# Morphology of Reactive PP/PS Blends with Hyperbranched Polymers

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**Summary:** To study the efficiency of different mechanism for reactive compatibilization of polypropylene/polystyrene (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 endgroups 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 like the unimodal distributed particles in the non-reactive PP-Ox/PS-Ox blends. Factors influencing the morphology are discussed.

**Keywords:** blends, hyperbranched polymers, morphology, reactive compatibilization

## 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, graft, or star-like copolymers at the interface during the melt mixing process. While the first two mechanisms are under investigation for past several years, 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 for compatibilization. Jannerfeldt et al. [1-3] investigated the grafting of aliphatic HBP onto a polypropylene (PP) chain. In 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.

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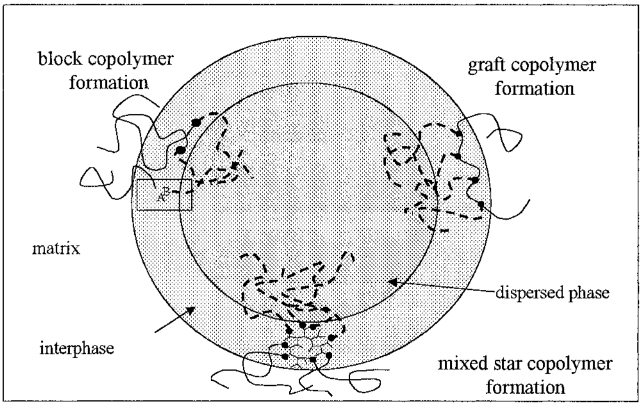
One of the goals of our work is the comparison of the different reactive compatibilization mechanisms, which are shown in Scheme 1. For this it is necessary to prepare proper reactive blend components. We used for this study the immiscible blend system PP/polystyrene (PS) since there are a variety of methods to synthesize or modify both components with different functionalities and PP and PS are stable during processing. As reactive compatibilization reaction the conversion of 2-substituted 1,3-oxazolines with carboxylic acids to mixed ester amides was chosen.

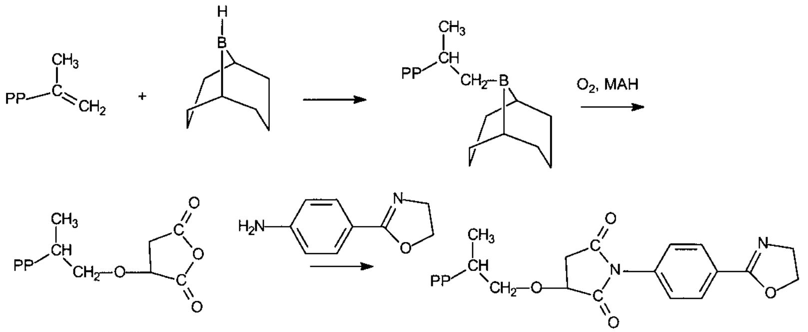


Scheme 1. Formation of block, graft, or star copolymers at the interface between immiscible polymers during melt mixing; A, B: different functionalities; black spots: coupling sites.

In previous studies the efficiency of the in-situ graft and block copolymer formation resulting in finer phase morphologies of reactive blends compared to the corresponding non-reactive blends was shown.[7,8] In this work we study the compatibilizing effect of the addition of polyfunctional carboxylic terminated HBP (which can react with 1,3-oxazoline terminated PP (PP-Ox) as matrix component as well as with 1,3-oxazoline terminated PS (PS-Ox) as dispersed phase component of the PP-Ox/PS-Ox blend) and compare the result with the in-situ compatibilization by the formation of PP-PS block- and graft-copolymers. The reason for the different behaviour will be discussed.

## Experimental

**Materials:** Non-reactive isotactic PP was obtained by metallocene polymerization.[4] The molecular weight determined by GPC with PP standard was $M_n$ = 21000 g/mol with a polydispersity (PD) of 2.05. The PP contains exactly one unsaturated endgroup per molecule, which can be converted into PP-Ox according Scheme 2.



Scheme 2. Synthesis of 1,3-oxazoline terminated PP (PP-Ox).

