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Infrared Monitoring of the Modification of Styrene Acrylonitrile Copolymers with Oxazoline and Its Interfacial Reaction with Acid-Containing Polymers

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Summary: The kinetics of the modification of styrene acrylonitrile (SAN) with aminoethanol to oxazoline-containing copolymers has been monitored with FTIR spectroscopy. Further, the interfacial reaction in bilayer samples of the oxazoline groups of these copolymers and the carboxylic acid groups of poly(ethylene-co-methacrylic acid) (PE-co-MA) copolymers has been studied by FTIR at different temperatures. The interfacial formation of ester-amides has been measured quantitatively by FTIR difference spectroscopy.

Keywords: FTIR; interfacial reactions; modification; PE-co-MA; SAN

Introduction

Reactive blending is an important and increasingly accepted method for the compatibilization of polymeric materials. Two or more immiscible polymeric components are functionalized with chemical units, which are co-reactive. During melt processing, the polymers chemically react to form copolymers at the interface between the two phases. These copolymers reduce the interfacial tension between the two phases, leading to better dispersion, and further promote adhesion between the phases.

The kinetics and extent of reaction between these functionalized polymers is a critical parameter in determining the resultant blend properties. The extent of reaction is usually measured by isolating the copolymer component from the reactive blend through selective extraction,[1–3] but in some cases nuclear magnetic resonance (NMR) spectroscopy has been used.[4,5] The reaction kinetics may also be followed by measuring the torque during blending,[2,3,6–8] however this method is indirect and difficult to interpret quantitatively. Reactive blending involves a complex process of diffusion, reaction and mixing at the same time. To understand the interfacial processes in more detail, bilayer film Fourier transform infrared (FTIR) experiments were designed by Scott and Macosko.[9] They studied a well defined interface which could be probed by infrared spectroscopy during the interdiffusion and reaction of two reactive polymers. Their study was based on a system of a styrene-maleic anhydride (SMA) copolymer and a low molecular weight poly(amide-11). The reaction between amine and anhydride is known to be very fast. Similar results were obtained by Orr et al.[10] for a poly(styrene) (PS)-anhydride and poly(methyl methacrylate) (PMMA)-amine system. They further studied the melt coupling reaction of PS and PMMA containing functional groups such as carboxylic acid, oxazoline, epoxy, aromatic primary amine, aliphatic primary amine, hydroxyl and cyclic anhydride. They found that the functional group pairs in order of

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increasing reactivity are acid/amine, hydroxyl/(anhydride or acid), aromatic amine/epoxy, aliphatic amine/epoxy, acid/oxazoline, acid/epoxy, aromatic amine/anhydride, and aliphatic amine/anhydride. To study a system with slower reaction rate, a system of acid and oxazoline-containing polymers was studied by Schäfer et al.[11] They studied a system of a high molecular weight copolymer of ethylene containing acid groups and a low molecular weight polymer containing oxazoline groups. To our knowledge, no study has been performed for a bilayer system of acid and oxazoline-containing high molecular weight polymers. Further, diffusion and reaction-controlled regimes in bilayer blend systems have also not been studied thoroughly.

In this work, we have studied the interfacial reaction between two higher molecular weight polymers, i.e. polyethylene-co-methacrylic acid (PE-co-MA) and styrene acrylonitrile oxazoline (SAN-Oxaz), produced by reaction of styrene acrylonitrile with aminoethanol in solution, the oxazoline functionality being of commercial interest due to its versatility to other functionalities.[13] The reaction kinetics was studied using Fourier transform infrared spectroscopy, focussing on the effect of temperature and oxazoline concentration on the interfacial reaction. The choice of this particular system was mainly governed by the experimental limitation of the FTIR analysis.

