Chemical Modification of Nitrile to Oxazoline Functionality on a Styrene-Acrylonitrile Copolymer in the Melt

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CHEMICAL MODIFICATION OF NITRILE TO OXAZOLINE FUNCTIONALITY ON A STYRENE-ACRYLONITRILE COPOLYMER IN THE MELT

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ABSTRACT

Oxazoline is a very interesting functionality for reactive extrusion and other applications. In this paper, we report the possibility of chemically transforming nitrile group attached to a copolymer of styrene and acrylonitrile (SAN) to oxazoline group using 2-amino-ethanol (AE). The chemical modification of SAN with AE was done in the molten state. Among various catalysts tested, zinc acetate turned out to be the most efficient. The effects of the catalyst concentration, temperature and mixing on the overall kinetics were studied. The formation of the expected oxazoline functionality was confirmed by infrared spectroscopy and by reacting with 1-naphthylacetic acid. The reaction between the oxazoline and the acid

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was very rapid as it went to completion within 2 minutes in the melt
at 180°C. The efficiency of an oxazoline modified SAN as compat-
ibilizing precursor was evaluated for SAN/PA 6 and SAN/PBT
blends.

INTRODUCTION

Blending existing immiscible polymers has become an important route to
obtain new materials. Multiphasic polymer blends may offer combinations of phys-
ical properties not achievable otherwise with single-phase materials. They may also
allow considerable savings over another alternatives, e.g., new polymers synthesized
from new raw materials. However, there are various problems with such phase-
separated blends. The interfacial tension between two immiscible polymers is often
high. Therefore the morphology of such a blend is often gross, thermodynamically
unstable and is prone to external perturbations (heat and/or shear). The interfacial
region is also very narrow and there is little penetration of the polymer chains from
one phase into the other and vice versa. Consequently, few entanglements are
formed across the interface and the interfaces are weak ($\sim$ 1 J/m^2).

It has been established for some time that addition of a block or graft
copolymer is effective at reducing the interfacial tension, promoting the interfacial
adhesion and stabilizing the morphology of the system. However, such copolymers,
also called (mistakenly) compatibilizers rather than interfacial emulsifiers, require
separate synthetic procedures which are often tedious and time-consuming. In fact,
for most blends of practical significance, interfacial emulsifiers may not be obtained
by this approach. This has then lead to "*in situ* compatibilization of immiscible
blends by reactive blending". In this way, instead of synthesizing interfacial
emulsifiers as a separate step, they are created during extrusion through interfacial
reactions between selected functional polymers [1, 2, 3].

However, the performance of *in situ* compatibilization of immiscible poly-
mer blends depends, among many other things, on the type of functional groups
involved. Oxazoline is known to be reactive toward numerous other functionalities
bearing labile hydrogen atoms such as carboxyl, amine, hydroxyl, phenol and
mercaptan [4] and useful for compatibilization of immiscible blends [5, 6, 7, 8].
Two methods have been explored to obtain oxazoline modified polymers. One
method is to copolymerize an oxazoline bearing vinyl monomer with a monomer of
interest. This method was originally developed by Dow Chemicals to obtain the so-
called reactive polystyrene (RPS). A second method is to free radically graft such a

monomer onto an existing polymer chain. This method was employed recently for compatibilizing polypropylene and poly(butylene terephthalate) blends by reactive extrusion.[7, 8] More recently, a third method has been reported in the literature [9, 10]. It concerns the chemical transformation of a nitrile attached to a macromolecular chain to oxazoline functionality with amino-alcohol in solution. The expected reaction scheme of the transformation of nitrile to oxazoline functionality is as follows:
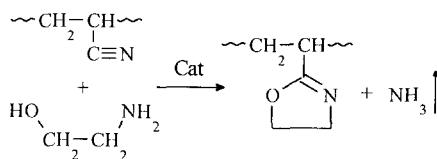
Quite a long time(10 to 20 hours) was necessary for the reaction to reach appreciable conversions (10 to 20%). In spite of the low reactivity, this method seems to be interesting as various copolymers of commercial use contain the nitrile group such as styrene and acrylonitrile copolymer (SAN), acrylonitrile, butadiene and styrene copolymer (ABS) and butadiene and acrylonitrile rubber (NBR).

