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Influence of interfacial reaction on morphology in modified PP/PS blends

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SUMMARY: In-situ compatibilization of blends has been studied for the system oxazoline grafted polypropylene/carboxylic acid terminated polystyrene. The reactive blends exhibit much finer morphologies than the corresponding non-reactive systems. Morphology is shown to depend on the degree of functionalization, viscosity ratio, blend composition, and mixing conditions.

Motivation

Melt blending of reactive polymers is expected to create block or graft copolymers which may act as in-situ compatibilizers at the interface between the immiscible components. This can lead to an improvement in the mechanical and other properties of multiphase blends. For polyolefins grafting with reactive monomers is commonly used to introduce active sites for reactive blending.

We have investigated the reaction between polypropylene, grafted with ricinol oxazoline maleinate (PP-g-Ox) by reactive extrusion, and carboxylic acid terminated PS, synthesized by the TEMPO method.

The morphology of the reactive blend depends not only on the reactivity of the blend system, but also on physical properties such as the viscosities and the interfacial energies of the blend components1,2). To separate these physical factors from the effect of graft copolymer formation we have compared morphologies of non-reactive and reactive blends with comparable viscosity ratios and similar interfacial tensions.

Materials and methods

Functionalized and non-reactive PS were synthesized by the TEMPO method3,4). The initiator used for the preparation of the carboxylic acid terminated PS was the commercially available 4,4'-azo-bis-(4-cyanopentanoic acid) (ABCP). The non-reactive PS was prepared using 2,2'-azo-bis-isobutyric acid nitrile (AIBN). To stabilize the product the TEMPO group was removed by oxidation with m-chloroperbenzoic acid5). The grafting of PP (Novolen® 1127 MX, BASF, Germany) with ricinol oxazoline maleinate (Henkel, Germany) was perfomed by means of a twin screw extruder (ZSK 30, Krupp Werner & Pfleiderer, Germany). The oxazoline content of the PP-g-Ox was 1.3 wt%.

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Melt rheology was investigated using a ARES rheometer (Rheometrics, USA) in nitrogen atmosphere. Frequency sweeps were performed in the linear viscoelastic range at 200°C using a parallel plate geometry. Surface and interfacial tensions of polymer melts were measured using the pendant drop method$^{6)}$ by use of a self made apparatus. SEC measurements on PS samples were performed at ambient temperature using modular chromatographic equipment with a refractive index detector. The molecular weigths of PP samples were determined using a PL-GPC 210 (Polymer Laboratories, UK) at 135°C with 1,2,4-trichlorbenzene (TCB).
Molecular weigths (PS or PP standards, respectively) and shear viscosities at 200°C are given in Table 1 together with the diameter of the PS particles, d_T, in the blends predicted by the Taylor equation ($d_T = \dfrac{4 \cdot \sigma_{12} \cdot (\lambda + 1)}{\dot{\gamma} \cdot \eta_m \cdot \left[\left(\dfrac{19}{4} \cdot \lambda\right) + 4\right]}$ with σ_{12} = 4.5 mN/m and γ = 6 s^{-1}).

Table 1. Molecular weights of the blend components, melt viscosity and viscosity ratio at 200°C and calculated PS particle size

Material	M_n g/mol	M_w g/mol	η at 800 Pa Pa s	$\lambda = \eta_{PS} / \eta_{PP\text{-}g\text{-}Ox}$ at 800 Pa	d_T µm
PP-g-Ox	36700	142500	133.5		
PS	24100	35500	16.1	0.12	6.3
PS-COOH 1	28300	38500	14.2	0.11	6.2
PS-COOH 2	47800	70100	137.7	1.03	11.4

The blends were prepared in a Miniature Mixing Reactor EK-3-5C (NCS, Japan). A material mass of 3 g, a temperature of 200 °C, a rotation speed of 60 rpm, and a mixing time of 30 min were used to produce PP-g-Ox based blends with different compositions. In a second series mixing time and mixing temperature were varied.
The particle size of the PS was investigated by SEM of cut surfaces after chemically etching the PS with xylene for 3 h. A SEM LEO 435 VP (Leo Elektronenmikroskopie, Germany) with an acceleration voltage of 10 kV was used.

