

## Effects of Compatibility in Rubber / Polypropylene Blends

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### Abstract

The solubility behavior of various elastomer additives, i.e. processing promoters (PRMs) was studied in EPDM, NBR and PP by using thermoanalytical and dynamic-mechanical methods. Binary rubber/thermoplastic blends containing selected PRM types were then investigated with regard to phase morphology, compatibilization and related final properties. The incorporation of some additives resulted in significant effects on the physical characteristics of the mixtures. It was demonstrated that the PRMs act as effective homogenizing agents, contributing to considerably improved dispersion and compatibility of the blend components.

### Zusammenfassung

Die Löslichkeit von verschiedenen kommerziellen Verarbeitungswirkstoffen (VAW's) in EPDM, NBR und PP wurde mit Hilfe thermischer und dynamisch-mechanischer Methoden untersucht. Anhand der erhaltenen Ergebnisse wurden dann einige VAW's ausgewählt und in kleinen Mengen in zweiphasigen Kautschuk/PP-Blends eingesetzt. Die Mischungen wurden bezüglich ihrer Morphologie, Verträglichkeit und Endeigenschaften untersucht. Es wurde festgestellt, daß bestimmte VAW's als gute bzw. wirksame Homogenisatoren, Dispersionsmittel und Verträglichmacher für die

beiden Polymerphasen dienen können. Damit tragen diese Zusatzstoffe deutlich zur Verbesserung der physikalischen Eigenschaften bei.

## Introduction

Polymer blends are an important class of engineering materials, as they exhibit synergetic effects due to them comprising useful properties [1-4]. Polyolefine blends have a commercially leading position due to a favorable cost-performance ratio, arising from versatile processing and final properties. A great deal of work has been carried out to improve the impact strength of polypropylene (PP) by blending with rubbers, particularly with the widely used EPDM or copolymer EPM [5]. Considerable efforts have been also directed to the area of thermoplastic vulcanizates (TPV) based on PP as continuous phase, in which the dispersed rubber particles are crosslinked [6]. Studies on elastomer modified polyolefines and other systems are extensively reviewed [7-10].

Most polymer blends are incompatible and immiscible, i.e. they show a limited mutual solubility and often high interfacial tension. The immiscibility primarily arises from the size of the chain molecules leading to a small entropy of mixing, and from chemical characteristics of the segments. However, properties of heterogeneous multiphase materials are crucially influenced by the morphology which, in turn, depends on the thermodynamic interactions between the components. One of the well established criteria for determining compatibility (or incompatibility) and phase structure of polymer blends is related to the changes of the glass transition (glass temperature  $T_g$ ) of the mixed components [11-13].

Great research efforts have been made in order to improve the homogenization and compatibility of polymer blends as well as their corresponding ultimate properties by means of phase compatibilization [6, 14]. For example, graft copolymers of EPDM and PP have been used to increase compatibility and phase dispersion in corresponding mixtures [15]. Coran and Patel [16] showed that the morphology of an NBR/PP blend could be controlled by adding block copolymers comprising compatibilizing segments of both polymers. In rubber blends and TPEs the use of suitable mineral (extender) oils has proven to be a valuable way of enhancing the

compatibility and/or related properties [5, 17, 18]. Advantageous solubility, partition and homogenizing effects have been clearly achieved by incorporating commercial and model (phenol and hydrocarbon) resins in neat rubbers and corresponding blends [19, 20].

The aim of this work is to examine the solubility behavior and compatibilizing effects of different chemical additives used otherwise as processing promoters (PRMs) in neat polymers (NBR, EPDM and PP) and corresponding two-phase blends (rubber/thermoplastic). The glass transition is used as a diagnostic aid for the elucidation of the phase morphology and related compatibility.

## Experimental

### Materials

Commercially available polymers were used for the experiments in this work:

- isotactic polypropylene (PP; P5000 / Vestolen GmbH)
- nitrile rubber (NBR; Perbunan NT 3465 / Bayer AG)
- ethylene-propylene-diene terpolymer (EPDM; Buna EP G 5450 )

Several types of processing promoters (PRMs) were obtained from RheinChemie (Mannheim). *Table 1* lists the additives with a general characterization detailing their chemical composition and thermal transitions (glass and melting temperatures  $T_g$  and  $T_m$ ), determined by calorimetric measurements on the neat PRMs.