The objective of this study was two-fold: to further explore this new route to synthesize oxazoline functionality by chemically modifying nitrile group attached to a macromolecular chain *in the molten state* and to test its ability to compatibilize immiscible blends. Specifically, the reactivity of the nitrile in a SAN was examined. The oxazoline modified SAN was then used as interfacial emulsifier precursor to compatibilize the blends of SAN with polyamide 6 (PA 6) or poly(butylene terephthalate) (PBT).

EXPERIMENTAL

Materials

The styrene and acrylonitrile copolymer (SAN) used in this study was kindly supplied by GE Plastics and contained 24.7 wt.% AN with a weight average molecular weight of 101 000 g/mole and a number average molecular weight of 45 600 g/mole. 2-Amino ethanol (AE) and 3-amino propanol (AP) were used as amino alcohol. Various catalysts were tested: zinc acetate (ZnAc), 2-hydroxypyridine (HP), dibutyltin oxide (DBTO), nickel acetate (NiAc) and zinc chloride (ZnCl$_2$). All amino alcohols and catalysts were purchased from Aldrich and used without further purification. The PA 6 (Ultramid 3) and PBT were kindly provided by BASF and DSM, respectively.

Reaction and Blending Procedures

A batch mixer of type Haake Rheocord was used for the chemical modification of SAN and blending of SAN with PA 6 or PBT. The chamber of the mixer had a capacity of 50 cm^3. Mixing was ensured by two sigma-shaped rotors rotating in opposite directions. For the chemical modification experiments, the temperature of the mixer was set at 150°C but that of the melt varied between 155 and 170°C, depending on the rotation speed of the rotors and the extent of reaction. Before studying the reaction in a systematic manner, several preliminary trials were made. It was found that AE was much more reactive toward SAN than AP. Also ZnAc turned out to be the most efficient catalyst. Thus only AE and ZnAc were used for subsequent kinetic studies. Since the solubility of AE and ZnAc in the molten SAN is low, they were charged to the mixer in different ways in order to see which one would best homogenize the reactive system and lead to highest conversions. It appeared that a good procedure was as follows: to solubilize ZnAc (or another catalyst) in AE and then add this homogeneous mixture to the SAN which was already molten in the mixer. To study the kinetics, small amounts (~ 1 g) of samples were taken quickly from the mixer at various chosen time intervals and then quenched immediately in liquid nitrogen to stop the reaction. For all reaction experiments, the amounts of SAN and AE were 50 and 10 g, respectively, unless specified otherwise. This amounted to a molar ratio of 0.68:1 for [AE]:[AN]. Thus the maximum conversion would be 68%.

Blending of the SAN with the PA 6 or PBT in the presence or absence of oxazoline modified SAN was done at a set temperature of 240°C for 10 minutes (the melting points of the PA 6 and PBT were 221 and 223°C, respectively). The rotation speed of the rotors was 64 revolutions per minute (rpm). Under those conditions, the actual temperature of the molten blends was about 248°C as a result of viscous dissipation. The PA 6 and PBT were dried at 100°C in an oven under vacuum for three days before use.

Determination of the Nitrile Conversion

Samples taken from the reaction were purified by dissolution in tetrahydrofuran and precipitation in methanol. This procedure was repeated once more to ensure a complete removal of ZnAc residue and AE. The conversions of the nitrile to oxazoline functionality of these samples were then measured by infrared spectroscopy (Fourier Transform Infrared Spectrometer Nicolet FX60). In Figure 1 are shown the IR spectra of the virgin and a modified SAN. The IR spectrum of the virgin SAN is characterized by the peak at 1602 cm^{-1} of the mono-substituted C=C
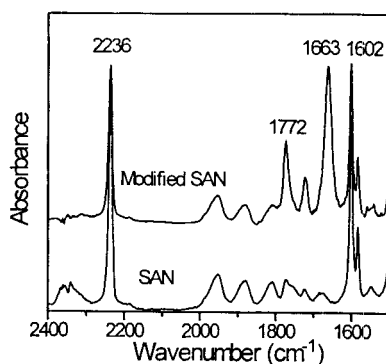
Figure 1.   Infrared spectra of the virgin and an oxazoline modified SAN.

