Macromol. Symp. **2003**, *202, 67—76*

Compatibilization of PA6/Rubber Blends by Using an Oxazoline Functionalized Rubber

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Summary: The compatibilization of blends of polyamide 6 with a nitrile butadiene rubber has been investigated. The procedure consists of two steps: modification of the nitrile groups of the rubber into oxazoline in the melt through condensation of ethanolamine with formation of a molecule of ammonia, followed by use of the modified rubber as a compatibilizing precursor which is melt mixed with the polyamide to produce the compatibilized blend. The modification reaction has been detected by NMR analysis and a rheological, mechanical and thermomechanical characterization has been carried out on the all the blends. The results indicate that the modification reaction occurs but the conversion of nitrile into oxazoline is relatively low. Use of the modified rubber in the preparation of binary polyamide/rubber blends, leads to an increase in viscosity, which is typical of compatibilized systems, and to enhanced tensile, impact and thermomechanical properties. These phenomena can be explained by the formation of in situ rubber/polyamide copolymers that act as compatibilizers, due to the reaction between oxazoline and the end groups of the polyamide. The presence of residual low molecular compounds, from the modification or from the purification of the rubber worsens all of the properties and inhibits the compatibilizing effect of the modified rubber.

Keywords: compatibilization; nitrile rubber; oxazoline; polyamide; reactive processing

Introduction

One of the most popular topics and targets of both scientific and industrial research is the preparation of high performance polymer blends with the final aim of producing new materials with improved properties as compared to those of the original polymer. The polymer couples are generally immiscible and incompatible, the final properties of the materials are generally poor and a proper compatibilizing technique is required to improve the otherwise weak interfacial adhesion, the gross morphology and the poor stability of the blend.[1-5]

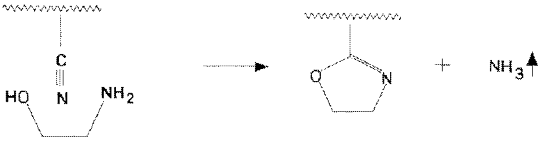
DOI: 10.1002/masy.200351207

A highly desirable result could be achieved by coupling of the impact resistance of rubber with the good mechanical and thermomechanical properties of polyamides but an appropriate compatibilization system has to be developed.

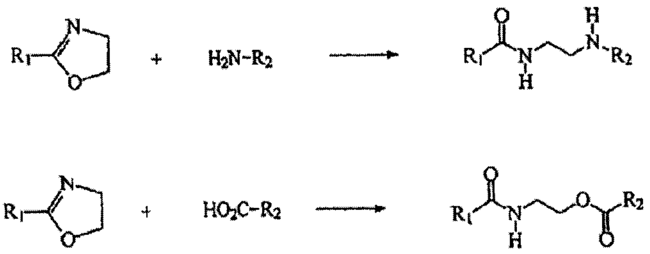
One of the most versatile methods for the compatibilization of incompatible A/B polymer blends is to add a graft A-g-B copolymer that locates at the interface, thus allowing a reduction of the interfacial tension with an enhancement of the dispersion and stabilization of the morphology.[1-3] The preparation of these copolymers can be achieved in a separate step or in situ, during the preparation of the polymer blend.[1-3,6] Of course, the second method is particularly desirable for industrial purposes and is relatively easy to achieve if one or both of the polymers contain functional groups able to react, such as maleic anhydride, acrylic acid, glycydil methacrylate, oxazoline.[6-11]

Oxazoline has been found to be highly reactive toward a number of other functional groups e.g. carboxyl, amine, phenol and mercaptan.[12] To graft an oxazoline ring to the polymer thus in situ it is possible to use compounds already containing an oxazoline ring[13-22] or to form it through condensation of ethanolamine on nitrile groups either in solution or in the melt.[23-27]

In the current work the nitrile groups of nitrile butadiene rubber (NBR) have been converted into oxazoline through reaction with ethanolamine in the presence of a catalyst. The modification reaction is depicted in Scheme 1. The modified rubber has then been used for the compatibilization of polyamide6/NBR blends. The possible method of formation of the compatibilizer is illustrated in Scheme 2.



