier. This ductility is preserved after mixing with small percentages of SMA 25, as seen in *Figure 12*. Binary blends of nylon 6 with SAN-g were also more ductile than comparable blends with ABS and SAN. The addition of SMA 25 to SAN-g further improves the ductility of its blends with nylon 6 as illustrated in *Figure 12*.

To further illustrate this, *Figures 13* and *14* compare

**Figure 13** Modulus and yield stress of nylon 6/(SAN-g/SMA 25 98/2) blends

the tensile and impact properties *versus* nylon content for 2% SMA 25 in SAN-g relative to the binary case with no compatibilizer. As might be expected, elongation at break exhibits a minimum for the binary. However, this is restored to an additive value when 2% SMA 25 is present. The notched Izod impact strength shows a more complex behaviour but this property is improved by the compatibilizer when nylon is the major phase. Yield stress and modulus are both increased slightly by the presence of SMA 25. To explore the effect of SMA 25 level, blends with a fixed fraction of nylon were prepared. The

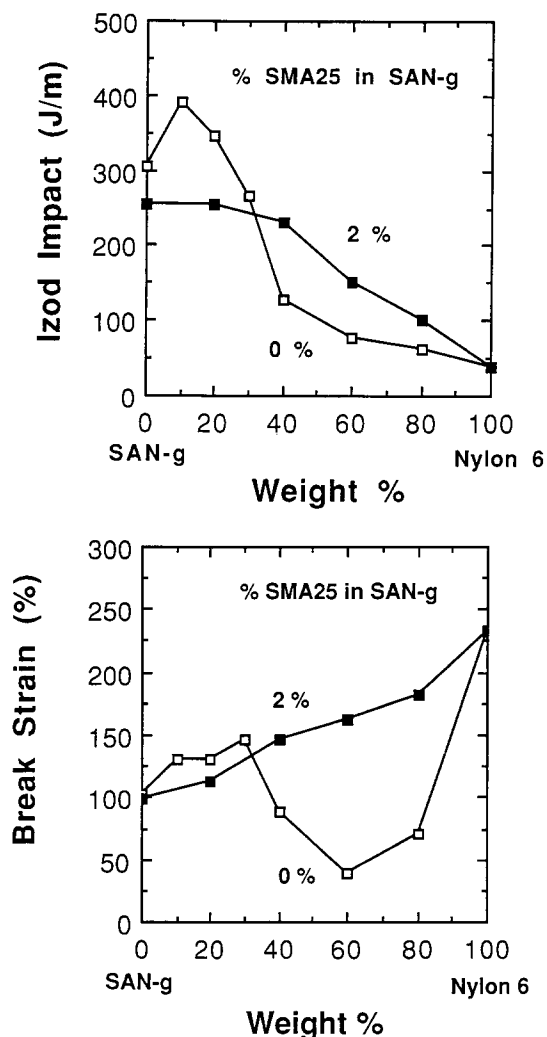


Figure 14 Impact strength and elongation at break for nylon 6/(SAN-g/SMA 25 98/2) blends

composition at the minimum of the percent elongation curve in Figure 14 (60% nylon 6) was selected for this purpose. Figure 15 shows how impact strength and elongation at break change as the amount of SMA 25 in SAN-g is increased.

Interestingly, there appears to be an optimum level at about 2 to 5% SMA 25. The initial increase, of course, reflects the benefits of coupling the phases and the attendant morphology changes. The decline may reflect a loss in optimum morphology, embrittlement by excessive reaction, and possibly other causes. High SMA 25 levels would embrittle the SAN-g itself owing to dilution of the rubber content and the very brittle nature of SMA 25. However, at these relatively low levels, we believe this is not the sole issue. Another factor is the relative stoichiometry of the functional groups. For blends containing 60% nylon 6, the SAN-g phase must contain 2.4% SMA 25 to have exactly as many MA units as there are nylon 6 amine end-groups, assuming this is the only reactive site in the nylon. Because this is very near the optimum level in Figure 15, it is tempting to suggest that stoichiometry may be an influential issue. Of course, full reaction of the SMA 25 molecule would result in an extreme level of grafting per molecule. It is hard to imagine that this would be well suited for an interfacial role.

