

Oxazoline-Containing Compatibilizers for Polyamide/SAN and Polyamide/ABS Blends

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ABSTRACT: Polyamide (PA) and acrylonitrile/butadiene/styrene copolymer (ABS) may appear as a mixture in the recycled plastic stream. The incompatibility of these blends results in a blend with poor mechanical properties. The aim of this work is to partially convert the nitrile groups of the acrylonitrile/styrene copolymer (SAN) into oxazoline groups by reaction with aminoethanol (AE). Such modified SAN (SAN-m) can react with the amine or carboxylic acid end groups of PA, and therefore used as compatibilizers for

blends of PA with ABS. SAN-m was found to reduce the SAN-domain size in the PA/SAN-blends. The initial acrylonitrile content of SAN-m had a strong influence on the degree of conversion into oxazoline groups and on the compatibilizing effect. Mechanical properties of SAN-m compatibilized PA/ABS blends were investigated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 449–455, 2002

Key words: compatibilization; blending; polyamides

INTRODUCTION

In situ or reactive compatibilization is an important route to achieve higher interfacial adhesion and better impact strength of polymer blends. The “effective” copolymers, which act as compatibilizers, are synthesized during the compounding operation at the interface between the phases (where they should be located to be effective). Ideally, only small amounts of compatibilizers are thus required. In the case of ABS/PA blends, two strategies have been used for compatibilization. One strategy involves the addition of a polymer that is compatible with the styrene-acrylonitrile copolymer (SAN) matrix of ABS, and can react with the amine or carboxylic acid end groups of the PA phase. In the other strategy, functional groups capable of reacting with PA are attached to SAN prior to blending with PA. Functional groups, such as acid or anhydride, epoxide, and oxazoline, which can react with the amine or carboxylic acid end groups of polyamide are used. The oxazoline functionality is particularly interesting because this group can easily react with both the carboxylic acid group and the amine group. Oxazoline groups can be grafted to a polymer,¹ and this approach has been used to produce reactive

polystyrene by Dow Chemical Co. Oxazoline groups are often attached to a polymer via a peroxide-initiated free radical grafting.^{2–5} Recently, another method was proposed for converting the nitrile groups of SAN or nitrile rubber into oxazoline with the aid of a metal salt catalyst in solution at 130 to 140°C^{6–9} or in the compounding equipment at 230 to 240°C in the absence of a solvent.^{9–13} 2-Aminoethanol (AE) and zinc acetate were shown to be an efficient reactant and catalyst, respectively, for this reaction. The reaction scheme is indicated in Figure 1. The nitrile content had a marked influence on the efficiency of the reaction between SAN and AE.⁷ It should, therefore, be interesting to explore the reactivity of AE towards a variety of SAN materials with different acrylonitrile contents. The number of available end groups of PA, which is related to the molecular weight, is also of interest.

In this work, the possibility of using this method to compatibilize PA/SAN blends was explored. SAN was functionalized according to the reaction scheme in Figure 1. The possible reactions between oxazoline-modified SAN (SAN-m) and PA are shown in Figure 2.

It was noted that the nitrile content of SAN prior to reaction with aminoethanol had a great influence on the compatibilizing effect on PA/SAN blends in terms of morphology, and in particular, the size of SAN domain was significantly reduced by high AN content SAN-m compatibilizer. The actual conversion rate of nitrile group to oxazoline group was characterized by Fourier Transform Infrared (FTIR). The yield of this conversion is low due to the limited reaction and volatile nature of the aminethanol. The PA/ABS blends compatibilized with SAN-m exhibited better

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mechanical properties than the simple immiscible PA/ABS blends.

EXPERIMENTAL

Materials

Three commercial grades of styrene-acrylonitrile copolymers were chosen to evaluate the importance of the acrylonitrile (AN) content. They contain 25 wt % AN (SAN-1) or 35 wt % AN (SAN-2 and SNA-3). SAN-3 has higher molecular mass than SAN-2. The polyamide 6 and ABS used were general-purpose grade Ultramide B3 (PA 6) and Terluran 967 K (ABS), both from BASF.