of the aromatic ring of styrene and that at 2236 cm^{-1} of C(N of acrylonitrile. The modified SAN yields an additional strong peak at 1663 cm^{-1}, characteristic of the expected oxazoline functionality. As for the peak at 1772 cm^{-1}, its origin is unclear for the moment. Since the peak at 1602 cm^{-1} should remain unchanged during the reaction while that at 2236 cm^{-1} cm diminishes, the ratio between the absorbance of the peak at 2236 cm^{-1} and that at 1602 cm^{-1} as the conversion of the nitrile to oxazoline functionality, provided that the intensity of this peak is proportional to the concentration of the nitrile in the SAN [11]. The validity of this method was confirmed by elemental analysis of modified SAN samples based on oxygen atom.

Observation of Blends' Morphology

The morphology of SAN/PA 6 and SAN/PBT blends was examined on fresh fractured and gold-sputtered surface using a scanning electron microscope (Streoscan 120 Cambridge Instruments).

RESULTS AND DISCUSSION

Efficiency of Various Catalysts

In Table 1 are gathered the conversions obtained after 30 minutes of reaction in the presence of a catalyst. ZnAc and ZnCl$_2$ turn out to be the best catalysts. Similar results were obtained by Hseih *et al.* [9, 10]. Also, the higher the conversion, the higher the melt temperature. This is because as the reaction proceeds, the amount of AE in the molten SAN reduces and the viscosity of the reactive system increases. Consequently the temperature of the melt rises.

TABLE 1. Comparison of the Efficiency of Various Catalysts in Terms of Conversion of the Nitrile to Oxazoline Functionality. (*) DBTO is Not Soluble in AE and the Mixture is like a Suspension.

SAN:AE:Cat (50:10:1.2 by wt.)	Without catalyst	ZnAc	$ZnCl_2$	DBTO*	NiAc	HP
Conversion (%) at 30 min.	< 1.0	8.0	6.0	3.8	< 1.0	< 1.0
Melt temperature (°C) at 30 min.	145	166	159	161	152	152

TABLE 2. Effect of the Amount of ZnAc on the Conversion. (a): A Desired Amount of a Solution of AE and ZnAc is First Mixed with SAN in a Cup; the Mixture is Then Charged to the Mixer. (b): A Desired Amount of a Solution of AE and ZnAc is Charged to the Molten SAN in the Mixer; (c): A Desired Amount of a Solution of AE and ZnAc is Added to the Molten SAN in the Mixer in a Successive Manner at 6, 10, 14 and 18 Minutes.

ZnAc content (g)	0	0.3	0.6		1.2		
Conversion at 60 min.	1.5	9.0[a]	13.0[a]	14.0[b]	13.0[b]	12.4[b]	13.2[c]

Table 2 shows the effect of the amount of ZnAc on the conversion. It appears that the conversion does not depend much on ZnAc's concentration. This may be explained by the heterogeneity of the reactive system. It is also noted that the way the catalyst is added to the mixer has little effect on the conversion. Successive addition of AE and ZnAc (procedure c) does not yield higher conversions than one-pot addition (procedure b). Successive addition may overcome the problem associated with low solubilities of AE and ZnAc in the molten SAN. However, it causes more loss of AE than the one-pot addition because of the low boiling point of AE (170°C/760 mmHg). In what follows, procedure b is retained.
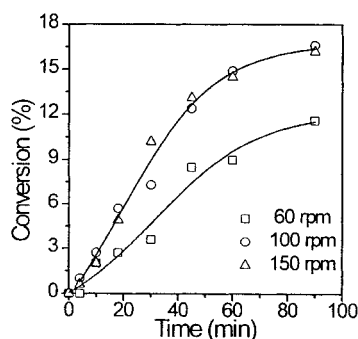
Figure 2. Effect of mixing on the conversion of the nitrile to oxazoline as a function of time.