**Table 1:** General characterization of the PRM types investigated

| Type | Chemical Composition                  | $T_g$ and/or $T_m$ [°C] |
|------|---------------------------------------|-------------------------|
| KT-1 | zinc salts of unsaturated fatty acids | $T_m=50-90$             |
| RP-1 | polyester based on natural oils       | $T_g=-38$ ; $T_m=-10$   |
| AF-1 | salts of natural fatty acids          | $T_m=50-120$ (2 peaks)  |
| AF-2 | fatty alcohols and fatty acid esters  | $T_m=20-100$ (3 peaks)  |
| AF-3 | pentaerithrit-tetrastearate           | $T_m=40-80$ (3 peaks)   |
| RS-1 | indene-cumarone resin                 | $T_g=-13$               |
| RS-2 | indene-cumarone resin                 | $T_g, T_m=90 - 100$     |
| RS-3 | unsaturated $C_9$ -hydrocarbons       | $T_g, T_m=55 - 65$      |
| RS-4 | phenol resin                          | $T_g=40$ ; $T_m=85$     |

### **Sample Preparation**

Each PRM type was first incorporated into the neat polymers by means of an internal mixer (Rheocord E3000). The rotor speed was adjusted to 50 rpm and the mixing time set at 10 min. The mixing temperature was 120°C for rubber materials and 185°C for those containing PP. In the next step, ternary systems consisting of rubber (NBR or EPDM), thermoplastic and PRM as compatibilizing agent were prepared. Rubber was allowed to melt with PP (weight proportion 70/30) in the kneader for 4 min at 185°C, then 10 phr PRM was added and mixed for 6 min. The blend was then molded at 185°C for 10 min in an electrically heated hydraulic press to prepare specimens of 2 mm thickness for physical measurements. After molding, the mix was cooled under pressure (200 bar) to room temperature (rate ca. 8°C/min).

### **Measurements**

*Differential scanning calorimetry.* DSC measurements were carried out using a DuPont 2920 CE calorimeter at a heating rate of 10°C/min. Sample weight amounted to ca. 10 mg. The glass transition was recorded at inflection point of the DSC curve.

*Dynamic mechanical analysis.* DMA measurements were performed on samples (10x60 mm<sup>2</sup>) using the automatic Brabender torsion-pendulum over a temperature range of -80 to 60°C with a heating rate of 1°C/min. The frequency of free oscillations did not exceed 9 Hz. The tan $\delta$ -peak maximum was assigned to the glass transition.

*Stress-strain measurements* were performed on selected blend samples. Dumbbell specimens were cut from the pressed sheets and tested at room temperature.

## **Results and Discussion**

### **Polymer / Additive Mixtures**

Materials containing EPDM or NBR were investigated by DSC at low temperatures to prove solubility of PRMs in rubbers. *Figure 1* shows DSC curves for different samples. Shifts of the glass temperature ( $T_g$ ) determined from the thermograms are considered as a reliable criterion for the assessment of corresponding solubility. This

standard is also applied to PP/PRM mixtures investigated by DMA, due to its high sensitivity to  $T_g$  of semicrystalline polymers. Some DMA curves are depicted in *Figure 2*. All determined  $T_g$ -values are summarized in *Table 2*.

The DSC results obtained for the rubber/PRM samples obviously reveal different effects of the additives on the thermal behavior of the polymers, indicating varied solubility of the PRMs in both rubber types. It can be seen that  $T_g$  of EPDM and NBR clearly remains unaffected in the presence of the PRM type KT-1. This result indicates the considerably low degree of solubility of the zinc salts of unsaturated fatty acids in the investigated polymers. Similar observations are made for other systems such as EPDM+RP-1 (polyester based on natural oils) and NBR+AF-3 (pentaerithrit-tetrastearate). It is noteworthy that although NBR and the AF types are expected to have similar characteristics regarding their polarity, only marginal compatibility effects of the components can be concluded from the DSC results. These may arise from a great nonpolar content of alkyl chain segments in these PRM mixtures as well as from a mismatch of other important features like molecular weight, crystallinity and processing properties of the materials.