Aminoethanol (AE) and zinc acetate dihydride [$\text{Zn}(\text{AC})_2$] were delivered from Aldrich, and 1.2% of $\text{Zn}(\text{AC})_2$ was dissolved in AE before the compounding step.

Functionalization and blending using a Brabender mixer

Fifty grams of SAN- x ($x = 1, 2, 3$) or ABS was fed into the Brabender batch mixer at 240°C , and 5 g of AE containing 1.2% $\text{Zn}(\text{AC})_2$ was then gradually added into the SAN- x melt over 2 min. Because the boiling temperature of AE is 170°C , some AE quickly vaporized from the vessel during the mixing at this processing temperature. The rotational speed of the mixing blades was 64 rpm. The total mixing time was 10 min (after addition of the AE), and the resulting products are coded SAN x -m.

Blending of SAN with PA was carried out by feeding the two materials together in the mixing chamber and processing them at a temperature of 240°C , the rotational speed of the mixing blades was 64 rpm. The total mixing time was 10 min.

Functionalization and compounding using a twin-screw extruder

A mixture of AE and 1.2% w/w $\text{Zn}(\text{AC})_2$ was added dropwise into the hopper of a twin-screw extruder (Werner & Pfleiderer ZSK 30 M 9/2) while pelletized SAN-2 was fed in. The AE : SAN-2 ratio was approximately 9 : 91 (by weight). The barrel temperature was 230°C , and the rotational speed of the screw 200 rpm. The resulting product was SAN with grafted oxazoline side groups (SAN-2-mE). ABS was blended with

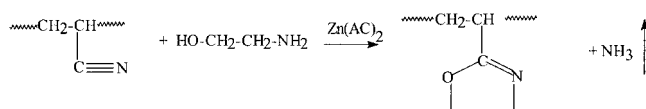


Figure 1 Reaction scheme for the transformation of nitrile group into oxazoline.¹⁴

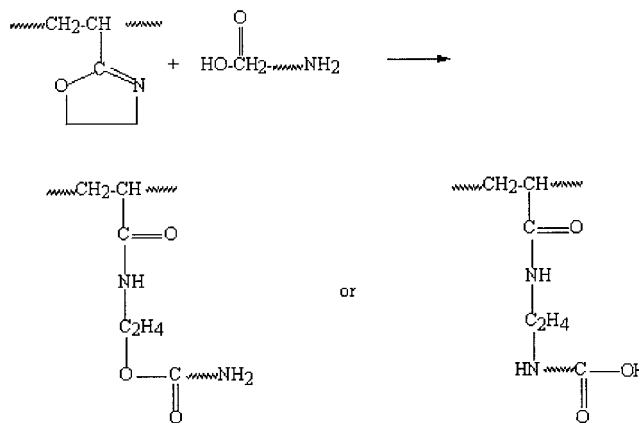


Figure 2 Reaction scheme of the PA carboxylic acid and amino end groups with the oxazoline group.^{2,4}

PA at 240°C , and at a screw speed of 200 rpm. The extrudates were pelletised with a granulator.

The SAN- m (both from the Brabender batch mixer and from the extruder) exhibited, to various extents, a brownish color (in contrast to the transparent character of SAN); this indicates some material change. It was noted that the volatile AE was lost to some extent upon heatup at processing temperature of 240°C . The extruded functionalized SAN has higher conversion rate and better compatibilization effectiveness than kneader mixed SAN. Such observation may be due to the difference in volatile rate of the AE in the different mixers.