Effect of Mixing

As the reactive system studied here is not homogeneous, mixing is expected to affect the overall reaction kinetics. Figure 2 shows the conversion as a function of time at three different rotation speeds of the rotors. A significant increase in the reaction rate is seen when the rotation speed is increased from 60 to 100 rpm. When the mixing speed is increased further, no additional contribution to the conversion can be detected. This implies that a minimum rotation speed is needed to ensure a fairly good dispersion of AE and ZnAc in the molten SAN. A further increase in the rotation speed does not improve or further the conversion.

However, it should be kept in mind that under mixing, the actual temperature of the reactive system is often higher than the set temperature. This temperature rise increases with increasing rotation speed. This is illustrated in Figure 3. When the rotation speed is 150 rpm, the melt temperature has reached 170°C, the boiling point of AE. Under this condition, there must have an appreciable loss of AE. This may explain the fact that the conversions obtained at 150 rpm are not higher than those at 100 rpm, despite a better dispersion of AE and ZnAc in the molten SAN and a higher temperature at 150 rpm.
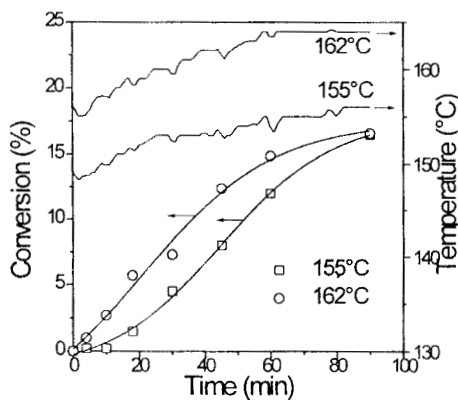
Effect of Temperature

In Figure 4 are shown the conversions at two different temperatures, both being below the boiling point of AE in order to minimize the loss of AE. As expected, the higher the reaction temperature, the higher the conversion. However, the conversion appears to level off at about 15% irrespective of the reaction
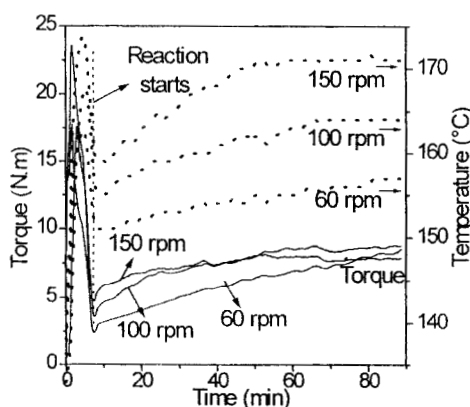
Figure 3.   Temperature and torque of the reactive system as a function of time at various rotation speeds. Dotted curves: temperature; solid curves: torque; vertical dashed line: demarcation between the addition of AE and ZnAc to the molten SAN and the start of the reaction.


Figure 4.   Effect of temperature on the conversion as a function of time.

temperature whereas the molar ratio between [AE] and [AN] is 0.68. A plausible explanation is that one AE molecule reacts with two adjacent AN groups of a SAN chain at the same time. Thus isolated AN groups cannot be converted to oxazoline. Moreover, because of its bulkiness, an oxazoline group once formed will reduce the accessibility of its neighboring AN groups. More work is needed to verify the point.

Reactivity of Oxazoline Modified SAN

If the reaction between SAN and AE indeed forms the expected oxazoline functionality, then the modified SAN should be able to react with a carboxyl group to form an ester-amide group. To confirm this, a modified SAN and 1-naphthylacetic acid (NAA) were mixed together in the batch mixer at 180°C with a rotation speed of 64 rpm. The expected reaction scheme is depicted below:
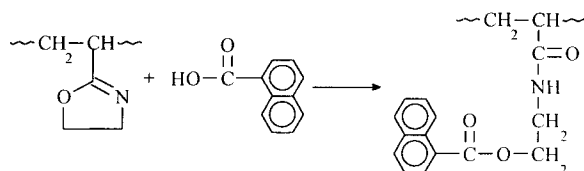

The advantage of using NAA as acid lies in its naphthyl group which is quite sensitive to ultraviolet. This makes easy a quantitative detection of the expected reaction. Moreover, it is convenient to work with NAA because of its powdery form at room temperature (melting point: ~130°C) and its low volatility at reaction temperatures.