Experimental

Materials

The styrene acrylonitrile copolymer (SAN) used in this study contained 28 wt% acrylonitrile and was obtained from DOW Chemicals. The number-average and weight-average molecular weight were 41 kg/mole and 91 kg/mole respectively. PE-co-Ma was a commercial sample provided by Sigma Aldrich. The acid content of the sample was 15 wt% with a MFI of 21 at 190 °C. As calibrant for the FTIR measurements, reactive polystyrene (RPS-1005) containing 1 wt% oxazoline was obtained from EPOCROS and used as received. 2-Aminoethanol (Sigma Aldrich) was used as purchased. 1,2-Dichlorobenzene (DCB), chloroform, methanol and dichloromethane were used as received (Aldrich Chemicals).

Synthesis of SAN-Oxazoline Copolymers

Styrene acrylonitrile (SAN) was first dissolved in dichlorobenzene. Then a specified amount of catalyst was added. Subsequently, 2-aminoethanol was introduced into the mixture. The reaction temperature was kept constant. Samples were taken at different intervals and purified in order to determine the conversion as a function of time. For purification, an equal volume of chloroform was added to the sample mixture for dissolution and then samples were precipitated with a 10 fold amount of methanol. The samples were also purified twice for complete removal of unreacted aminoethanol. The purified samples were dried at 45 °C under vacuum for 2 days before analysis.

FTIR Analysis of Modification of SAN

For FTIR analysis, 15 mg of the modified polymer was dissolved in 1 ml dichloromethane. Spectra were recorded on a BioRad Excalibur 3000 infrared apparatus. The intensity of the stretching vibration of C=N of the oxazoline group at 1664 cm^{-1} was used to quantify the oxazoline formation. The samples were calibrated using a calibration curve obtained from RPS-1005 samples. The calibration curve was obtained by measuring the area under the 1664 cm^{-1} peak for different concentrations of RPS-1005 in dichloromethane. The phenyl stretching vibration at 1494 cm^{-1} from styrene was used as reference.

Bilayer Sample Preparation

First, PE-co-Ma samples were melt pressed at 180 °C to a thickness of 0.5 mm. Then, a thinner film of approx. 500–600 nm of SAN-Oxaz was spincoated on top of it from a 10 wt% of SAN-Oxaz in chlorobenzene

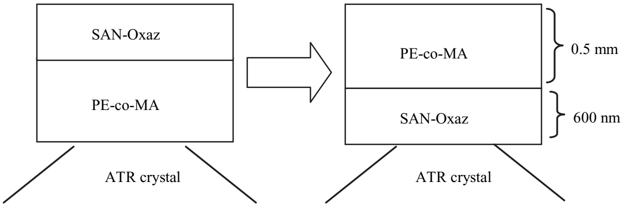

Figure 1.
Schematics of the bilayer sample of PE-co-MA and SAN-Oxaz.

solution. The sample was put in an oven at 50 °C for 2 hrs to remove the residual solvent.

FTIR Analysis of the Bilayer Samples

The bilayer sample was put upside down as shown in Figure 1 on to the Golden Gate Heated Attenuated Transmission Reflectance (ATR) top plate. The thinner SAN-Oxaz film (approx. 500 nm) was positioned at the bottom and thicker PE-co-MA film (approx 0.5 mm) was positioned at the top. The bilayer sample was covered with a steel cover with a continuous nitrogen supply. The heated ATR top plate is operational from ambient temperature to 200 °C by a dedicated Eurotherm 3000 series temperature controller. The angle of incidence of the ATR was 45° with diamond as the ATR crystal material. Thus, the penetration depth was in the order of 1.5–2 μm for the spectral range of interest (1000–2000 cm^{-1}). The thinner sample was used at a maximum thickness of approx. 600 nm to get the information from the interfacial region. The spectra were taken using the same BioRad Excalibur 3000 FTIR apparatus, but now coupled to a MCT-detector. Thirty scans were accumulated for each spectrum and the measurements were repeated in different time intervals in order to study the reaction kinetics.