All of the mechanical properties shown here are

averages. In most cases, the range associated with testing 10 or more samples was relatively narrow. This was not the case near the maximum in Figure 15, and simply reporting the average fails to give the full picture. This is illustrated by the histogram of Izod values shown in Figure 16 for 28 specimens containing 4% SMA 25 prepared on two separate occasions. A significant number

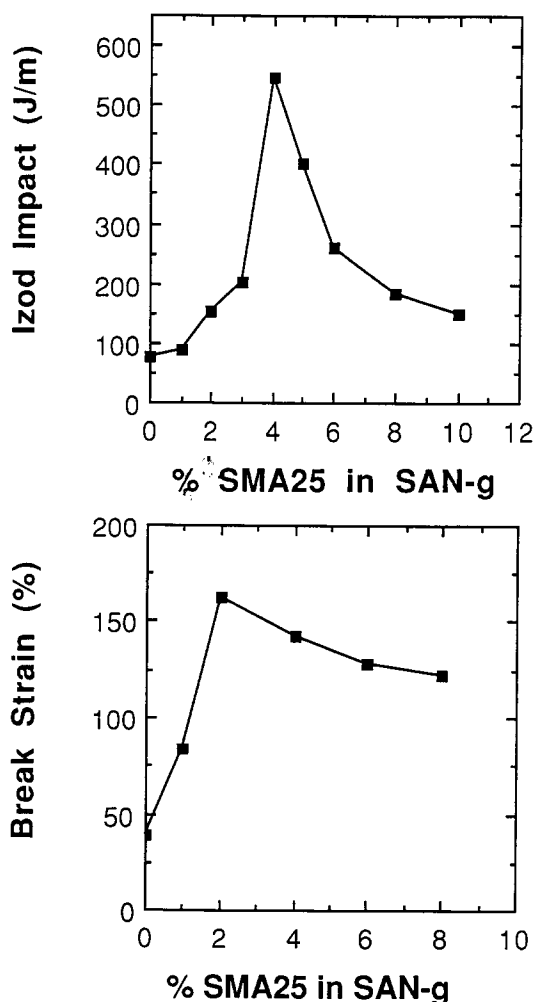


Figure 15 Effect of the amount of SMA 25 on impact strength and elongation at break for 60/40 nylon 6/(SAN-g/SMA 25) blends

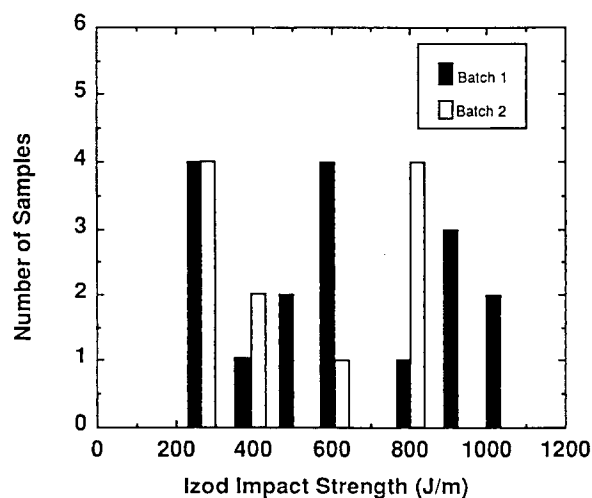


Figure 16 Distribution of impact strength values for two sets of 60/40 nylon 6/(SAN-g/SMA 25 96/4) blends

of these samples were in the super-tough range; however, the average is diminished by some specimens that were much less tough. Outside the 3–5% SMA 25 range, the deviation about the average was more normal and none of the specimens exhibited super-toughness. By process optimization, it may be possible to achieve super-toughness consistently for specimens having the optimum SMA 25 level.