A mixture of 45 g modified SAN (17% conversion) and 10 g NAA was charged to the mixer. This amounts to a molar ratio of 1.5 for [-COOH]: [oxazoline]. The time zero for the reaction was taken as the moment where the reactive mixture got molten (it took about 2 minutes). To evaluate the reaction rate, samples were taken quickly from the mixer at different reaction times and then quenched immediately in liquid nitrogen to stop the reaction. After removal of NAA residue according to the purification procedure described in the Experimental section, the samples were dissolved in chloroform at a polymer concentration of about 0.3 g/l and then analyzed by UV.

Figure 5 shows the UV spectrum of the AE modified SAN and those after 2 and 60 minutes of reaction with NAA. Clearly, NAA is fixed onto the AE modified SAN chains because after reaction with NAA, the UV spectrum of the AE modified SAN is more like an superposition of the UV spectra of NAA and SAN. This is further supported by the IR spectra of the AE modified SAN before and after reaction with NAA. In this latter case, three additional peaks appear in the IR spectrum: one at 1738 cm^{-1} corresponding to the ester of the ester-amide group, the other two at 1656 and 1538 cm^{-1}, characteristic of the amide of the ester-amide group. The peak of the amide at 1656 cm^{-1} is overlapped with the oxazoline functionality. The chemical modification of SAN also results in an increase in glass transition: the glass transition of the virgin SAN is 110°C while that of an AE
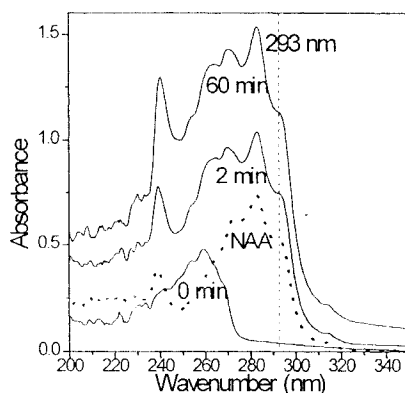
Figure 5.   UV spectrum in chloroform of an AE modified SAN (17% of the nitrile was reacted with AE) and those after 2 and 60 minutes of reaction with NAA. Dotted curve: NAA. In this study, the peak at 293 nm was used for quantitative measurement. According to an unpublished work [12], the extinction coefficient of NAA at 293 nm in chloroform at room temperature is 4274 liter. mole^{-1} cm^{-1}.
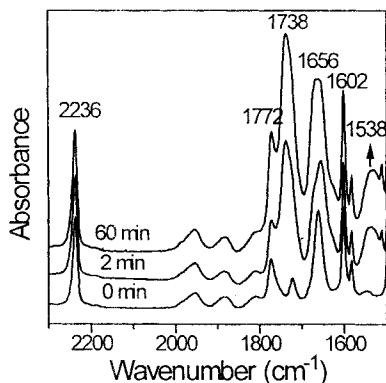
Figure 6.   IR spectrum of an AE modified SAN (17% of the nitrile is reacted with AE) and those after 2 and 60 minutes of reaction with NAA.

modified SAN (17% conversion) is 114°C. This means that the conversion of the nitrile to oxazoline functionality tends to reduce segmental mobility of the SAN chains. All the above results tend to confirm that the desired reaction between SAN and AE does have taken place.