Results

Physical factors influencing the blend morphology

The viscosity ratios of the blend components were determined from the viscosity functions (Fig. 1) at a constant shear stress of 800 Pa. This corresponds to the shear stress of the matrix component transferred to the dispersed particles at a shear rate of $\gamma = 6\ s^{-1}$, which was calculated to be the shear rate during mixing in the Miniature Mixing Reactor. The viscosity of PS and PS-COOH 1 at 800 Pa and 200°C is approximately the same, so that the viscosity ratios in both blends are comparable (about 0.1). Blends with PS-COOH 2 exhibit a viscosity ratio of about 1. Under these conditions the mixing efficiency of the Miniature Mixing Reactor is very good in spite of the low shear rate.

Direct measurements of interfacial tensions between PP-g-Ox and PS-COOH were not successful. At 200°C the surface tension of PP-g-Ox and PS-COOH are 19.7 mN/m or 28.0 mN/m, respectively, which are identical with that of the non-modified polymers. However, measurements of interfacial tensions of PS and both PS-COOH against another polar modified PP, which cannot react with the PS-COOH, did not show significant differences (Fig. 2).

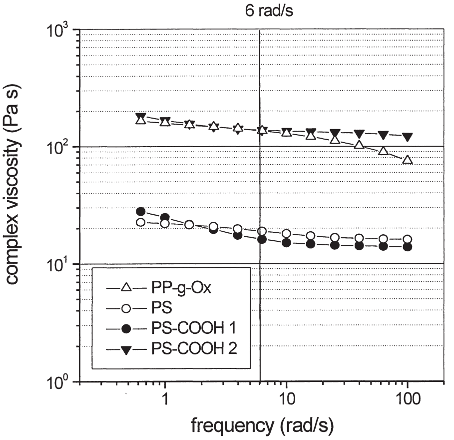


Figure 1: Melt viscosity functions of the blend materials at 200°C

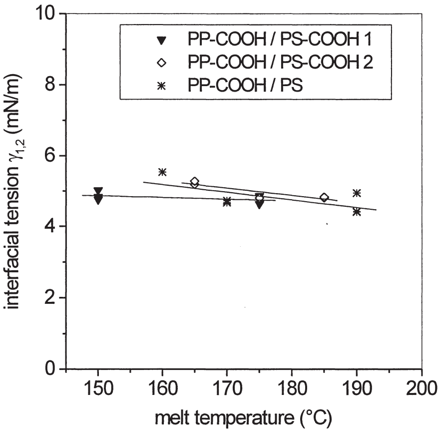
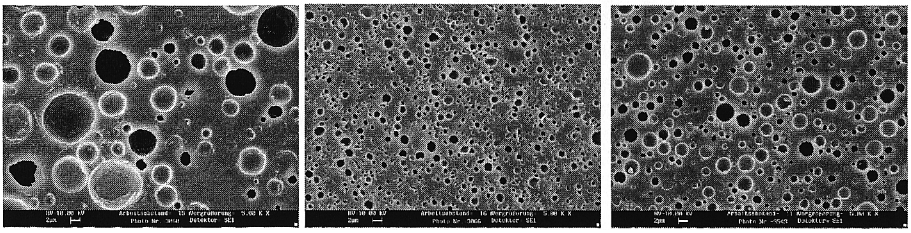


Figure 2: Interfacial tension of non-reactive PP/PS-systems as a function of temperature

This means that the effect of the reduction of interfacial tension by modification without reaction can be excluded for this system. Therefore, morphology differences between the reactive and non-reactive blends can be caused only by the interfacial reaction.

Comparison of reactive and non-reactive blends with different compositions

The particle size is smaller in all in-situ compatibilized blends. It was observed that with rising content of PS in non-reactive blends a significant increase in the particle size and particle size distribution caused by coalescence occurs, which is less pronounced in the reactive blends. Figure 3 shows micrographs of blends with 30 wt% PS.



PP-g-Ox / PS
$\lambda = 0.12$, COOH : Ox = 0

PP-g-Ox / PS-COOH 1
$\lambda = 0.11$, COOH : Ox = 0.51

PP-g-Ox / PS-COOH 2
$\lambda = 1.03$, COOH : Ox = 0.30

Figure 3: SEM on etched surfaces of PP-g-Ox / PS = 70/30 blends (frame size 64x48 µm)

The differences in the morphology between the non-reactive and the reactive blends show that the relation between both basic processses of morphology development, drop breakup and coalescence, is changed. If an interfacial reaction occurs the coalescence process is inhibited due to the immobilization of the interface. The reduction of interfacial tension caused by the copolymer formation at the interface also changes the breakup process. Furthermore, changes in viscosities and viscosity ratios occur during interfacial reaction.