SMA 14 is just outside the boundary for miscibility with the SAN phase of SAN-g as defined in Figure 2. Thus, it is not as likely as SMA 25 to function in the idealized manner suggested by Figure 1. Figure 17 shows that the elongation at break can be improved considerably by SMA 14, but the more critical Izod values show much less impressive improvements. In addition to their differences in miscibility, SMA 14 has only about one half the reactive groups that SMA 25 does. It is interesting to note that it takes at least twice as much SMA 14 to reach maximum elongation at break as it does of SMA 25. For the former compatibilizer, the impact strength does not go through a maximum in the range examined.

Similar experiments were conducted with the Imide material described in Table 1, and the results are shown in Figure 18. Its presence toughens the blends equally well if not better than SMA 14, but the blend does not reach the super-tough range, like that found for SMA 25. The Imide has a considerably lower level of functionality than either SMA copolymer, albeit of a different type.

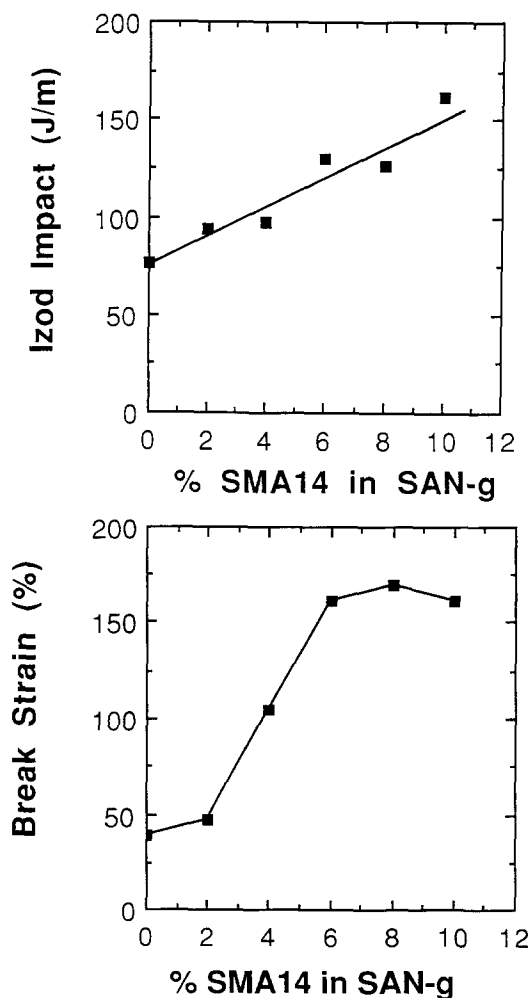


Figure 17 Impact strength and elongation at break for 60/40 nylon 6/SAN-g blends compatibilized by SMA 14