**Table 2:** Influence of the additives on the glass temperature of the polymers

| PRM-type<br>(10 wt.%) | EPDM                          |              | NBR                  |                    | PP                   |                    |
|-----------------------|-------------------------------|--------------|----------------------|--------------------|----------------------|--------------------|
|                       | $T_g/^\circ\text{C}$<br>(DSC) | $\Delta T_g$ | $T_g/^\circ\text{C}$ | $\Delta T_g$ (DSC) | $T_g/^\circ\text{C}$ | $\Delta T_g$ (DMA) |
| -----                 | -53.6                         | 0.0          | -28.4                | 0.0                | 17.5                 | 0.0                |
| KT-1                  | -53.6                         | 0.0          | -28.5                | 0.1                | 17.0                 | 0.5                |
| RP-1                  | -53.4                         | 0.2          | -28.9                | 0.5                | 15.5                 | 2.0                |
| AF-1                  | -53.0                         | 0.6          | -27.9                | 0.5                | 16.0                 | 1.5                |
| AF-2                  | -52.9                         | 0.7          | -27.8                | 0.6                | 14.5                 | 3.0                |
| AF-3                  | -52.5                         | 1.1          | -28.6                | 0.2                | 13.0                 | 4.5                |
| RS-1                  | -52.7                         | 0.9          | -26.6                | 1.8                | 14.5                 | 3.0                |
| RS-2                  | -52.7                         | 0.9          | -26.5                | 1.9                | 18.5                 | 1.0                |
| RS-3                  | -51.4                         | 2.2          | -25.1                | 3.3                | 21.0                 | 3.5                |
| RS-4                  | -52.4                         | 1.2          | -25.3                | 3.1                | 18.0                 | 0.5                |

A certain solubility of some PRMs can be estimated, for example, by the change detected in  $T_g$  of EPDM, when RS-3 (unsaturated hydrocarbon resin) and the stearate-type AF-3 are added. In comparison, the influence of other additives (such as AF-2: fatty alcohol and acid esters and RS-2: indene cumarone resin) is obviously weaker. This can be explained by their higher polarity and, thus, limited solubility in the nonpolar EPDM.

Considering the data of the NBR mixtures, solubility effects of RP-1 may be assumed due to the small change observed in the glass transition region of both components. However, the most pronounced effect on  $T_g$  (increase) of NBR is observed by incorporation of the resins, particularly, the types RS-3 (unsaturated hydrocarbons) and RS-4 (phenol formaldehyde resin). This is generally explained by a significant solubility of these additives in the nitrile rubber, due to a good match of the polarity and a favorable molecular weight.

The DMA curves obtained for the PP/additive mixtures generally indicate a marginal to significant influence of the PRMs on  $T_g$  of PP (see *Table 2* and *Figure 2*). It is obvious that the incorporation of the hydrocarbon resin RS-3 results in a great increase of  $T_g$ , while the phenolic resins RS-4 and KT-1 (zinc salts of unsaturated fatty acids) cause a negligible effect. Addition of the indene cumarone resin RS-1 and the additive RP-1 shifts the glass transition of PP to lower temperatures, i.e. towards its own  $T_g$  or main thermodynamic softening (see *Table 1*). However, an interesting result is the clear  $T_g$  decrease, i.e. plasticizing effect determined for PP in the presence of the AF additives based on fatty acids. These PRMs exhibit overall high melting (softening) temperatures and, thus, were expected to enhance  $T_g$  of PP. Therefore, the multiphase AF types seem to act as effective plasticizers due to their significant (presumably nonpolar) low-molecular content having a low  $T_g$  and, thus, crucially influence the observed behavior.