Results and Discussion

This part is divided into two sections. The first section discusses the kinetics of the modification reaction of SAN to SAN-oxazoline, while the second section describes the monitoring of the interfacial reaction of the SAN-Oxaz with PE-co-MA.

Kinetics for the Modification Reaction of SAN to SAN-Oxazoline by FTIR

The reaction was monitored by recording FTIR spectra of samples taken after specified times. In Figure 3, the FTIR spectrum for pure SAN is shown and compared with the modified SAN. A new peak was formed at 1664 cm^{-1}, characteristic for the stretching vibration of the C=N group of oxazoline. The peak at 2239 cm^{-1}, which can be assigned to the stretching vibration of the C≡N group in acrylonitrile, decreases during the modification. The extinction coefficient for the nitrile group is found to be much lower than for the oxazoline group. Therefore, all kinetic data were calculated based on the oxazoline conversion. The calibration curve for oxazoline was obtained using a RPS-1005 sample.

From Figure 3, it can be observed that only oxazoline is formed during the reaction with no side products. The kinetics scheme is shown in the Figure 2. The rate of

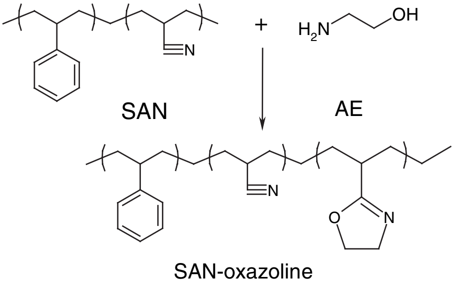

Figure 2.
Kinetic scheme of the formation of SAN-Oxazoline from SAN.

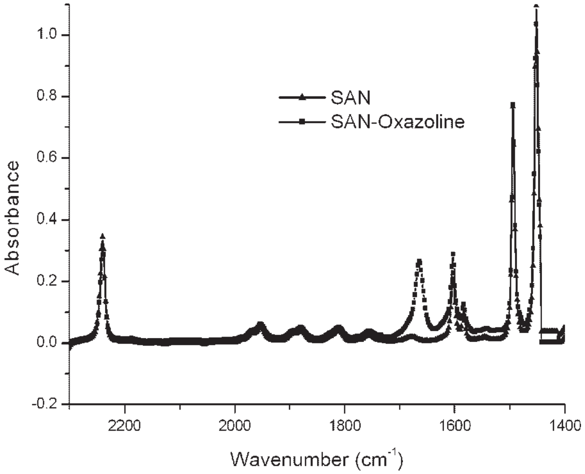

Figure 3.
Infrared spectra of pure SAN and SAN-oxazoline.

formation of oxazoline can be expressed as:[12]

$$\frac{C_{\text{SAN-oxaz}}}{C_{\text{AE},0}(C_{\text{AE},0} - C_{\text{SAN-oxaz}})} = kt \tag{1}$$

The SAN-oxazoline concentration was determined from the FTIR experiments as a function of time for different temperatures. The oxazoline concentration increases smoothly with time as shown in Figure 4. As expected, increasing the reaction temperature results in an increase in the rate of oxazoline formation to 150 °C.

Equation (1) was used for the evaluation of kinetic parameters of the reaction study. The reaction rate constant k can be computed using the experimentally determined $C_{\text{SAN-oxaz}}$ values at each temperature. Next, the activation energy of the reaction according to the Arrhenius equation was determined together with the values of the frequency factor $k_0 = 6.4 \times 10^{4}$ g/(mmol · min) and the activation energy $E_A = 20.74$ cal/mmol.