Scheme 1. Reaction of conversion of nitrile into oxazoline.



Scheme 2. Reaction of oxazoline with amine and carboxyl groups.

Experimental

Materials and Preparation

The rubber used in this work was kindly supplied by Enichem Elastomeri (a nitrile content of 30%). The polyamide 6 (PA6) was the ASN27 grade, supplied by Rhodia. The functionalizing agent employed was 2- ethanolamine (EA) and the catalyst used according to previous works[23–28] was zinc acetate, both purchased from Aldrich. All the materials were used as received without further purification.

The functionalization was performed in a Brabender (PLE 330) batch mixer between 160 °C and 180 °C and a speed of 64 rpm, requiring about 10 minutes. A solution of EA and catalyst (100:6 w/w) was added to molten rubber (rubber/solution 75/25 w/w) and the mixer was closed in order to avoid reactant loss through vaporisation. The rubber was then removed from the chamber and either used as it was or after further purification, consisted of solubilization it in tetrachloroethane followed by precipitation from methanol in order to remove any trace of reactants and low molecular weight compounds and drying under vacuum at 85 °C to remove any remaining solvent.

80/20 w/w binary blends of polyamide and rubber (modified and unmodified) were also prepared using the same apparatus as used for the functionalization process. The conditions employed were : 220 °C, a rotational speed of 64 rpm and about 10 minutes mixing time, until a constant value of torque was reached. Both the polyamide and the rubber were dried overnight in a vacuum oven before processing.

Characterization

The modification reaction was investigated by CP MAS NMR using a Bruker 200AC spectrometer operating at 4.7 Tesla and equipped for solid state analysis. Samples were spun at 5000 Hz in 7 mm diameter zirconia rotors with Kel-F caps. The 50.32 MHz ^{13}C CP MAS NMR spectra were obtained using the standard Bruker cross polarization pulse sequence with high power dipolar decoupling during acquisition, 3 ms Contact Time, 30 seconds Relaxing Delay, and were processed with 20 Hz exponential line broadening. ^{13}C chemical shifts were externally referenced to solid sodium 3-(trimethyl-silyl)-1-propane sulfonate at 0 ppm. The magic Angle condition was adjusted observing ^{79}Br resonance in a rotor containing 5% of KBr.[29]

Tensile tests were carried out using an Instron 1122 (United Kingdom) tensile testing machine on samples cut from sheets obtained by compression moulding (Carver laboratory press) at 220 °C.

Impact tests were carried out using a CEAST (Italy) impact test machine on notched samples at –20 °C. Thermomechanical properties were evaluated using a Rheometric DMTA V (USA) in the range 20-110 °C at a frequency of 1 Hz.

Results and Discussion

Modification

FTIR analysis, not reported here, is not useful for monitoring the conversion of the nitrile group of NBR into oxazoline. This is probably due to the poor degree of achieved conversion during the modification reaction. It is worth noting that this is not a negative result as, for compatibilization purposes, even very low conversions are sufficient to obtain a good performance of the modified polymer. Even if the effectiveness of the modified rubber as a compatibilizing agent can be used as indirect evidence of the modification reaction, direct investigations have been carried out by using ^{13}C NMR in the solid state analysis. These results are reported in Figs. 1a-b.

In Fig. 1a the spectrum of neat NBR is reported. The two signals characteristic of the rubber can be clearly seen due to the aliphatic and aromatic carbon atoms, respectively, centered at 31ppm and 130ppm.

The same peaks are also present in the spectrum of the modified rubber (Fig. 1b), but in this case additional weak peaks are also present. In particular the signal centered at 61 ppm can be attributed to the carbon atoms bonded to the nitrogen in the oxazoline ring[30] grafted onto the main backbone of the polymer. Their relative weakness confirms the very low conversion achieved in the modification reaction. Different reaction temperatures have also been employed, but the characteristics of the different materials obtained are exactly the same, at least in the range of conditions investigated in the present work. A separate study on the degradation of the rubber,[31] showed that a slightly higher reaction temperature led to less degradation, probably due to the lower melt stress resulting from the reduced melt viscosity,. Thus, all the functionalized rubber used for compatibilization purposes was prepared at 180 °C.