In general, the determined effects of the PRMs on EPDM, NBR and PP are primarily attributed to the major influence of polarity (or nonpolarity) and chemical structure of the components. It is well known that materials of totally dissimilar chemical nature are largely immiscible and incompatible due to their different solubility parameter, which is a basic property of all materials. Considering the results by these terms, it

becomes obvious that, for example, the predominantly polar phenol resin (RS-4) is excessively able to form efficient interactions with the polar NBR, controlled by hydrogen bonds. In contrast, alkyl substituents would determine the PRM solubility in the nonpolar EPDM. The resin type RS-3, which consists of unsaturated hydrocarbon chains, seems to match the polarity (nonpolarity) of each investigated polymer and thus yields satisfactory solubility and compatibility effects. This is illustrated in *Figure 3* by DSC thermograms obtained for the RS-3/polymer mixtures at higher temperatures. The solubility behavior of the hydrocarbon resin RS-3 arises from favorable chemical composition and structure, promoting the formation of well-balanced (physical) intermolecular forces and (probably chemical) interactions between the PRM molecules as well as the PRM/polymer molecules.

The molecular weight, content and processing conditions are also important parameters determining the compatibility level of materials. Therefore, the limited solubility of RP-1 (polyester) in NBR can be attributed to a critical molecular weight of this PRM, resulting in quite small mixing entropy. The insolubility of KT-1 (zinc salts) in the polymers is influenced by the high content of this PRM, which usually used as lubricant in low quantities (< 3 phr). An exact elucidation of the solubility behavior of the AF-types (based on fatty acid esters) is indeed difficult, since these PRMs are mostly mixtures of components, which presumably possess individual characteristics and, thus, exhibit different effects on the polymers.

### ***Polymer Blends***

Considering the results obtained above, some PRMs (RP-1, AF-3, RS-1, RS-3; content 10 wt.%) were selected and incorporated in the blends NBR/PP and EPDM/PP (ratio 70/30) for homogenizing and compatibilizing purposes. The DMA spectra of the blends are depicted in *Figures 4 and 5*.

It can be observed that the storage modulus ( $G'$ ) of the EPDM/PP blends (*Figures 4a and 4b*) significantly decreases at low temperatures ( $T < 40^\circ\text{C}$ ) in the presence of all PRMs, except the resin RS-3, which causes an increase of stiffness compared to the blend without additive. With increasing temperature the reduction or rise of the  $G'$  values diminishes as the glass transition and rubbery plateau occur. However, the

most remarkable modulus decrease determined over the whole range of temperature measurement is assigned to RP-1 (polyester based on natural oils) and RS-1 (indene cumarone resin).

On the corresponding  $\tan\delta$  curves, an obvious increase of the damping values can be observed for both PRMs, particularly in the relaxation region of the blend components (EPDM: -50 to -20°C, PP: 0-20°C). The initial thermal transition of RP-1 is detected at -15°C and the glass temperature of EPDM (ca. -41°C) remains unaffected, while in the presence of RS-1 the own PRM transition is non-detectable and the relaxation characteristics of the polymers are slightly influenced. In contrast, the  $\tan\delta$  curves of the blends containing RS-3 (unsaturated C<sub>9</sub>-hydrocarbons) and AF-3 (pentaerithrit-tetrastearate) reveal significant effects on the glass transition behavior of the polymer components. This is proven by the pronounced peak-shift of EPDM to higher temperatures ( $T_g$  increase of 4-5°C) and a broadening (disappearance) of the relaxation shoulder of PP.

The effects of  $\tan\delta$  and  $G'$  indicate a high degree of solubility of RS-3 and AF-3 in both polymers (EPDM and PP), resulting in efficient homogenizing, dispersing and compatibilizing effects. This can not be assumed for RP-1 because no noticeable changes are detected for  $T_g$  of the corresponding components. These assumptions are largely confirmed by the results of mechanical measurements. The mechanical properties (tensile strength  $\sigma_{max}$  and elongation at break  $\epsilon_b$ ) of the investigated blends are illustrated in *Figure 6*.

In general, the incorporation of the PRM types leads to a decrease in the tensile strength and a considerable rise in percentage elongation. It is apparent that the change level depends on the chemical nature of the additive and its content. For example, the resin RS-3 marginally lowers  $\sigma_{max}$  and clearly enhances  $\epsilon_b$ , indicating an improved phase connectivity. Considering other additives, the same tendency is detected, with the indene-cumarone resin (RS-1) yielding the most remarkable influence. Therefore, it is assumed that the use of smaller quantities of these additives would result in a well-balanced mechanical behavior.