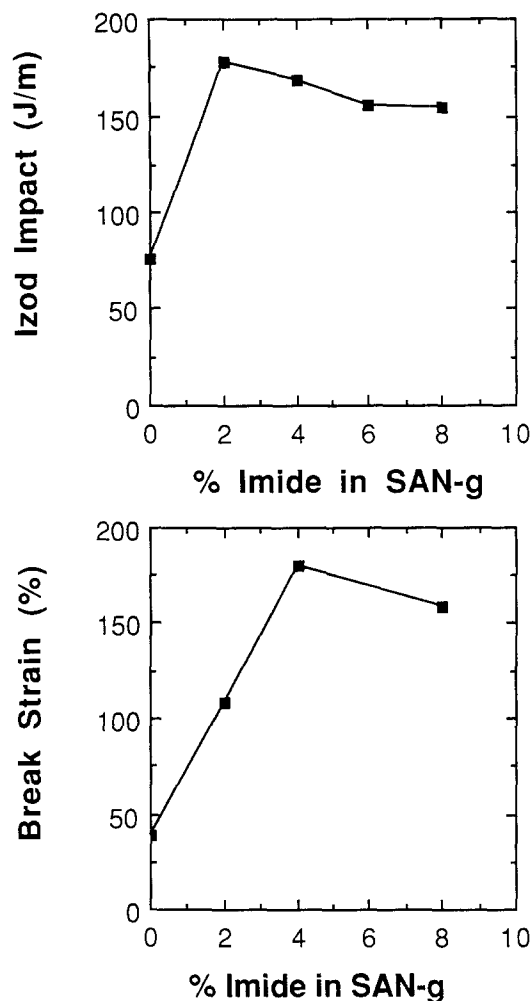


Figure 18 Impact strength and elongation at break for 60/40 nylon 6/SAN-g blends compatibilized by methyl methacrylate/methyl glutarimide copolymer (Imide)

Clearly the most efficient design of a reactive compatibilizer is complex, and not yet completely understood.

INTERFACIAL ADHESION

One of the premises of compatibilization is placement of chemical bonds across the interface. In the solid state this leads to improved interfacial adhesion. It then seems logical to determine in a direct manner whether adhesion improvements do occur⁶. Lap shear adhesion measurements of laminates provide a useful guide. Using the standardized procedure described earlier, it was found that the average shear stress for interfacial debonding of N6/SAN 25/N6 laminates was about 670 kPa, which is in the range for other immiscible polymer pairs. Replacement of SAN 25 with polystyrene gives a value of 350 kPa, which evidently reflects the more favourable interaction with nylon caused by the polar AN units. Similar measurements for R-SAN gave an average shear stress of 2700 kPa. This must be interpreted as a minimum for the adhesion because some samples broke in the nylon 6 layer rather than at the interface. There is no question that the oxazoline functionality reacts effectively with nylon 6 at the interface under these conditions.

Similar measurements were made using mixture of SMA 25 in SAN 25 as the interlayer. The results are shown in Figure 19. Each point is the average of 5 to 10 determinations, as were the previously mentioned values.

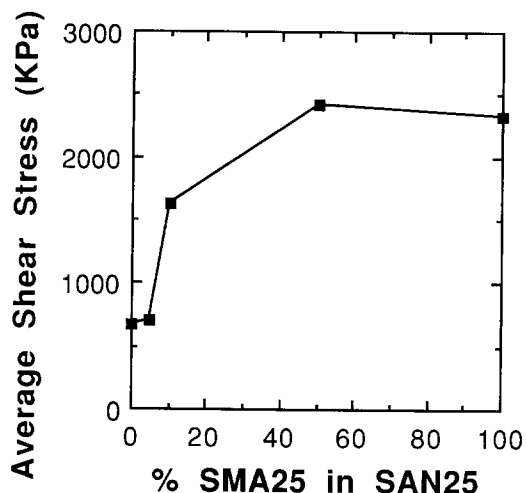


Figure 19 Lap shear adhesion strength between nylon 6 and SAN 25/SMA 25 mixtures bonded at 240°C for 10 min

For this system, each specimen failed by interfacial debonding. The adhesion is increased several fold by reaction of nylon 6 with the SMA 25. However, the response is not simply proportional to the amount of SMA 25, probably because at some point there is an over abundance of MA units and the extent of reaction at the interfaces is limited by the availability of nylon amine ends.

CHEMICAL CHARACTERIZATION

A solvent extraction procedure¹⁶ was developed to gain another more quantitative way of assessing the extent of chemical reaction in these systems. In order to see changes in morphology with composition, extruded pellets of blends of N6/SAN-g 80/20, 60/40, 40/60 and 20/80 were immersed for 2 days in a solution of 88% formic acid or in methyl ethyl ketone, MEK. In formic acid solution, which is a solvent for polyamides, the 80/20 composition disintegrated after a few hours to give a milky solution. For the other compositions the pellets swelled, but did not disintegrate after 2 days. The fact that the N6/SAN-g 60/40 pellets did not disintegrate suggests that at this composition, the nylon 6 and SAN-g phases are present in a cocontinuous state. The cocontinuous morphology is formed between 20 wt% and 40 wt% of SAN-g in the blend. In a similar system, Lavengood and Silver³¹ found that the cocontinuous morphology is formed at 25 wt% of ABS in the blend. None of the pellets immersed in MEK disintegrated, but they swelled more as the percentage of SAN-g increased. MEK is a solvent only for the SAN phase. Therefore, there is not enough soluble material in the blends to cause disintegration. The same experiment was repeated with the N6/(SAN-g/ SMA 25 98/2) series, and similar results were obtained.