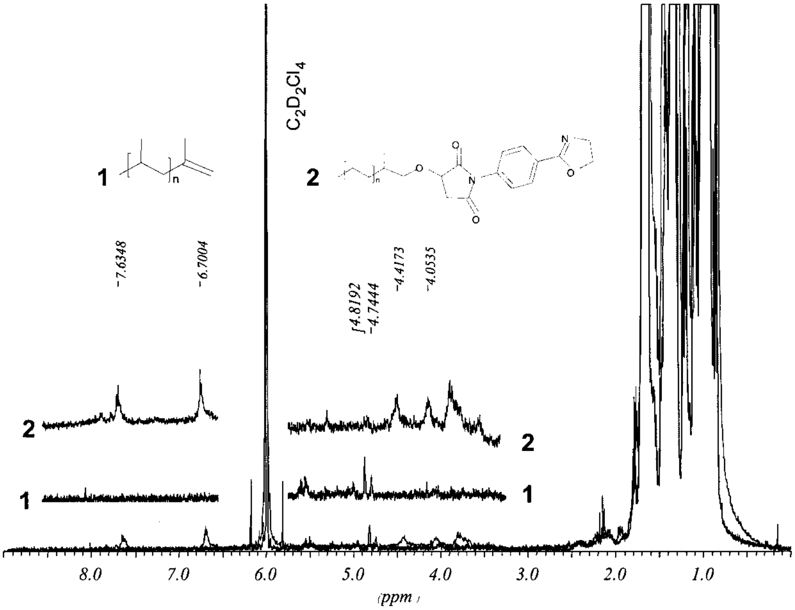


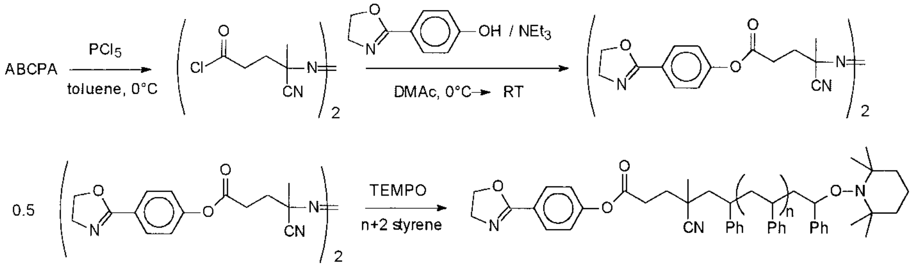
Fig. 1. $^1$H-NMR spectra of the PP (1) and the oxazoline terminated PP-Ox (2) in $C_2D_2Cl_4$, 120 °C. The signals at 4.05 ppm and 4.42 ppm indicate the methylene protons of the oxazoline; the signals at 4.82 ppm, 4.74 ppm indicate the vinylidene-endgroup of the PP.

The hydroboration product is added to a solution of maleic anhydride (MAH) in THF. When small amounts of oxygen are added, MAH terminated PP as an intermediate product was formed. This can be converted into the PP-Ox by reaction with 2-(4-aminophenyl)-1,3-

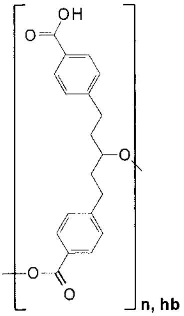
oxazoline under the same conditions as described in.[5] The hydroboration and the conversion of PP-MAH to PP-Ox were done in dispersion. To improve the accessibility of the unsaturated sites in the dispersed PP particles small amounts of benzene were added to the tetrahydrofurane (THF) used as solvent. During the reactions no changes in the molecular weight could be observed. However, the conversion is not complete.

From comparison of the $^1$H-NMR spectra (Fig. 1) of the unsaturated PP with that of the PP-Ox we calculated a functionality of 35 %, that means about every 3$^{rd}$ PP chain contains one 1,3-oxazoline endgroup.

Oxazoline-terminated PS was prepared by "living" radical polymerization using the TEMPO-method under analogous conditions like used for the synthesis of carboxylic terminated PS-COOH.[6-8] The initiator for the synthesis of PS-Ox was prepared by conversion of 4,4'-azo-bis(4-cyanopentanoic acid) (ABCPA) into the bischloride (Scheme 3). The product was dissolved in N,N-dimethylacetamide (DMAc) and slowly added to an equimolar mixture of 2-(4-hydroxyphenyl)-1,3-oxazoline and triethylamine (small excess) at 0 °C, stirred at room temperature for few hours and than carefully added to a saturated ice cooled sodium chloride solution. The precipitate was filtered off and washed with ice water. The functionality of the PS-Ox is about 75 %. The molecular weight is $M_n$ = 28000 g/mol (PD = 1.2). Before using the PS in the blends the TEMPO group was removed by oxidation with m-chloroperbenzoic acid.[9] For comparison a non-reactive PS with Mn = 30000 g/mol (PD = 1.25) was synthesized using AIBN as initiator under similar conditions.



Scheme 3. Syntheses of PS-Ox by the TEMPO-method.