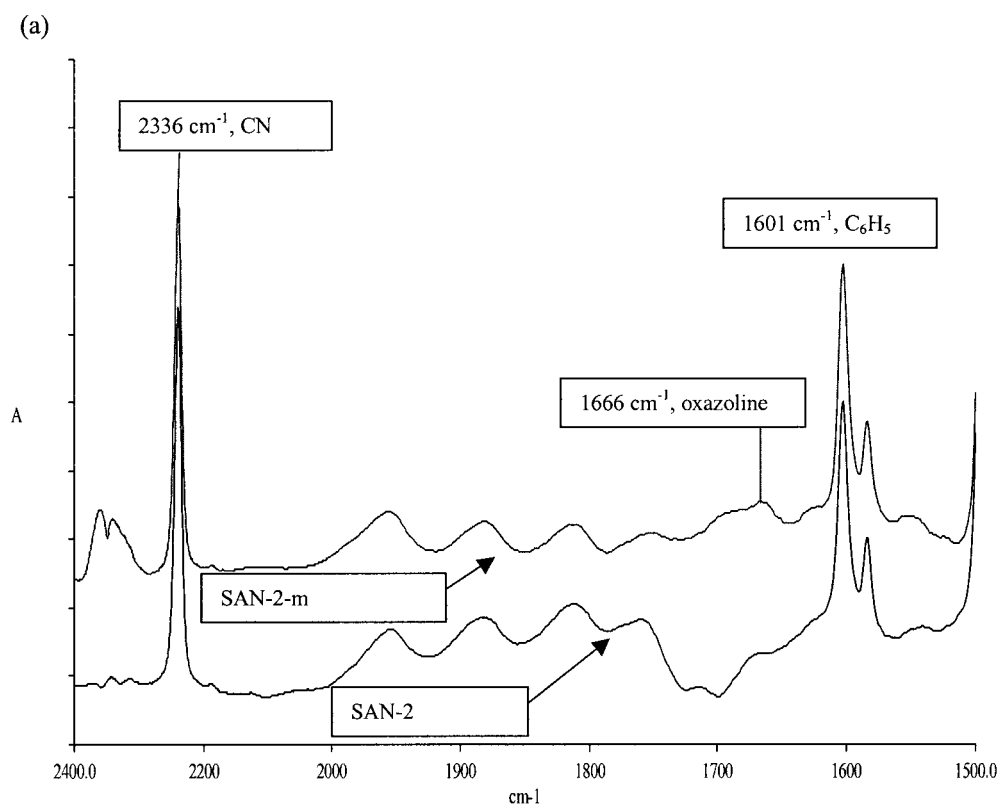
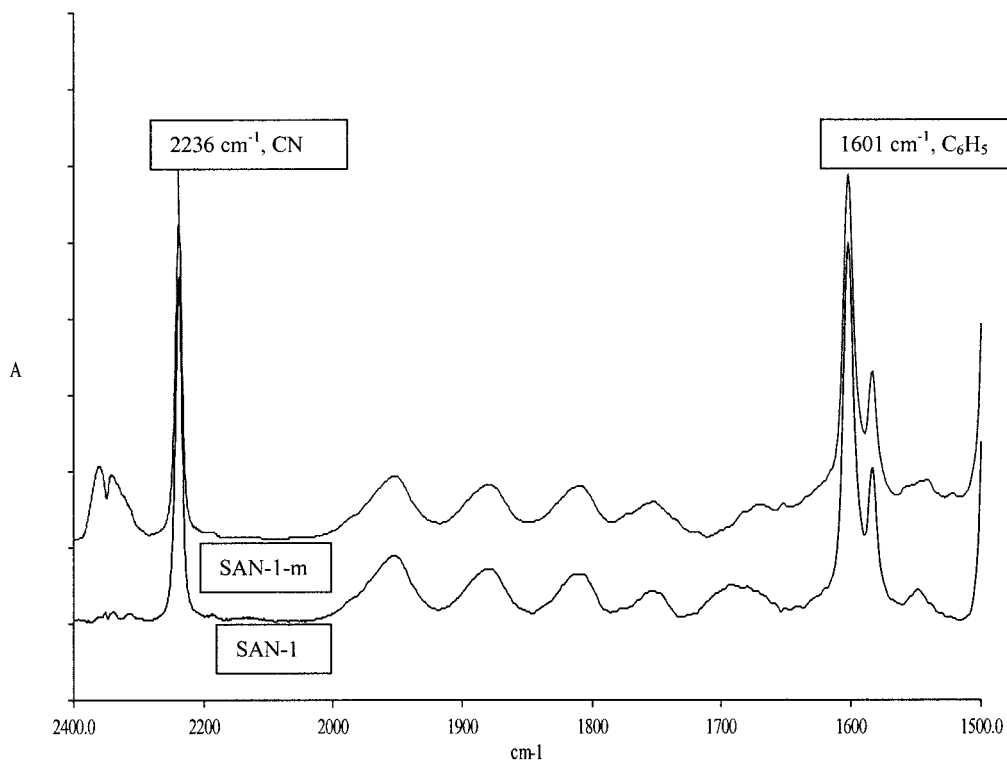
Injection molding

Mechanical test specimens were prepared by injection molding with an Engel 330/80 press at a melt temperature of 240°C and a mold temperature of 50°C .