This type of experiment using an 88% formic acid solution was repeated for the N6/(SAN-g/SMA 25) 60/40 compositions where the weight per cent of SMA 25 in SAN-g ranged from 0 to 10. Both SAN-g and SMA 25 are not soluble in formic acid. The viscosity and translucency of the formic acid solutions formed during the extraction increased with the SMA 25 content and gave a totally milky solution at 10 wt% of SMA 25 in SAN-g. Therefore, some other species than pure nylon are extracted from the pellets when there is chemical

reaction occurring in the blend. After soaking for 4 days in solvent, the insoluble material was separated from the dissolved material, and the formic acid was removed from each by drying to constant weight in a vacuum oven. The recovery of total solids from these operations was always over 98%. Differential scanning calorimetry for both the insoluble and soluble recovered materials was performed to determine the amount of nylon 6 in each on the basis of the magnitude of melting endotherm observed. The amount of insoluble material increased while the amount of soluble material decreased as more SMA 25 was present. The amount of unextracted nylon 6 in the insoluble phase is shown in Figure 20 relative to the total nylon 6 in the original blend. The small value found at 0% SMA 25 suggests that most unreacted nylon is extracted by this procedure and that the amount not extractable is essentially that which is bound to SAN-g by reaction with SMA 25.

Repeat experiments indicated reasonably good reproducibility as seen in Figure 20. The amount of nylon 6 that could not be extracted initially increases rapidly as SMA 25 is added to SAN-g and then seems to either level off or increase much less rapidly. If every MA unit reacted with one nylon chain the amount of unextractable nylon 6 should rise linearly with SMA 25 content up to 2.4% at which point all of the nylon would be grafted. This serves as a useful point of reference for judging the reaction efficiency.

Similar experiments were conducted for the Imide compatibilizer, and the results are shown in Figure 21. From these limited data, it appears that the amount of nylon 6 reacted is essentially independent of the amount of Imide in the SAN-g phase and that the extent of reaction levels off at a lower value than observed for SMA 25. The functionality of the Imide is about one order of magnitude less than that of SMA 25. Thus, it is not at all clear why the amount of reaction should become insensitive to the amount of Imide because it appears to be the limiting reactant in these blends.

Selected experiments were done with 60/40 nylon 6/(SAN 25 + SMA 25) blends to examine how the lack of any rubber phase might change the extent of reaction. The unextracted nylon 6 relative to total nylon 6 was found to be 5.5% using 2% SMA 25 and 20% using 5%

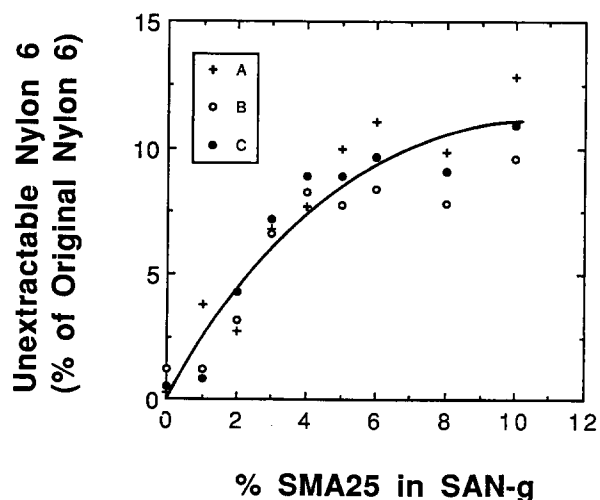


Figure 20 Amount of unextractable (grafted) nylon 6 as a function of SMA 25 content for 60/40 nylon 6/SAN-g blends. A, B and C denote the results of three separate analyses