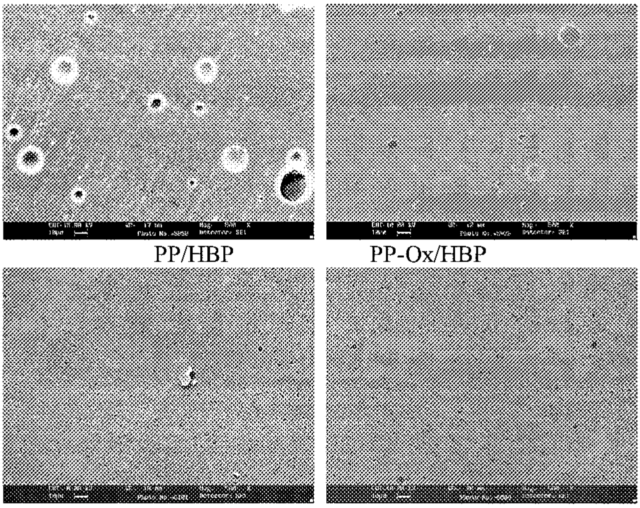
Scheme 4. Chemical structure of the HBP-COOH.

The carboxylic terminated hyperbranched polymer HBP-COOH (Scheme 4) with $M_n$ = 26000 g/mol (GPC, PS standard) was obtained by condensation of 1,5-bis-(4'-carboxyphenyl)pentan-3-ol in presence of dibutyltindiacetate as catalyst. After 90 min stirring the product in argon atmosphere at 210 to 250 °C a vacuum of 0.06 mbar was applied for additional 4.5 h until no bubble development was observed. Details and the synthesis of the monomers are described in.[10] Even considering the uncertainties of the molecular weight determination (PS calibration, hyperbranched nature of the product) we have to expect a very high functionality of the HBP molecules in the range of almost 100 COOH groups per molecule.

**Methods:** The blends in the composition PP/PS = 2/1 (by weight) plus 5 wt-% HBP 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 strands coming out of the Micro Compounder were cryo cut by a microtome to analyse the morphology by means of an SEM LEO 435 VP (Leo Elektronenmikroskopie). The dispersed phases were etched under different conditions. Etching with THF for 4 h at room temperature dissolves the PS as well as the HBP phase. Etching with NaOH/water for 4 h dissolves only the HBP phase. The etched samples were sputtered with gold and analysed with an acceleration voltage of 10 kV. The viscosity and the viscosity changes during annealing were measured with an ARES rheometer (Rheometrics) using a parallel plate geometry (1.2 - 1.8 mm gap) under nitrogen atmosphere. Frequency sweeps (0.1 - 100 rad/s, 5 % strain) and time sweeps (60 min, 10 rad/s, 20 % strain) were performed at 200 °C. Infrared spectroscopy was performed using a IFS 66 (Bruker) in transmission mode on thin films prepared by solution casting from THF on KBr plates.

## Results

The HBP is insoluble in both PP and PS, independent of the reactivity of the thermoplastics. However, the distribution of the HBP in PS is much finer than in PP (Fig. 2). This can be explained by the interactions between the polymers and the different viscosity ratios between the dispersed phase (HBP) and the matrix components. Due to the aromatic interactions between the HBP and the PS a better compatibility as compared to HBP/PP is achieved. In addition, the surface tension of HBP which is expected to be high because of the extremely high content of functional groups is more similar to that of PS (28.0 mN/m at 200°C [8]) than to that of PP (19.7 mN/m at 200°C[8]). Also the viscosity ratio which is next to the interfacial tension dominating the particle size when mixing non-reactive fluids[11] is different for both systems (Fig. 3). Assuming the validity of the Cox-Merz-rule the viscosity ratio was calculated for a shear rate of 100 $s^{-1}$ that is, even if we do not know the mean shear rate in the Micro Compounder, a value typical for extrusion processing. The viscosity ratio $\lambda$ changes from about 1 for HBP in PS and PS-Ox to about 3.5 for HBP in PP-Ox, and about 6.4 for HBP in PP. In the blend of PP-Ox with HBP a significant reduction in particle size is seen compared to the nonreactive mixture. whereas only marginal changes occur in the blend of PS-Ox with HBP. In addition to the rheological changes, a reduced interfacial tension due to the functionalization and the desired reaction may cause this reduction.


PP/HBP PP-Ox/HBP

PS/HBP PS-Ox/HBP

Fig. 2. Distribution of 5 wt% HBP in PP, PP-Ox, PS, and PS-Ox (frame size 240x180 µm).