The influence of a changed viscosity ratio is clearly visible when comparing blends prepared with PS-COOH 2 (Fig. 3). The measured mean number average particle diameter d_n for this reactive blend with a viscosity ratio of about 1 is 1.71 μm. It is much higher than in the reactive blend with the lower viscosity ratio (d_n = 0.82 μm) but still much finer than in the non-reactive blend with the low viscosity ratio (d_n = 3.59 μm). It is to consider that also the functionality is changed, PS-COOH 2 contains much less reactive sites than PS-COOH 1.

The formation of graft copolymers was proven by selective extraction coupled with SEC, FTIR, and ^{1}H NMR. In addition, DSC, DMA and melt rheology were used to investigate the differences between reactive and non-reactive blends. While DSC and DMA did not show significant differences, the melt rheological properties are significantly changed. Although the viscosities of reactive and non-reactive PS are very similar, the reactive blend with 30 wt% PS-COOH 1 exhibits higher viscosity (Fig. 4). The zero shear viscosity is almost doubled. This indicates an increase in the amount of interface in the reactive blend which is a result of finer dispersion as well as higher interactions at the interface between matrix and particles.

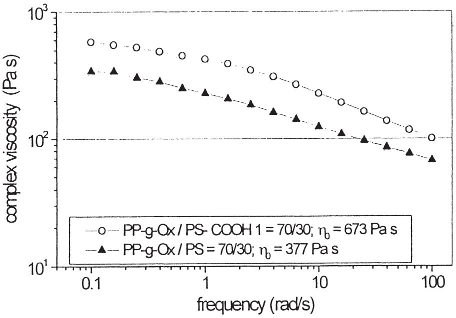


Figure 4: Melt viscosity functions at 200°C for reactive and non-reactive PP-g-Ox / PS blends

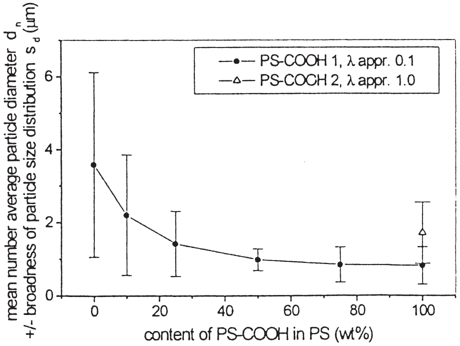
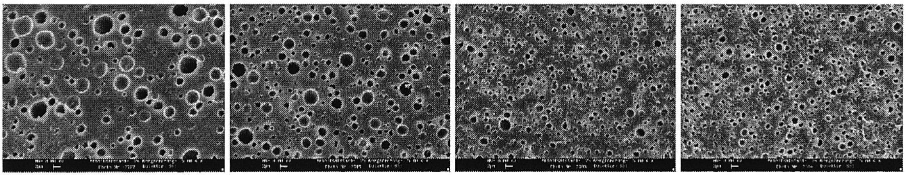


Figure 5: Particle diameter d_n of PP-g-Ox / PS = 70 / 30 blends by changing the ratio of PS/PS-COOH

In order to study the influence of the degree of functionalization on the morphology a series of PP-g-Ox / PS = 70/30 blends were prepared. PS-COOH 1 was mixed in different compositions with the non-reactive PS. In this way the ratio between carboxylic acid groups and oxazoline groups was varied between 0.05 and 0.51 whilst maintaining a constant viscosity ratio. Micrographs are shown in Figure 6, the quantitative evaluation is given in Figure 5. The results show that the addition of more than 50 wt% of modified PS led to no further improvement in the dispersity. This means that complete functionalization of the PS is not necessary for the in-situ compatibilization.