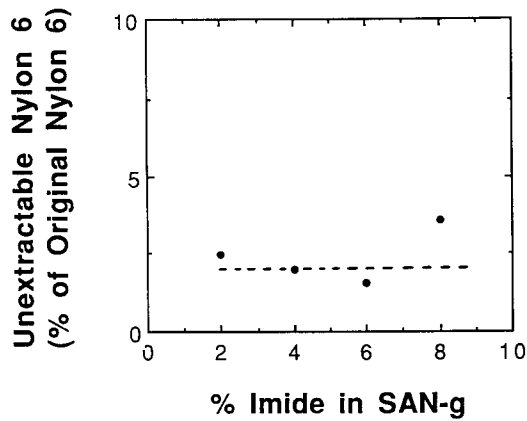


Figure 21 Amount of unextractable (grafted) nylon 6 as a function of acrylic-glutarimide copolymer (Imide) content for 60/40 nylon 6/SAN-g blends

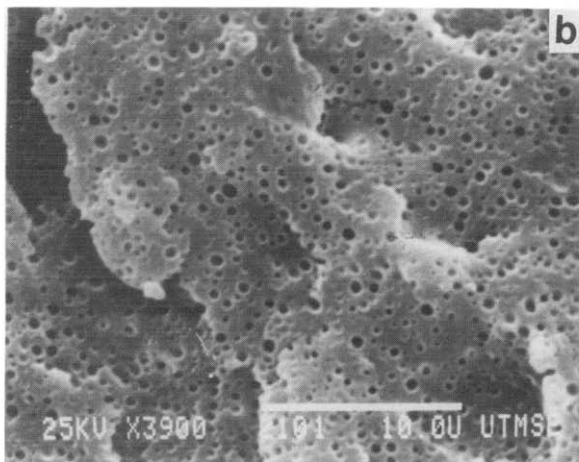
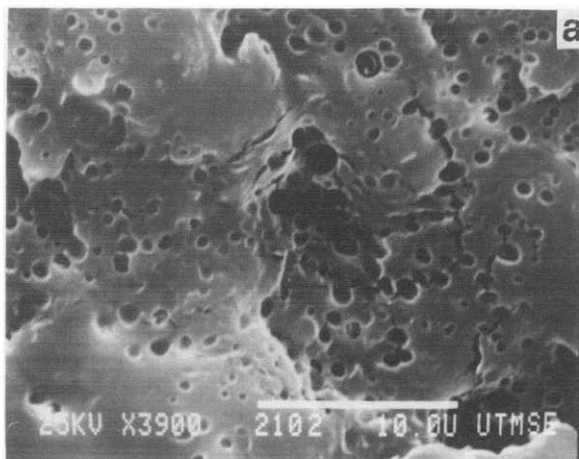


Figure 22 SEM photomicrographs of 75% nylon 6 blends with (a) SAN 25 and (b) R-SAN. Blends were prepared by two extrusion passes. Samples were cryofractured and etched for 5 h in methyl ethyl ketone

SMA 25. These values are about twice those found for the corresponding cases using SAN-g. Thus, the rubber phase appears to limit the extent of reaction which could reflect more limited access of functional groups to each other (diffusion, surface area, mixing patterns, etc.) rather than inherent chemical effects. Clearly there are many interesting and important questions that demand further work.

