Macromol. Symp. **2004**, *214*, 279-288

Influence of Reactive Compatibilization on the Morphology of Polypropylene/Polystyrene Blends

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Summary: To study the efficiency of different mechanisms for reactive compatibilization of polypropylene/polystyrene blends (PP/PS blends), main chain or terminal-functionalized PP and terminal-functionalized PS have been synthesized by different methods. While the *in-situ* block and graft copolymer formation results in finer phase morphologies compared to the corresponding non-reactive blends, the morphology development in the ternary blend system PP/PS + HBP (hyperbranched polymer) is a very complex process. HBP with carboxylic acid end groups reacts preferably with the reactive sites of the oxazoline functionalized PS (PS-Ox) and locates mainly within the dispersed PS-Ox phase. A bimodal size distribution of the PS-Ox particles within the oxazoline modified PP (PP-Ox) matrix phase is observed with big PS-Ox particles (containing the HBP as dispersed phase) and small PS-Ox particles similar in size to the unimodal distributed particles in the non-reactive PP-Ox/PS-Ox blends. Factors influencing the morphology are discussed.

Keywords: blends; morphology

Introduction

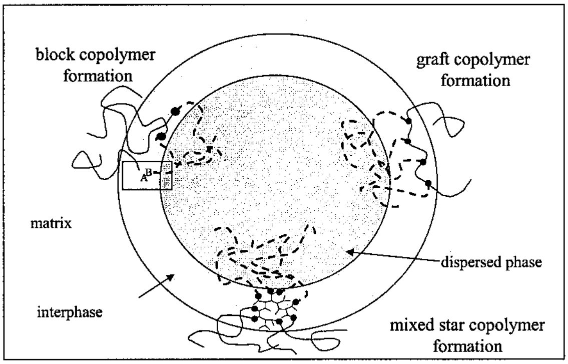
The compatibilization of immiscible blends can be done by the addition of emulsifiers (so called compatibilizers) as third component or by the use of reactive polymers, which can create block or graft copolymers at the interface during the melt mixing process. The *in-situ* formed compatibilizers reduce the interfacial tension, enhance the interfacial adhesion, stabilize the interphase during melt processing, and reduce in this way the tendency of coalescence, resulting in finer dispersions compared to non-reactive blends. This can lead to an improvement in the mechanical and other properties of multiphase blends. While the mechanisms of block- and graft copolymer formation have been widely studied over the past several years, a third mechanism, the *in-situ* formation of mixed star copolymers at the interphase of two immiscible polymers, due to the addition of highly functional hyperbranched polyesters (HBP), is a rather new approach to compatibilization. Jannerfeldt et al. [1-3] investigated the grafting of aliphatic HBP onto a polypropylene (PP) chain. In

DOI: 10.1002/masy.200451020

this way the number of reactive sites per molecule is increased. The effect of this grafted PP in blends with polyamide 6 on interfacial properties and blend morphology was reported.

However, the morphology of the reactive blends 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 components, as has been shown by Pötschke et al. [4,5]

To compare the different reactive compatibilization mechanisms (Scheme 1) and to separate the physical factors from the effect of copolymer formation we have compared morphologies of non-reactive and reactive blends (which are able to form graft, block, or star-like copolymers during melt mixing), considering the viscosity ratios and changes in interfacial tensions due to the chemical modification. For these studies we have chosen the blend system polypropylene/polystyrene (PP/PS), which may be considered as a model for PS/elastomer blends. Advantageous for PP and PS is that there exist different chemical pathways by which to obtain main chain or endgroup functionalised polymers. As model reaction for the compatibilizer formation the conversion of 1,3-oxazolines with carboxylic acid, which is known as fast and selective, has been used.



Scheme 1. Formation of block, graft, or star copolymers at the interface between immiscible polymers during melt mixing; A, B: different functionalities; black spots: coupling sites [9]

Materials – Synthetic Strategies

The necessary end group and main chain functionalized reactive PP and PS were synthesised by different synthetic pathways. Their characterisation is given in the corresponding citations, if not mentioned here.