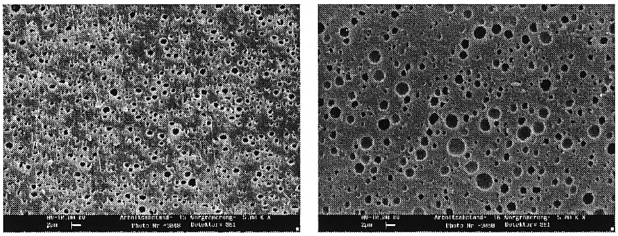
PS/PS-COOH 1 90/10 75/25 50/50 25/75

COOH: Ox 0.05 0.13 0.25 0.38

Figure 6: SEM of etched surfaces of PP-g-Ox/PS = 70/30 blends with varying PS/PS-COOH 1 ratio (frame size 64x48 μm)

The influence of mixing conditions on morphology

In non-reactive blends with 30 wt% PS the morphology after 10 and 20 min is very similar and coarsens slightly during further mixing. In reactive blends with 30 wt% PS-COOH the final morphology is reached after about 10 min despite the low shear rates. Since there are morphology differences between blends with similar ratio between carboxylic acid to oxazoline groups but different viscosity ratios it can be concluded that for this blend system the morphology development occurs either prior or parallel to the morphology stabilization by the interfacial reaction.



T = 180°C T= 220°C

Figure 7: SEM of etched surfaces of PP-g-Ox/PS-COOH 1 = 70/30 blends by variation of the mixing temperature (frame size 64x48 μm)

In contrast to the expected higher reaction rate with rising temperature the variation of the melt mixing temperature (180°C to 220°C) showed the smallest particles at the lowest mixing temperature (Fig. 7). This can be explained by the temperature dependence of the matrix viscosity (180°C η_m= 165 Pas, 220°C η_m = 66.7 Pas) and the viscosity ratios (180°C λ= 0.48 and 220°C λ= 0.08) caused by different viscosity - temperature dependencies of PS-COOH 1 and PP-g-Ox (Fig. 8). In Figure 9 the Taylor diameters calculated for an increase in temperature are compared with the measured values. This result shows that in reactive blends physical factors such as viscosities are also very important for the morphology development. It can be concluded that in the first step the morphology development is dominant and that after reaching a constant particle diameter the reaction stabilizes the interface against coalescence.

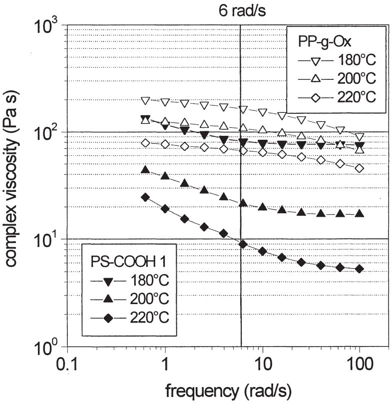


Figure 8: Melt viscosities of PP-g- Ox and PS-COOH 1 at different melt temperatures

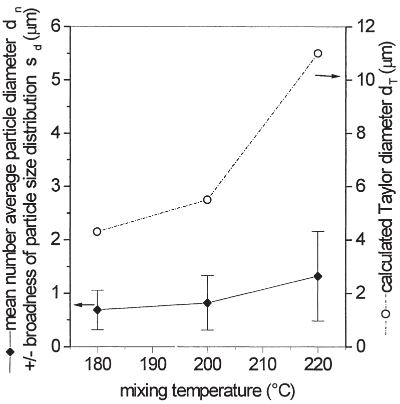


Figure 9: Measured particle diameter d_n of PP-g-Ox/PS-COOH 1 = 70/30 blends and calculated Taylor diameter d_T at varied mixing temperatures

Summary and Conclusion

We studied the in-situ compatibilization of multiphase polymer blends during melt mixing using the system oxazoline grafted polypropylene / carboxylic acid terminated polystyrene.

The in-situ formation of graft copolymers at the interface between the blend components results in a finer dispersion and a lower dependence of the particle size on the composition. This can be explained by the reduction in interfacial tension between the components and by the steric stabilization of the interface which leads to a hindrance of the coalescence as well as to easier drop breakup.

It was found that in-situ compatibilization does not require complete functionalization. Even the addition of small amounts of polymers able to react to form interfacially active graft copolymers shows a significant effect on the morphology.

For the morphology development in this reactive blend system physical factors, especially the viscosity and the viscosity ratio, also play an important role and cannot be neglected.

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