IR spectroscopy

Fourier Transform Infrared (FTIR) spectra were obtained with a Perkin-Elmer System 2000 apparatus. The samples were dissolved in chloroform, and 30 scans were taken for each spectrum. Three adsorption peaks are here of interest: the $\text{C}=\text{C}$ vibration of styrene at 1601 cm^{-1} (reference), the $\text{C}\equiv\text{N}$ vibration of the acrylonitrile at 2236 cm^{-1} , and the characteristic $\text{N}=\text{C}$ band of the oxazoline group at 1664 cm^{-1} . The spectra were normalized with regard to the reference peak intensity at 1601 cm^{-1} , which was unaffected by the functionalization.

According with the reaction scheme in Figure 1, it is assumed that the reduction of the $\text{C}\equiv\text{N}$ peak intensity corresponds to the conversion of nitrile to oxazoline. The degree of conversion α can be expressed as:



(b)

Figure 3 IR-spectra of (a) SAN-1 and SAN-1-m, (b) SAN-2 and SAN-2-m. The y-axis is absorption intensity. The spectra are normalized with respect to the reference peak at 1601 cm⁻¹.

TABLE I
Degree of Conversion of the SAN-m Samples

Sample/reference	$[A_{C=N}]_{SAN-m}/[A_{C=N}]_{SAN}$ at 2237 cm^{-1}	$[A_{OXA}]_{SAN-m}$ at 1664 cm^{-1}	Degree of conversion α , %
SAN-1-m/SAN-1	0.0409/0.0447	Not detectable	Not detectable
SAN-2-m/SAN-2	0.0527/0.0541	0.0021	3
SAN-2-mE/SAN-2	0.0510/0.0541	0.0043	6
SAN-3-m/SAN-3	0.0640/0.0734	0.0081	13

$$\alpha = \frac{[A_{CN}]_{SAN} - [A_{CN}]_{SAN-m}}{[A_{CN}]_{SAN}}$$

where $[A_{CN}]$ is the intensity of the absorption peak at the wave number 2236 cm^{-1} , normalized with respect to the reference peak at 1601 cm^{-1} .