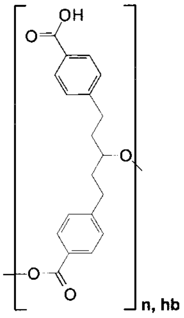
The PS were synthesized by the TEMPO method. The initiator used for the preparation of the carboxylic acid terminated PS (**PS-COOH**) was the commercially available 4,4'-azo-bis-(4-cyanopentanoic acid) (ABCPA) [6-8]. The non-reactive PS was prepared using 2,2'-azo-bis-isobutyric acid nitrile (AIBN). To stabilize the product the TEMPO group was removed by oxidation with m-chloroperbenzoic acid [7]. Oxazoline-terminated PS (**PS-Ox**) was obtained analogously but the ABCPA initiator was converted into an bisoxazoline by conversion the ABCPA-chloride with (4-hydroxyphenyl)-1,3-oxazoline [7,9]. The degree of the PS functionalization was about 75 %. An alternative route to obtain PS-Ox is the atom transfer radical polymerization (ATRP) [7,10,11] which results in high functionalities, but the remaining bromide end group may result in unfavourable side reactions.

PP grafted with oxazoline (**PP-g-Ox**) was prepared by grafting of PP (Novolen 1127 MX, BASF, Germany) with ricinol oxazoline maleinate (Henkel, Germany). The oxazoline content of the PP-g-Ox was 1.3 wt% [8]. Alternatively, main chain oxazoline-functionalised PP was obtained by copolymerisation of propene with different unsaturated 1,3-oxazolines [12,13]. The detailed structure and analysis of the **PP-co-Ox** used in the blends is given in [13].

Carboxylic terminated PP (**PP-COOH**) with different molecular weights and therefore viscosities could be obtained by hydrosilylation of peroxidic degraded PP with 4-pentenoic acid [7]. The pentenoic acid had to be used in the trimethylsilyl ester form to suppress the poisoning effect of the free acid on the platinum catalyst. The peroxidic degraded PP (and therefore also the hydrosilylation product PP-SOOH) is a mixture of monofunctional, bifunctional and nonfunctional polymer chains. The hydrosilylation with oxazoline monomers is not possible due to side reactions of the hydrosilylation agent with the oxazoline ring.

To achieve better control over the functionality, metallocene catalysed PP, which obtains exactly one unsaturated endgroup per polymer chain, may be used. Such PP with an molecular weight of Mn = 21000 g/mol with a polydispersity (PD) of 2.05, was used to prepare oxazoline-terminated PP (**PP-Ox**) by a hydroboration reaction. After the hydroboration with 9-borabicyclo[3.3.1]nonane, maleic acid anhydride can be coupled to the PP in the presence of oxygen. The resulting maleic terminated PP offers the opportunity for a large variety of further modification reactions [14]. We prepared PP-Ox by its conversion with 2-(4-aminophenyl)-1,3-oxazoline under the same conditions as described by [14]. During the reactions no changes in the molecular weight could be observed. However, the conversion was incomplete. We calculated a functionality of 35 %, that means about every 3rd PP chain contained one 1,3-oxazoline endgroup.

Polyfunctional hyperbranched polyester (HBP-COOH, Scheme 2) with Mn = 26000 g/mol was obtained by polycondensation of the AB_2 type monomer 1,5-bis-(4′-carboxyphenyl)pentan-3-ol. Details are given in [9].