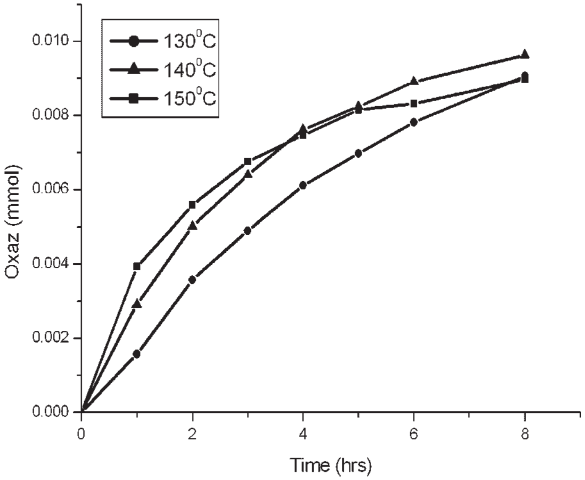

Figure 4.
Production of SAN-oxazoline vs. time at different temperatures in solution.

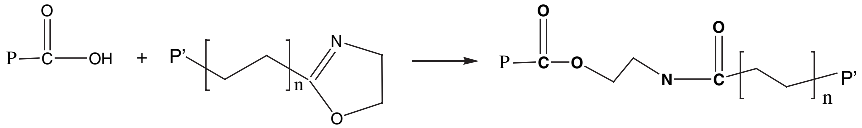

Figure 5.
Overall reaction between acid and oxazoline.

Monitoring of Interfacial Reaction between SAN-Oxazoline and PE-co-MA

For the interfacial monitoring, bilayer samples were prepared as discussed in the experimental section. The samples were placed upside down as shown in Figure 1 onto the ATR crystal. First, the sample was heated to 120 °C, which is above the melting point of PE-co-MA and T_g of SAN-Oxaz. Then, the temperature was increased to the specified reaction temperature. During the reaction, the spectral changes were followed. Figure 5 shows the overall reaction of the ester-amide formation by the nucleophilic attack of the carboxylic acid at the oxazoline ring via a ring opening reaction.[13] Figure 3 and 6 show the original spectra of SAN-Oxaz and PE-co-MA respectively. For PE-co-MA, the interesting spectral range is around 1600–1800 cm^{-1}, i.e. the strong carbonyl stretching vibration of the acrylic acid at approx. 1680 cm^{-1}. Similarly for SAN-Oxaz, the characteristic band of C=N is at 1664 cm^{-1}. During the initial annealing at 120 °C for 30 min, melting of PE-co-MA occurs and no reaction product (ester-amide) was found. A peak at 1740 cm^{-1} developed at higher temperatures, which can be attributed to dissociation of intermolecular carboxylic acid dimers.[14,15]

The reaction can be observed above 150 °C. Figure 7 shows the spectra of the bilayer films after annealing at 120 °C for 30 min and then reacting at 190 °C. The reaction can be evaluated by the change of the absorption bands associated to the oxazoline and amide and ester groups. The oxazoline band at 1664 cm^{-1} decreases with time, whereas the formation of amide I (C=O stretching vibration) and ester can be observed at 1680 and 1730 cm^{-1} respectively. Also a weak shoulder at 1530 cm^{-1} develops which might be assigned to an

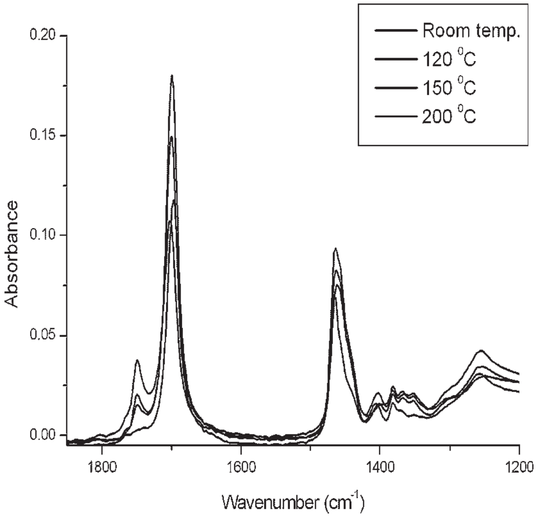

Figure 6.
FTIR spectra of PE-co-MA at different temperatures.