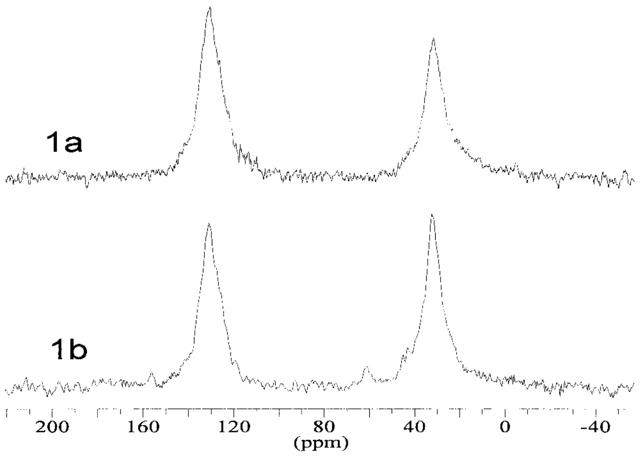


Fig. 1. Solid state ^{13}C NMR spectra of: (a) unmodified NBR, (b) modified and purified NBR.

Compatibilization

In Fig. 2 the torque obtained during the modification reaction is reported for the following blends: PA6 with modified and unpurified NBR (PA6/NBR mod.); PA6 with modified and purified NBR (PA6/NBR mod. pur.) and PA6 with pure NBR which has been previously processed under the same functionalization conditions (PA6/NBR lav.).

The mixing torque is a measure of the power absorbed during processing of the rubber and is strictly related to the melt viscosity of the material inside the mixing chamber. As can be clearly seen, the curve with the lowest torque values is that obtained for the binary blend containing modified and unpurified NBR. This can be explained by the presence of low molecular weight residual reactants that act as plasticizers lowering the melt viscosity of the blends to values even lower than that displayed by the uncompatibilized PA6/NBR lav. blend. The presence of these compounds has been also confirmed by the generation of smoke products in the chamber during the preparation of the blend.

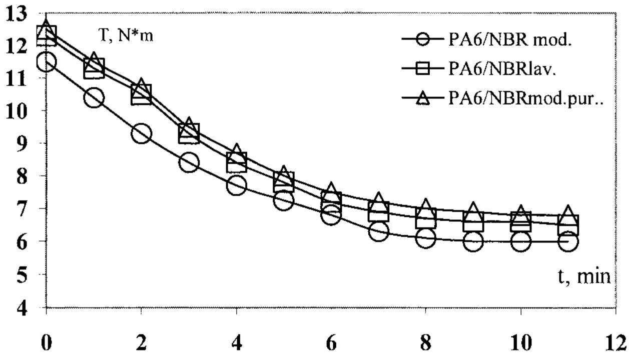


Fig. 2. Mixing torque as a function of time of compatibilized and uncompatibilized PA6/NBR.

The situation is different when the rubber is purified prior being added to the PA6. In this case no smoke products are detected during processing and the viscosity is higher than that of the uncompatibilized blend. This phenomenon is expected as the reaction between the oxazoline modified NBR and the PA6 leads to the formation of NBR-PA6 copolymers that, localizing at the interface of the two polymers, can act as compatibilizers for the blend. This, causes a greater interaction between the phases with the consequent increase of the melt viscosity. It is clear that this phenomenon also occurs when modified and unpurified NBR is used, but in this case the increase in the viscosity is overcome by the plasticizing effect caused by the presence of the low molecular weight compounds.

In Table 1 the tensile mechanical properties of the three binary blends are reported. The mechanical results confirm the results of the rheological analysis.

The mechanical properties of the blend containing unpurified modified NBR show the worst properties as compared with the other blends, especially for the uncompatibilized blend. Once again, this is due to the presence of residual low molecular weight compounds that act as defects in the solid state and induce premature rupture exhibiting low values of tensile stress, elongation at break and of the breaking energy. This effect is more intense than the plasticizing effect evidenced by the lowering of the elastic modulus.

Table 1. Mechanical properties of compatibilized and uncompatibilized PA6/NBR binary blends.