In Figure 7 is shown how fast the oxazoline reacts with NAA. The conversion of the percentage of the oxazoline to the ester-amide group has reached
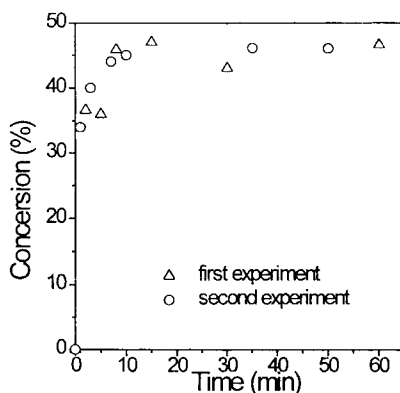
Figure 7. Kinetics of the reaction between an oxazoline modified SAN (17% of the nitrile is converted to oxazoline) and NAA in the melt at 180°C. Molar ratio of [-COOH]:[oxazoline] = 0.95. Rotation speed = 64 rpm.

the ultimate value within less than 5 minutes. However, the ultimate conversion is limited to about 46%, which is well below the maximum attainable (100%). Nevertheless, this agrees qualitatively with results reported elsewhere [7].
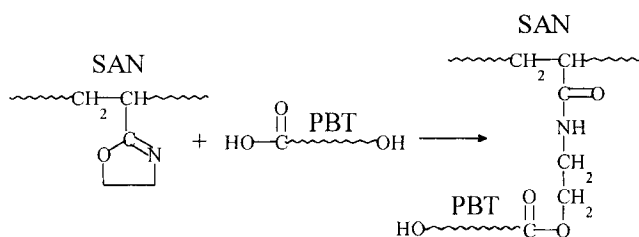
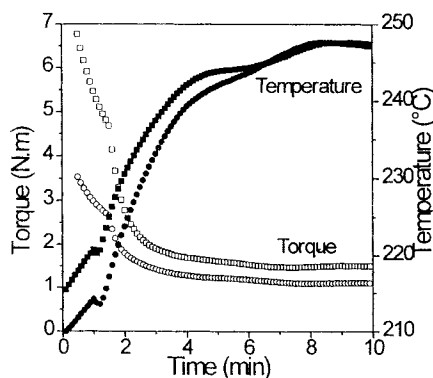## Compatibilizing Efficiency of Oxazoline Modified SAN:

We tested the efficiency of an oxazoline modified SAN as compatibilizer precursor for the SAN/PA 6 and SAN/PBT blends. The expected compatibilizing reactions can be depicted below:

For the SAN and PA 6 system:
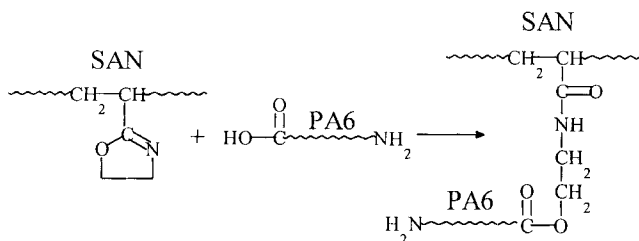

For the SAN and PBT system:

Figure 8. Torque and temperature of the mechanical and reactive SAN/PA 6 blends when subjected to mixing. Mechanical blend: SAN/PA 6 = 70/30 by weight; reactive blend: oxazoline modified SAN/SAN/PA = 14/56/30 by weight. (○, ●): torque and temperature of the mechanical blend; (π, ■) torque and temperature of the reactive blend. Rotation speed: 64 rpm.

The composition of SAN and PA 6 (or PBT) was 70/30 by weight. The ability for the oxazoline modified SAN (17% nitrile converted to oxazoline) to make SAN/PA 6 and SAN/PBT blends compatible can be appreciated first by torque and temperature changes during blending in the bath mixer. As can be seen from Figure 8, the torque and temperature of the SAN/PA 6 blend in the presence of the oxazoline modified SAN are notably higher than those of the corresponding mechanical blend. This infers that the oxazoline modified SAN must have reacted with the terminal carboxylic group of the PA 6, which generates a graft copolymer (SAN-g-PA 6). This latter brings about an increase in the viscosity of the blend due to the molecular weight build-up and/or a change in morphology and interfacial adhesion. Similar observations were also made for the SAN/PBT mechanical and reactive blends.