MORPHOLOGY

The phase morphology is, no doubt, a very important aspect of the properties of these systems; however, the scanning electron microscopy techniques used in this work lead to only a rather limited understanding. We expect that formation of graft copolymer at the interface should result in a decrease in domain size through lowering of interfacial tension^{5,45}, i.e. a surfactant effect. Although the effect is not dramatic in *Figure 22*, there is evidence for smaller particles of R-SAN when it is dispersed in nylon 6 than when SAN 25 is incorporated in the same manner. *Figure 23* shows a comparison of blends containing 25% SAN 25 and 25% (SAN 25 + 5% SMA 25) (note that the SAN 25 controls in *Figures 22* and *23* may not be compared directly owing to differences in processing and preparation techniques). Addition of SMA 25 causes dramatic change from a simple dispersion of SAN 25 spheres in nylon 6 to an entirely different shape in which the SAN 25 + SMA 25 tends towards a phase that is narrowed in one dimension and tends to be cocontinuous. If a high concentration of rubber particles of fixed dimension were included in this phase as in SAN-g, one might expect a tendency towards dispersing them individually. This would have a significant toughening effect.

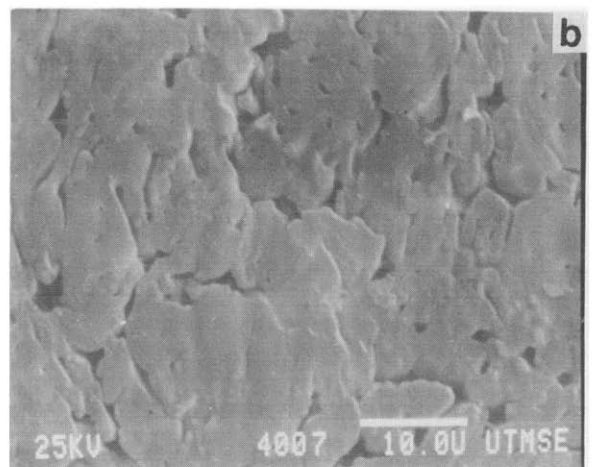
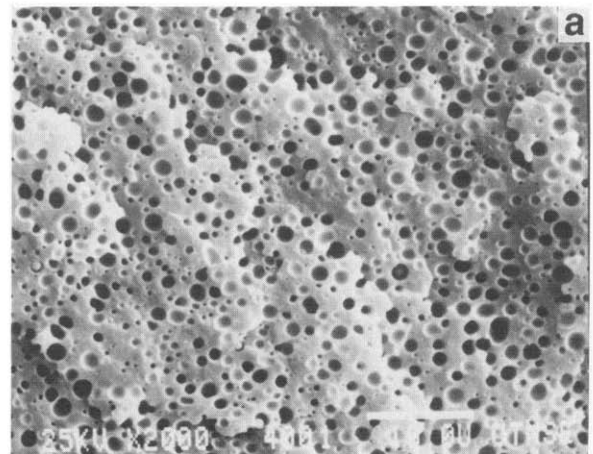


Figure 23 SEM photomicrographs of 75% nylon 6 blends with (a) SAN 25 and (b) SAN 25/SMA 25 95/5 mixture. Each blend was prepared by a single extrusion step. Samples were cryofractured and etched for 12 h in methyl ethyl ketone. (Photographs courtesy of Y. Takeda)