Scheme 2. Chemical Structure of HBP-COOH

Methods

All blends were prepared by melt mixing at 200 °C. Most of the blends forming graft- or block-copolymers. A Miniatur Mixing Reactor EK-3-5C (NCS, Japan) was used (rotating piston in a fixed cylinder with 4 shear edges in the bottom; 3 g; shear rate about 6-10 s^{-1}; 30 min. – if not mentioned otherwise). The blends in the composition PP/PS = 2/1 (by weight) plus 5 wt-% HBP and the blends based on PP-co-Ox were prepared by melt mixing using a Micro Compounder (DACA Instruments; two conical co-rotating screws with a bypass allowing the material to circulate for defined periods; capacity of 4.5 cm^3) at 200 °C with 100 rpm for 5 min, if not otherwise mentioned. The shear rate was much higher than in the other mixing equipment (similar to shear rates in conventional twin screw extruders) but could not be quantified.

The particle size of the PS was investigated by SEM of cut surfaces after chemically etching the PS with xylene or THF for 3 h. A SEM LEO 435 VP (Leo Elektronenmikroskopie, Germany), with an acceleration voltage of 10 kV, was used. Selective etching of the HBP phase was performed with NaOH/water at room temperature for 4 h.

Melt rheology was investigated using a ARES rheometer (Rheometrics, USA) in a 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, using a self made apparatus. SEC measurements of PS samples were performed at ambient temperature using modular chromatographic equipment with a refractive index detector. The molecular weights of PP samples were determined using a PL-GPC 210 (Polymer Laboratories, UK) at 135°C with 1,2,4-trichlorbenzene (TCB).

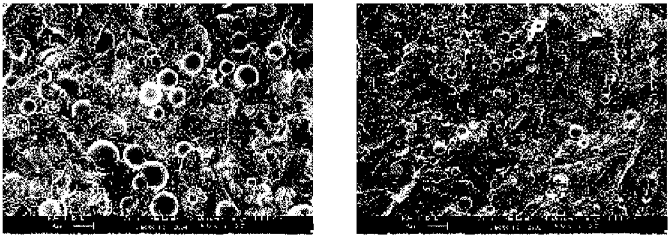
Results and Discussion

The morphology development when melt mixing immiscible polymers is a combined process of drop deformation and break up on the one hand and coalescence on the other hand. From the Taylor-Equation given below, the minimum particle diameter d_T which can be reached by mixing of two immiscible fluids in dependent on the shear rate $\dot{\gamma}$, matrix viscosity η_m, viscosity ratio between dispersed and matrix phase λ, and interfacial tension σ_{12} can be calculated. Even if this relation is valid only for Newtonian fluids, this relation can be used for the estimation of the smallest achievable diameter in polymer mixtures. But the same factors influencing the drop deformation and break up also influence the coalescence, which coarsens the morphology. However, there exists no good theoretical model for the description of all the correlations during the process of coalescence. In addition, with increasing dispersed phase content the coalescence probability increases strongly. Therefore only morphologies with similar compositions can be compared with each other.

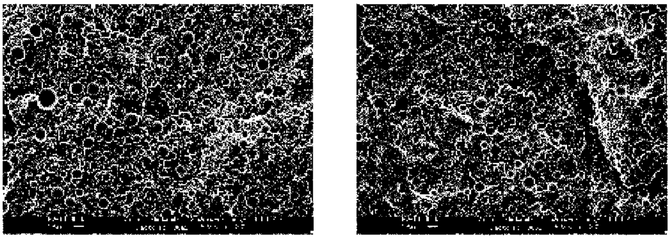
$$d_T = \frac{4 \cdot \sigma_{12} \cdot (\lambda + 1)}{\dot{\gamma} \cdot \eta_m \cdot \left[\left(\frac{19}{4} \cdot \lambda\right) + 4\right]} \quad \text{Taylor-Equation}$$

In [8] we showed that the interfacial and surface tensions of polymers are not, or only slightly, affected by reactive modification. Therefore, when comparing reactive with non-reactive blend systems, changes in the morphology can be caused only due to the chemical reactions. When no reactions occur then the interfacial tension will be constant. Otherwise we noticed a strong effect of the reactive sites on the viscosity of the polymers, even if the molecular weight is not changed during the process of chemical modification [9]. Therefore, the viscosity ratio has to be determined for each polymer combination.