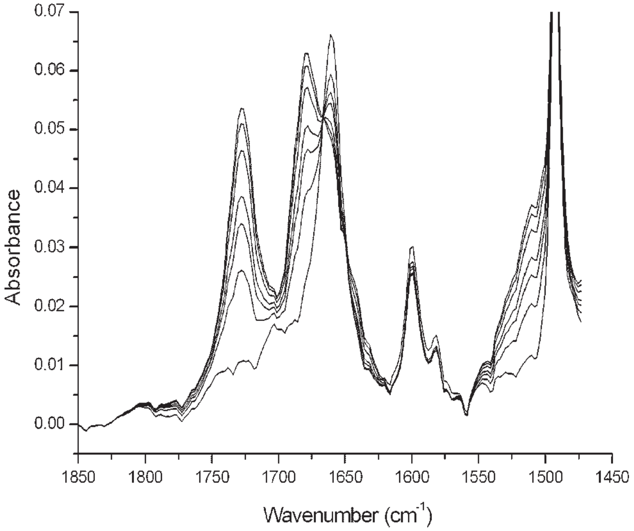

Figure 7.
FTIR spectra of bilayer specimen of PE-co-ma and SAN-Oxaz taken after annealing 30 min at 120 °C (0 min) and subsequent times reacted at 190 °C.

amide II band (N–H deformation and C–N stretching vibration). This was also observed in other polymer systems.[3]

Since not all bands were completely separated, all further analysis was done by applying difference spectroscopy. All spectra were subtracted from the spectrum obtained after pretreatment for 30 min at 120 °C. Figure 8 shows the difference spectra obtained at 190 °C as a function of time. The band at 1664 cm^{-1} from oxazoline clearly decreases with time. Similarly, the band at 1730 cm^{-1} from the ester group and also at 1680 cm^{-1} from the amide I increase with time. The peak at 1680 cm^{-1} can be integrated quantitatively.

Figure 9 shows the increase of the peak area of the carbonyl band of the ester-amide as a function of reaction time for different temperatures. At lower tempera-

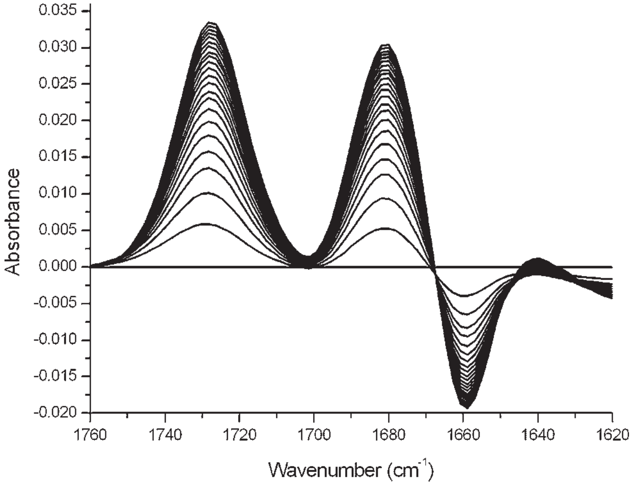

Figure 8.
FTIR difference spectra of the bilayer system measured at 190 °C as a function of time.

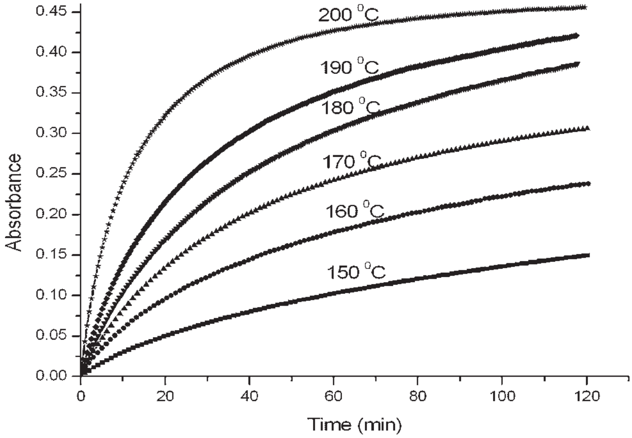

Figure 9.
Peak area of the amide I peak vs. reaction time at different temperatures.