The compatibility capacity of the oxazoline modified SAN can also be evaluated by morphology observations. As can be seen from the SEM micrographs shown in Figure 9, PA 6 is indeed better dispersed in SAN with the oxazoline modified SAN than without. In the mechanical blend, the mean diameter of the PA 6 phase of the mechanical blend is about 2 μm. It is largely reduced to less than 0.5 μm in the reactive blend. Apparently, the interfacial adhesion between the SAN and PA 6 phases is also enhanced. As for the SAN/PBT system, the
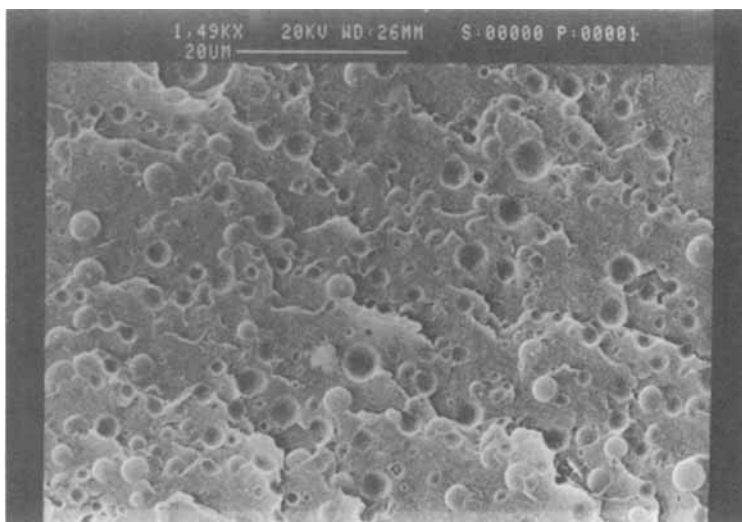
Mechanical blend
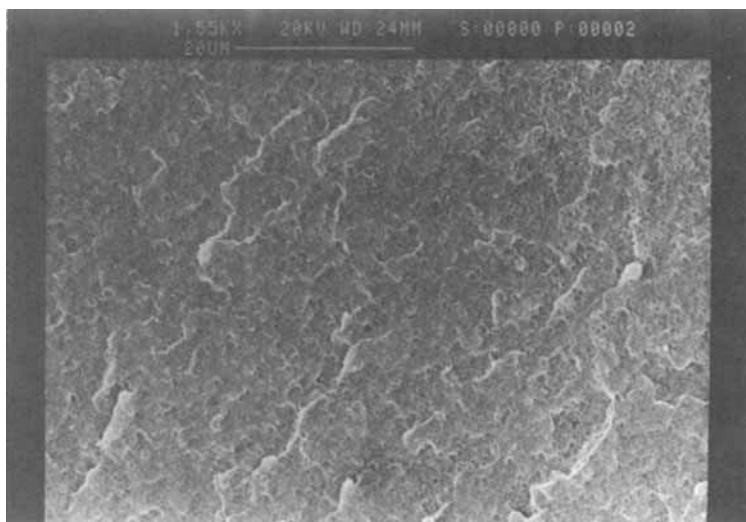
Reactive blend

Figure 9. SEM micrographes of the SAN/PA 6 mechanical and reactive blends. Mechanical blend: SAN/PA 6 = 70/30 by weight; reactive blend: oxazoline modified SAN/SAN/PA 6 = 14/56/30 by weight.

presence of an oxazline modified SAN also reduced the particle size of the dispersed phase (PBT).

CONCLUSION

In this paper, we have reported the possibility of chemically transforming a nitrile attached to a macromolecular chain to oxazoline functionality. Specifically, we have shown that appreciable amounts of the nitrile of a styrene and acrylonitrile copolymer (SAN) can be converted to oxazoline when reacted with 2-amino ethanol (AE) in the melt in the presence of zinc acetate as catalyst. Because AE is not soluble in the molten SAN, adequate mixing is necessary for homogenizing this immiscible reactive system. The oxazoline modified SAN has been found to be very reactive toward carboxyl group. When 1-naphthlylacetic acid is used as acid, the reaction carried out in the melt at 180°C has gone to completion within about 2 minutes. This explains the good compatibility efficiency of oxazoline modified SAN in SAN/PA 6 and SAN/PBT blends. Extension of this work to reactive extrusion is underway.

ACKNOWLEDGEMENTS

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