The particle size is smaller in all in-situ compatibilized blends. It was observed that with increasing PS content 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. Fig. 1 gives an example of the influence of reactivity on the final morphology when forming block-copolymers in-situ [7]. At unfavourable viscosity ratios, λ greater than 1, the effect of the reactivity is clearly visible, while at favourable viscosity ratios, λ near 1, the reactive system has only a slightly improved phase morphology compared to the non-reactive system. The favourable viscosity ratio results in even finer PS distribution than in the reactive system with more different viscosities. In this case the physical factors dominate the blend morphology.



PP1-COOH/PS, λ=1.6 PP1-COOH/PS-Ox, λ=2.2

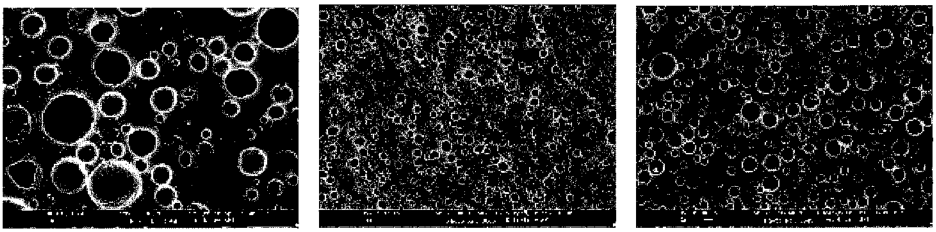


PP2-COOH/PS, λ=0.6 PP1-COOH/PS-Ox, λ=0.9

Figure 1. Influence of the block-copolymer formation and viscosity on the morphology of PP/PS = 70/30 blends, SEM of cryofractures (frame size 310x220 μm) [7]

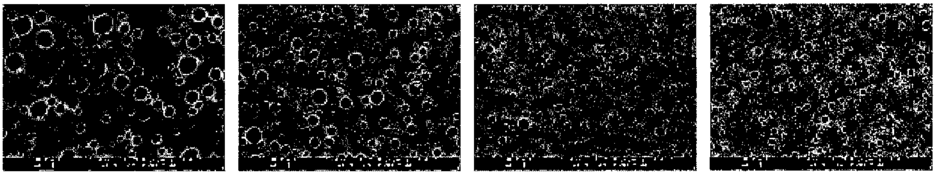
The in-situ graft-copolymer formation seems to have a stronger influence on the morphology, probably due to the higher content of reactive sites in graft copolymers compared to endgroup modified polymers. The influence of a changed viscosity ratio is clearly visible when comparing blends prepared with PS-COOH 2 (Fig. 2) [8]. The mean number average particle diameter d_n for this reactive blend with a viscosity ratio of about 1 is much higher than in the reactive blend with the lower viscosity ratio but still much finer than in the non-reactive blend with the low viscosity ratio. It must be noted that the functionality is also changed; PS-COOH 2 contains much fewer reactive sites than PS-COOH 1 does.

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-COOH1 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 3. 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. This is an important fact since polymers in which every chain contains reactive sites are accessible only by a limited number of methods.



PP-g-Ox / PS	PP-g-Ox / PS-COOH 1	PP-g-Ox / PS-COOH 2
λ = 0.12, COOH : Ox = 0	λ= 0.11, COOH : Ox = 0.51	λ= 1.03, COOH : Ox = 0.30

Figure 2. Influence of the graft-copolymer formation and viscosity on the morphology of PP/PS = 70/30 blends, SEM of cryofractures (frame size 64x48 μm)