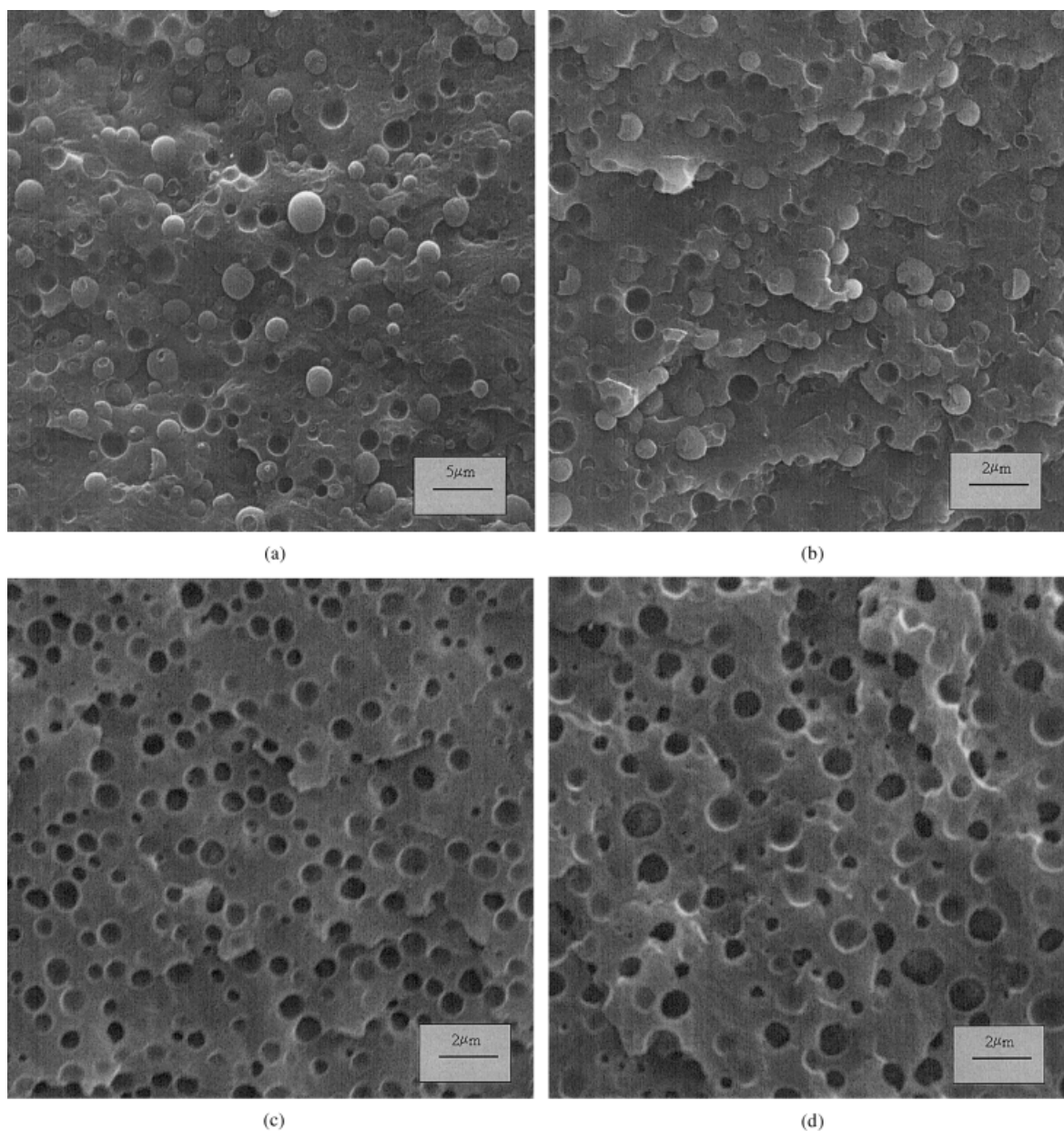


Figure 4 SEM micrographs of cryo-fractured surfaces of PA 6/SAN-blends, specimens shown in (c) to (f) were etched by acetone in order to reveal the morphology. (a) PA6/SAN-1 80/20, (b) PA6/SAN-1/SAN-1-m 76/19/5, (c) PA6/SAN-1/SAN-2-m 76/19/5, (d) PA6/SAN-2/SAN-2-m 76/19/5, (e) PA6/SAN-1/SAN-3-m 76/19/5, and (f) PA6/SAN-2/SAN-3-m 76/19/5.