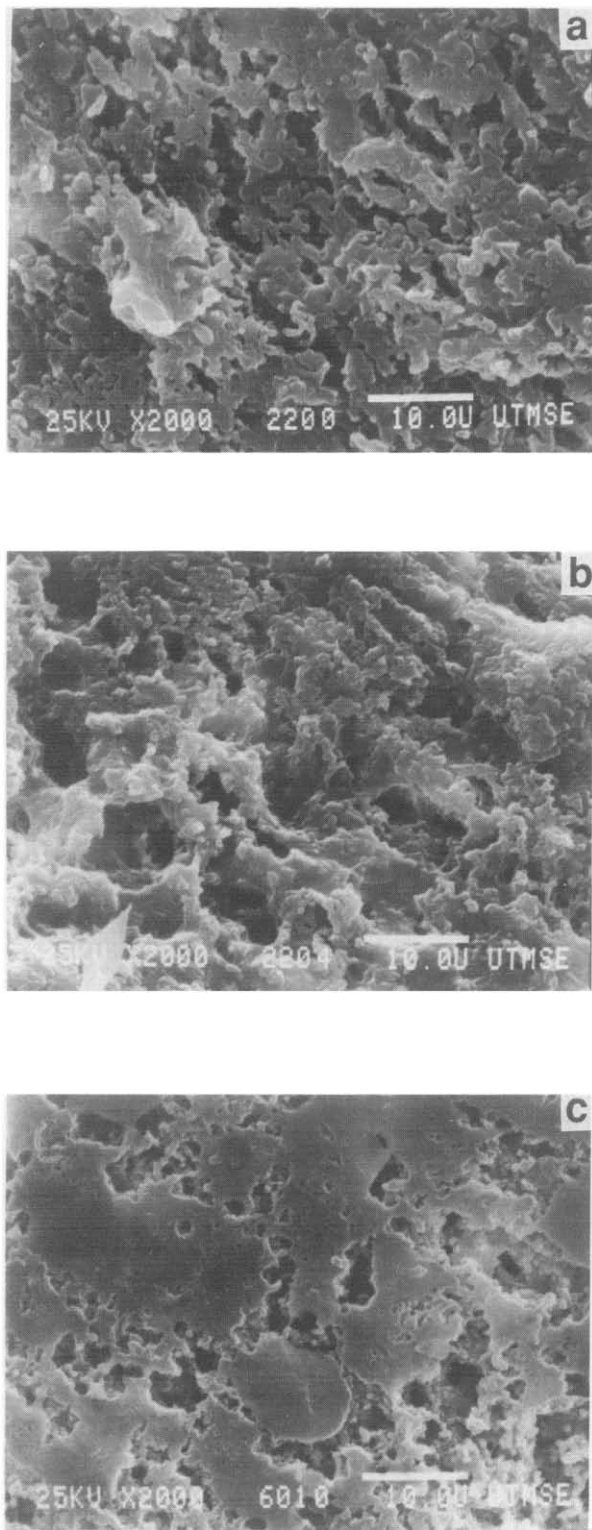


Figure 24 SEM photomicrographs of 60/40 blends of nylon 6/(SAN-g/SMA 25) containing (a) 0% SMA 25, (b) 4% SMA 25 and (c) 10% SMA 25. Samples were cryofractured and etched for 1 h in formic acid solution

For nylon 6 blends with SAN-g, the SAN-g cannot be conveniently extracted from fracture surfaces because of the high fraction of SAN-g that is crosslinked with rubber particles having SAN chains grafted to them. Photomicrographs of surfaces treated in this way suggest a dramatic reduction in the size of the regions that can be extracted as SMA 25 is added. However, the results are very difficult to interpret unambiguously, therefore we will

not discuss them further. It is also possible to etch away the soluble nylon 6 from a fracture surface using formic acid solutions, but this evidently takes some SAN-g material with it. *Figure 24* shows a series of photomicrographs prepared in this way. These show that SAN-g tends to form a somewhat cocontinuous skeletal phase and with some evidence that the dimensions are smaller when there is 4% SMA 25 present. At 10% SMA 25 there are large islands ($\approx 10 \mu\text{m}$) of unextractable material. Thus, in one sense the 4% SMA 25 may reflect an optimal morphology. However, transmission electron microscopy studies are required before any firm conclusions can be reached.

CONCLUSIONS

Most of the literature suggests that reactive coupling of the phases in immiscible polymer blends requires functionality on both materials. The approach outlined here relaxes this requirement by having the functionality on a polymer molecule that is added to one of the phases. Here we focused on nylon 6 blends with ABS and SAN materials, where the former has functional groups but the latter do not. In general, neither phase must contain chemically bound functionality because appropriate additives could be designed for each phase. We believe that, to be most effective, these functional additives should be miscible with their intended phase. The work presented here has demonstrated that the approach can be useful, but much remains to be learned before systems can be rationally designed. We hope to address some of the most important issues in future papers.

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