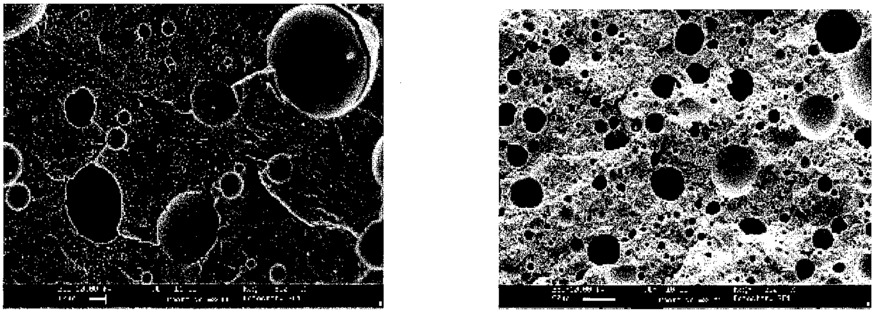


PS/PS-COOH 1	90/10	75/25	50/50	25/75
COOH: Ox	0.05	0.13	0.25	0.38

Figure 3. SEM of etched surfaces of PP-g-Ox/PS = 70/30 blends with varying PS/PS-COOH 1 ratio (frame size 64x48 μm)

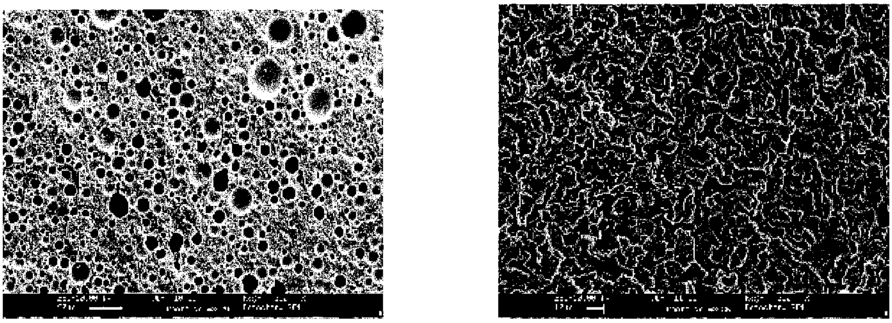
Contrary to this finding we found in another system based on PP-co-Ox/PS-COOH a continuous change in the morphology with an increasing amount of reactive polymers. When the nonreactive PP was completely replaced by the reactive copolymer even phase inversion was observed (Fig. 4). [13]

More complex is the situation when trying to use HBP-COOH as compatibilizing agent in blends based on PS-Ox and PP-Ox [9]. When melt mixing PP with PS and PP-Ox with PS-Ox (in both blends the components cannot react with each other) the PP-Ox/PS-Ox blend has a much finer morphology that the PP/PS blend. The reason is the changed viscosity ratio, even if the molecular weights of the reactive polymers are nearly equal to those of the non-reactive polymers. The addition of HBP-COOH which should form compatibilizing mixed stars at the interphase, due to the reaction with both oxazoline-modified polymers, did not result in a finer morphology. In contrast, very big holes were observed after etching with THF which is a solvent for the PS and HBP (Fig.5).



PP/PP-*co*-Ox/PS-COOH (66.7/0.0/33.3)
Ox/COOH = 0

PP/PP-*co*-Ox/PS-COOH (60/6.7/33.3)
Ox/COOH = 0.5



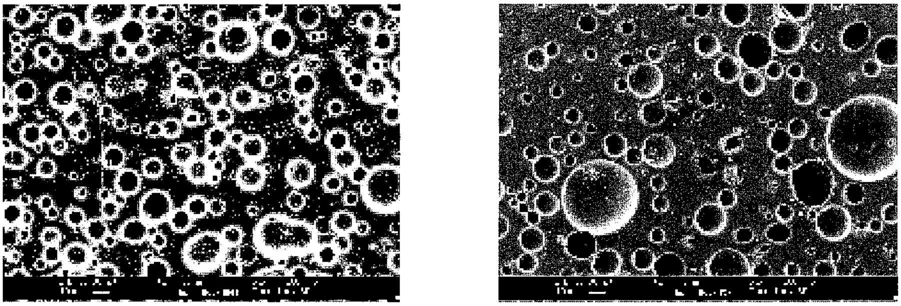
PP/PP-*co*-Ox/PS-COOH (41.7/25/33.3)
Ox/COOH = 1.8