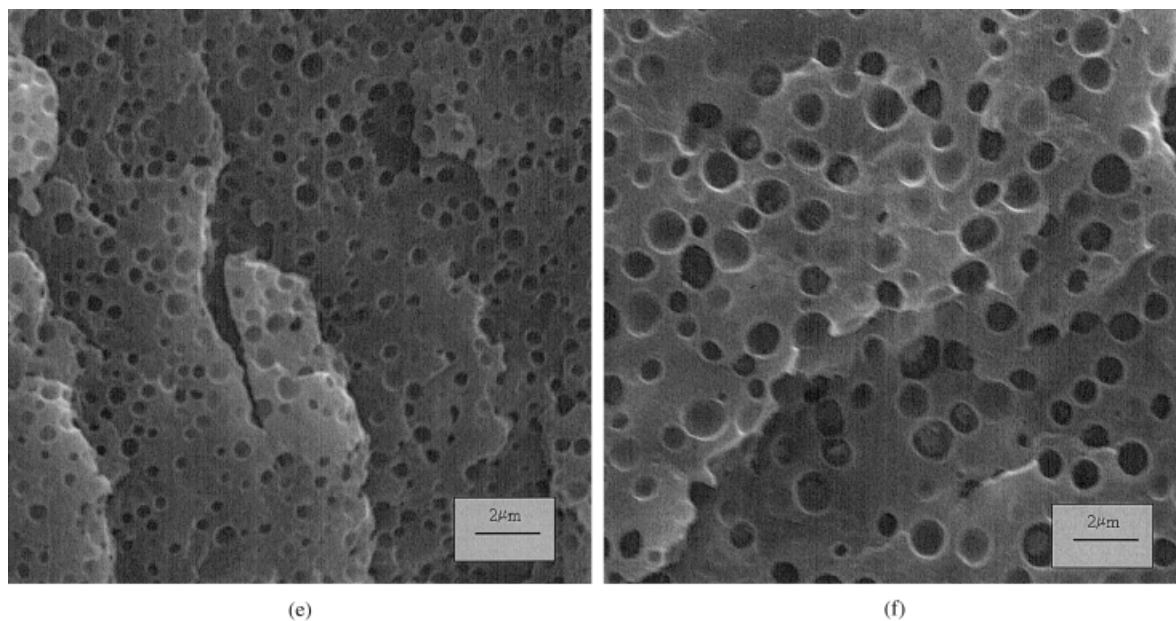


Figure 4 (Continued from the previous page)

Mechanical properties

The tensile properties were determined at a temperature of $22 \pm 1^\circ\text{C}$ and a relative humidity of $55 \pm 10\%$ according to ISO 527-2, using a crosshead speed of 5 mm/min and an initial clamp distance of 10 mm, corresponding to a strain rate of 0.0008 s^{-1} . The notch Charpy impact strength was measured using a Frank KMO 79 impact tester according to ISO 179 standard specimen type 2.

Scanning electron microscopy (SEM)

The morphology of the specimens was studied by observing cryo-fractured surfaces using a Digital Scanning Electron Microscope Zeiss DSM 940A. The specimen surfaces were coated with a thin gold layer about 50 \AA thick.

An etching technique was used to remove the SAN-phase to reveal the morphology of the blends. Acetone, which is a solvent for SAN but not for PA, was employed for this purpose. The specimen was cryo-fractured, then etched in acetone for 10 min and rinsed in methanol.

RESULTS AND DISCUSSION

Degree of nitrile group conversion in SAN

The FTIR spectra were used to characterize the degree of the conversion. Seven samples were used, including the three unmodified SAN-samples, i.e., SAN-1, SAN-2, SAN-3, and their corresponding oxazoline conversion products from the Brabender mixer, i.e., SAN-1-m, SAN-2-m, SAN-3-m, as well as SAN-2-m

from the extruder (SAN-2-mE). Examples of these spectra are shown in Figure 3.

The results of the IR-measurements are summarized in Table I. No oxazoline peak for SAN-1-m was detected after mixing SAN-1 and AE at 240°C for 10 min, although there was a slight decrease in the $\text{C}\equiv\text{N}$ peak intensity. However, as shown later, 5% of SAN-1-m can reduce the domain size of SAN in the PA6/SAN-1 76/19 (76% PA6 and 19% SAN-1) blend, compared to the blend without SAN-1-m. It was also noted that SAN-1 changed from crystal clear transparency to a brownish color after the conversion reaction. SAN-1-m was therefore clearly different from the original SAN-1, and trace amounts of oxazoline groups may have been formed. In case of SAN-2-m, Figure 3 clearly shows that oxazoline groups have been formed. The extruder was more efficient in converting the nitrile groups into oxazoline groups, considering the fact that the residence time was 10 min in the Brabender batch mixer and only 2 to 3 min in the extruder. SAN-3-m exhibited the highest degree of conversion of 13% (Table I). The fact that the degree of conversion increased with increasing nitrile content is in agreement with results obtained in a solution reaction.⁷ Although SAN-2 and SAN-3 had the same AN content, the nitrile conversion of the higher molar mass SAN-3 was higher with respect to SAN-2.