Material	Modulus MPa	Tensile Stress MPa	Elongation at Break %	Energy to Break J
PA6	300	60	335	-
PA6/NBR lav.	640	36.3	75	4.96
PA6//NBR mod.	574	36.0	70	3.91
PA6/NBR mod. pur.	625	38.6	101	5.72

The situation is completely different for the blend containing purified modified NBR. In this case the modulus is comparable with that of the uncompatibilized blend while all the other properties are enhanced. This improvement in the mechanical properties of the blend is be ascribed to the presence of copolymers that locate at the interface between PA6 and NBR and increase the interfacial adhesion and therefore the tensile properties.

To further verify the effectiveness of modified NBR as compatbilizer impact tests have been performed at –20 °C. This temperature is compatible with possible outdoor applications of rubber toughened PA6. The relative results are reported in Table 2.

Table 2. Impact strength measured at –20 °C of compatibilized and uncompatibilized PA6/NBR binary blends.

Blend	Impact strength, J/m^2
PA6/NBR lav.	3940
PA6//NBR mod.	2300
PA6/NBR mod. pur.	5250

The trend is the same as that displayed foe the tensile properties. Once again, the lowest value is obtained for the modified and unpurified NBR and the highest is obtained for purified modified NBR blend. As before, the presence of low molecular weight compounds is the responsible for the low value obtained . The conclusion is that the removal of reactants is crucial to the obtainment of good properties for these materials.

To confirm the presence of in situ formed compatibilizers, thermomechanical tests have been performed on neat polyamide, on the uncompatibilized binary blend and on the compatibilized blend with purified modified NBR. The curves of tan δ as a function of temperature for the above mentioned materials are reported in Fig. 3.

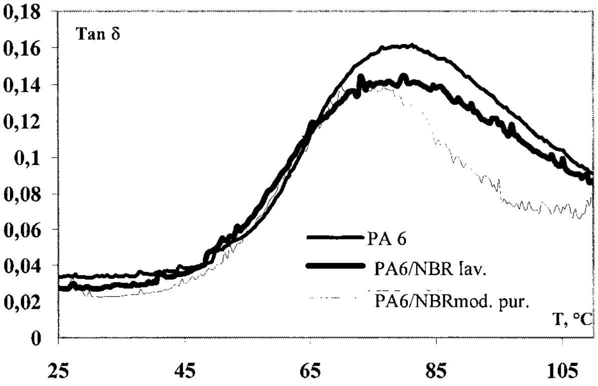


Fig. 3. Tan δ as a function of temperature for neat PA6, for the binary uncompatibilized blend PA6/NBR lav. and for the compatibilized blend with purified modified NBR.

Can be clearly seen in the figure, the curves for the neat polyamide and the uncompatibilized blend show approximately the same tan δ peak while the curve corresponding to the compatibilized blend shows a peak at a slightly lower temperature.

As the tan δ peak is associated with the glass transition temperature of the phase, a reduction of the peak temperature corresponds to a lowering of the glass transition temperature.

When no interactions between the polyamide and other phases are present, such as in the case of the uncompatibilized blend, there are no differences between the glass transition temperature of the polyamide phase in the blend and of the polyamide alone. However, in the compatibilized blend there is an interaction between the phases, resulting from the presence of in situ formed NBR-g-PA6 compatibilizers at the interface of the polymers. A qualitative explanation of this phenomenon is that the presence of these copolymers significantly reduces the crystallinity of the polyamide phase and weakens the connection between the crystalline and amorphous phase. As a consequence a reduction in the energy required for this transition, and therefore of the temperature of the transition, can be expected.

Conclusions

In this work compatibilization of NBR/PA6 blends has been investigated. The nitrile groups of the rubber have been modified with oxazoline by a condensation reaction that employes ethanolamine in the presence of a catalyst. Degree of conversion is very small and not easy to detect but it is nevertheless efficient for compatibilization purposes.

Binary blends of PA6 with modified and unmodified NBR have been prepared in a batch mixer. The results indicate that the modified rubber is able to improve the tensile and the impact properties of the blends but only if a proper purification stage is carried out in order to completely remove residual low molecular weight compounds. The formation of in situ NBR-g-PA6 copolymer at the interface can be reasonably invoked to explain the increased compatibility of the blends.

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