Dynamic mechanical spectra of the NBR/PP blends reveal interesting effects of the



PRMs (*Figures 5a and 5b*). In comparison to the blend without additive, a PRM addition reduces the  $G'$  values at low temperatures. In the temperature range of the rubbery plateau this modulus decrease clearly diminishes. However, the additives RP-1 and AF-3 exhibit a much more significant influence on the modulus than other PRMs. On the corresponding  $\tan\delta$  curves a remarkable decrease is observed above the glass temperature of NBR through the incorporation of AF-3. In presence of the other additives an apparent increase of the  $\tan\delta$  values is observed within and above the relaxation region of the rubber phase. For the blend containing the polyester RP-1 only a marginal change in the relaxation position of NBR is noticeable, while the stearate AF-3 lowers  $T_g$  slightly. This indicates a partial plasticizing or lubricating effect of the PRM. The unsaturated resin RS-3 yields, as in EPDM/PP blend, a less pronounced influence on the relaxation intensity, but it considerably shifts the glass transition of NBR to higher temperatures (from  $T_g = -11^\circ\text{C}$  to  $-6^\circ\text{C}$ ). A similar effect of a relaxation peak shift is also obtained by adding the indene cumarone resin RS-1.

It should be noted that in all NBR/PP blends the glass transition of PP can not be separately detected since the  $T_g$ -regions of both polymers lie in a close temperature interval, and due to the low content of the thermoplastic (30 wt.%). However, consideration of the characteristics of the overall relaxation observed in the range of  $-30^\circ\text{C}$  to  $30^\circ\text{C}$  allows a reliable assessment of compatibilization effects.

For the blend containing the additive RP-1, an improved homogenization of the multiphase morphology can be assumed due to the well-formed relaxation peak including the thermal transitions of all three components. In contrast, the viscoelastic behavior resulting from the addition of AF-3 indicates, with regard to DSC and stress-strain results, an excessively limited compatibility between the polymer components. Addition of the PRMs based on fatty acids (AF-types) to an NBR/PP blend simultaneously causes an evident reduction of its tensile strength and elongation at break. This is primarily due to lower load transfer between the phases.

As mentioned above, both resins RS-1 and RS-3 yield a significant influence on the dynamic mechanical behavior of an NBR/PP blend, corresponding to the well-developed relaxation peaks and emerged transitions of NBR and PP. These changes indicate an improvement of the dispersion, homogenization and compatibility in the

blends. Results of the stress-strain tests support this assumption and indicate that the contents of the resins (in particular RS-1) have to be reduced in order to obtain an improvement in both properties, i.e. tensile strength and break elongation.

## Conclusions and Outlook

The glass transition of NBR, EPDM and PP is clearly affected by the incorporation of some processing promoters (PRMs). This is due to the good solubility and partition of these additives arising from their favorable chemical nature and additional factors. The changes observed in  $T_g$  are highly dependent on characteristic features like chemical composition and polarity of the components.

Some PRMs exhibit a significant influence on the dynamic mechanical properties of binary rubber/polypropylene blends. An interesting effect is the inward shifting of the glass temperatures of the polymer components.

All thermal, viscoelastic and mechanical effects observed for the polymer/PRM mixtures and rubber/PP/PRM blends indicate that several additives act as efficient agents contributing to the improvement of dispersion, homogenization and compatibility in the blends.

Further studies have to be carried out on blends containing PRMs to yield satisfactory effects of compatibility. The influence of the blend composition, additive content and processing conditions on the morphology and ultimate properties of the materials is a worthy target of investigations. However, the final purpose of these efforts is to attain thermoplastic elastomers comprising useful properties.

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## Figures

**Figure 1** DSC curves of polymers in the presence of processing promoters (PRMs).

**Figure 2** Influence of PRM incorporation on the glass transition of neat PP.

**Figure 3** Solubility of hydrocarbon resin (RS-3) in polymers investigated.

**Figure 4a-b** Temperature dependence of storage modulus  $G'$  and loss factor  $\tan\delta$  (DMA spectra) of EPDM/PP blends containing different additives.

**Figure 5a-b** Effects of PRM incorporation on the DMA spectra of NBR / PP blend .

**Figure 6** Influence of different PRMs on tensile strength ( $\sigma_{max}$ ) and elongation at break ( $\epsilon_b$ ) of polymer blends investigated.