PP/PP-*co*-Ox/PS-COOH (0.0/66.7/33.3)
Ox/COOH = 4.8

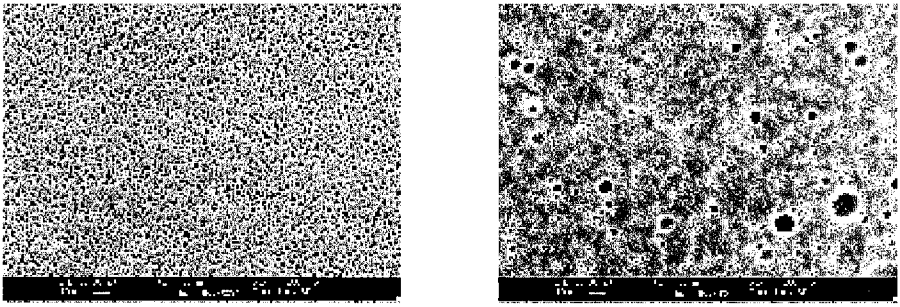
Figure 4. SEM of etched surfaces of PP/PP-co-Ox/PS-COOH blends with varying PP/PP-co-Ox ratios (frame size 233x187 μm)

The reason for this a typical behaviour is the much better compatibility of the HBP to PS and PS-Ox than that to PP or PP-Ox. HBP is immiscible with both polymers but, due to the aromatic character, the HBP forms much smaller particles in PS than in PP. In reactive PP-Ox the HBP-COOH distribution is somehow improved but still much more worse than in PS or PS-Ox. Therefore, when mixing all components together the HBP locates favourably within the PS phase, as well in reactive as in non-reactive blends. This results in an increase in the PS-Ox viscosity, which finally causes the formation of big PS-particles filled with rather finely distributed HBP. The size of the filled PS particles increases with time. Beside this PS phase another part of PS which contains no HBP inclusions has about the same size as it does in the blend free of HBP. Etching the three-component blend with NaOH/water dissolves only the HBP phase and reveals the phase in phase morphology (Fig.6).

PP/PS (λ= 6.8)

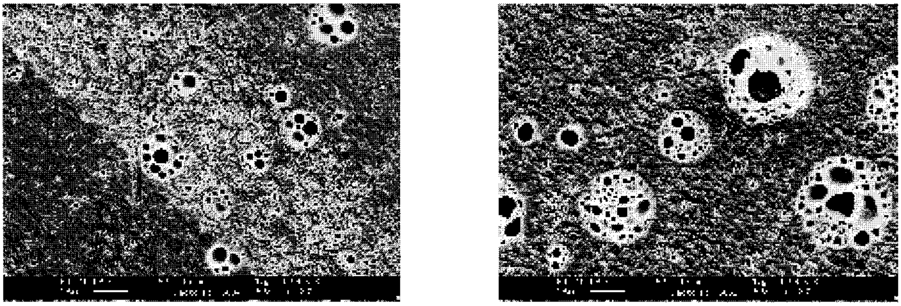


PP-Ox/PS-Ox (λ= 3.0)



no HBP 5 wt% HBP-COOH

Figure 5. SEM of etched surfaces of PP/ /PS blends (2/1) with and without addition of 5 wt% HBP-COOH etched with THF (frame size 240x180 μm)



5 min. mixed 30 min. mixed

Figure 6. Time dependence of the three-phase morphology of PP-Ox/ /PS-Ox (2/1) + 5 wt% HBP-COOH etched with NaOH/water (frame size 116x86 μm)

The phase in phase morphology has similarities to the structure of high impact PS (HIPS). Unfortunately, the rather low molecular weights of our polymers result in very brittle blends and mechanical properties have not been determined.

Acknowledgement

The authors are grateful for the support of this work by the Deutsche Forschungsgemeinschaft (Collaborative Research Centre 287) and the Max-Buchner-Forschungsstiftung.

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