tures, the reaction is very slow and the curve seems to increase even after 2 hrs of reaction. On the other hand, at higher temperatures, the curve has a steep increase followed by a plateau region. From the initial slopes, the reaction rate constants can be obtained. The initial slopes are plotted against the reciprocal temperature in Figure 10 resulting in a straight line indicating that the reaction is not diffusion controlled in the temperature range investigated. Further studies on trilayer system, containing a non-reactive interlayer of SAN are underway.

The effect of different oxazoline-concentrations in SAN-Oxaz on the bilayer reaction was studied and the results are shown in Figure 11. It is found that the final yield of amide I is directly related to the oxazoline concentration in SAN-Oxaz.

Conclusions

FTIR spectroscopy can be used to study the kinetics of the modification reaction of SAN into SAN-Oxazoline. The frequency factor and the activation energy were found to be *6.4* × *10*^{4} g/(mmol · min) and *20.74* cal/mmol respectively. Further, FTIR spectroscopy proved to be a powerful tool for studying the kinetics of interfacial reactions

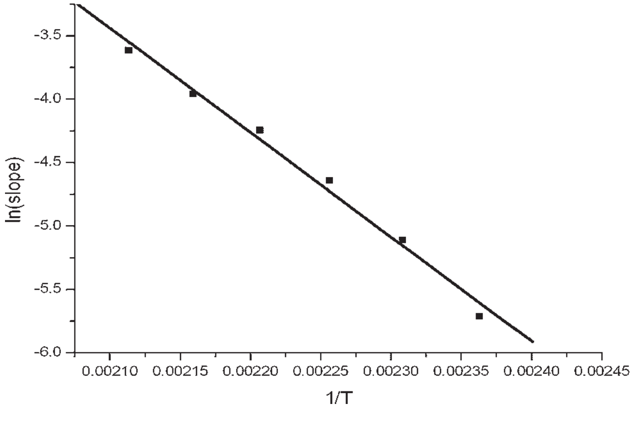

Figure 10.
The initial slope of the interfacial reaction rate as determined from the absorbance of the amide I peak vs. 1/T.

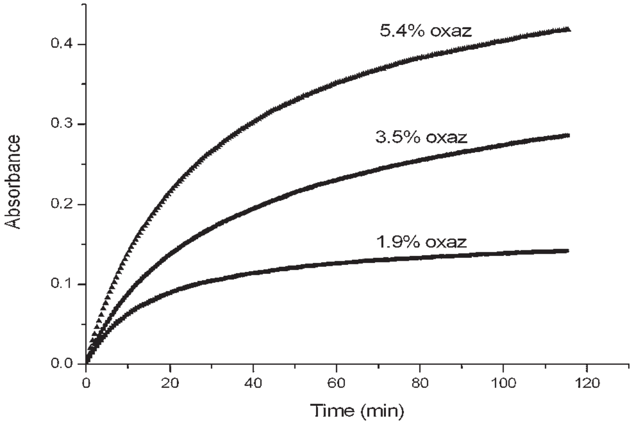

Figure 11.
Effect of oxazoline concentration in SAN-Oxazoline on the interfacial reaction.

in bilayer systems of functionalized polymers even for higher molecular weight polymers. For the system of PE-co-MA/SAN-Oxaz, the temperature dependence of the interfacial reactions was obtained quantitatively by using FTIR difference spectroscopy. These results show that in this case the system is only reaction controlled, and not diffusion controlled. These observations can contribute to a more quantitative understanding of the reactive blending process.

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