Morphology

The morphology of a polymer blend can indicate the compatibility of the components. SAN and PA are not compatible, and the blend exhibited a coarse two-

TABLE II
Mechanical Properties of Injection-molded Specimens

Composition	Tensile modulus (GPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)
ABS	2.3	40	35	14	13.0
ABS/SAN-2-mE 100/5	2.1	45	35	10	5.5
PA6/ABS 80/20	2.0	43	40	6	2.8
PA6/ABS/SAN-2-mE 80/15/5	2.1	No yield	49	9	3.2

phase structure. The maximum domain size of the SAN-1-phase was about 3.5 μm in a PA6/SAN-1 80/20 blend, as shown in Figure 4(a). When 5% of SAN-1-m was added to the PA6/SAN-1 76/19 blend, the SAN-1-domain size was reduced to 1.5 μm [Fig. 4(b)]. The addition of 5% SAN-2-m had an even better compatibilizing effect on the PA6/SAN-1 76/19 blend. The phase boundaries became so blurred that no SAN-1-domains could be distinguished. By using acetone to dissolve the SAN-1-phase, it was revealed that 5% of SAN-2-m reduced the SAN-1-domain size to a maximum of 1 μm [Fig. 4(c)]. However, SAN-2-m had a less pronounced compatibilizing effect in the PA6/SAN-2/SAN-2-m 80/15/5 blend; the SAN-2-domain size being 1.5 μm [Fig. 4(d)]. SAN-3-m can further reduce the SAN-1-domain size. In the PA6/SAN-1/SAN-3-m 80/15/5 blend, it was smaller than 0.8 μm , as shown by the etched surface in Figure 4(e). SAN-3-m was less effective in the SAN-2-containing blends, the domain size here being 1.4 μm , as shown in the case of the PA6/SAN-2/SAN-3-m 80/15/5 blend in Figure 4(f).

It has been reported that the difference in acrylonitrile content between two different SAN-copolymers should not exceed 4% if they are to be miscible.¹⁵ If the nitrile groups are converted to 2-oxazoline groups, the SAN-m composition will change, which may influence the miscibility of SAN-m and SAN. Moreover, the oxazoline groups will react with the amine and the carboxylic acid end groups of PA in the PA/SAN/SAN-m blends and this will further change the structure of the SAN-m. All these factors may influence the interaction between SAN and the SAN-m compatibilizer, and may therefore affect the compatibilizing effect of SAN-m.

It is known that the higher the acrylonitrile content of the SAN copolymer, the better the chemical resistance. It has also been reported that, with a higher the nitrile content in SAN, more oxazoline groups (high degree of conversion) will be produced from the reaction between SAN and AE in solution.⁷ The FTIR experiments performed here showed that this also occurred in a bulk reaction. The morphology study indicated, furthermore, that SAN-m derived from SAN with a high acrylonitrile content had a better compatibilizing effect on the PA/SAN-blends. The ini-

tial SAN used for the oxazolization does not necessarily have to be of the same composition as the SAN used as blend component.

Mechanical Properties

SAN-2-mE had a pronounced influence on the mechanical properties of ABS (Table II). Only 5% of SAN-2-mE was sufficient to reduce the Charpy impact strength to less than half of that of neat ABS. It is therefore not suitable to use this compatibilizer in a system containing ABS as the major component. The mechanical properties of the binary PA6/ABS 80/20 blend were as expected poor. Adding 5% SAN-2-mE to the system improved the tensile strength, but also the elongation at break and the impact strength were improved (Table II). This compatibilizing effect on mechanical properties agrees to the same effect on morphology.

CONCLUSIONS

The nitrile groups in SAN copolymers were converted to oxazoline group by a condensation reaction with aminoethanol, both in a Brabender batch mixer and in a twin-screw extruder. The latter method appeared to be more efficient, probably due to less loss of the volatile AE upon heatup.

Morphological studies indicated that such modified SAN copolymers could be used as compatibilizers for PA/SAN blends and PA/ABS blends. A higher nitrile group content in the SAN copolymers increased the yield of oxazoline groups in modified SAN-m and further enhanced the efficiency of SAN-m for reducing the SAN-domain size in a PA/SAN/SAN-m blend. SAN-m produced from a SAN grade with higher nitrile content was more efficient. It was not very critical for the SAN grade used for producing SAN-m to have the same composition as the SAN used in the PA/SAN blends. SAN-m exhibited a compatibilizing effect with regard to the mechanical properties of PA/ABS blends.

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