Surprisingly, the distribution of the PS-Ox in the PP-Ox/PS-Ox blends is much finer than that of PS in the PP/PS blends (Fig. 4, left micrographs) though polymers with very similar molecular weights have been used and a change in the interfacial tension or a reaction between the two oxazoline terminated polymers is not expected. The reason is the strong influence of the functional groups on the viscosity of the PP. Fig. 3 shows that the viscosity of PP-Ox is higher than that of PP, whereas the viscosity of both PS is similar. The viscosity ratio between the dispersed phase (PS, PS-Ox) and matrix component (PP, PP-Ox), again calculated for 100 rad/s, changes from about 6.8 for the non-functionalized blend components to about 3.0 for the functionalized blend components.

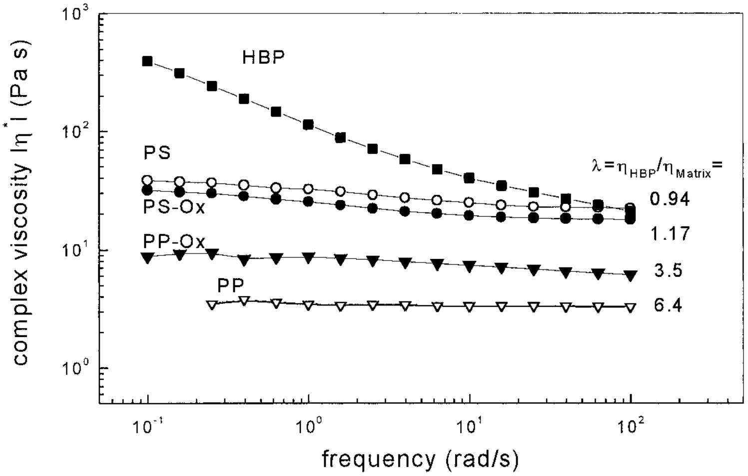
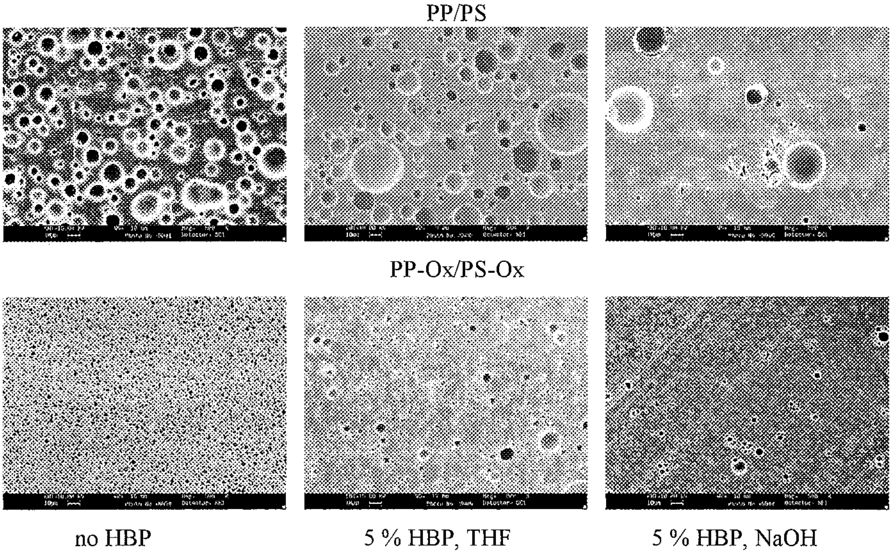


Fig. 3. Viscosity at 200 °C and viscosity ratio at 100 rad/s of the blend components.


PP/PS

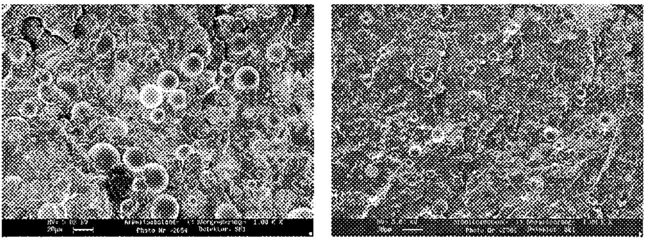
PP-Ox/PS-Ox

no HBP 5 % HBP, THF 5 % HBP, NaOH

Fig. 4. Morphology of PP/PS=2/1 blends with and without addition of 5 wt% HBP (frame size 240x180 μm).

The strong influence of the viscosity ratio between the reactive blend components on the morphology development was already found for the formation of graft copolymers using oxazoline grafted PP and carboxylic acid terminated PS.[8] In case of the in-situ block copolymer formation during mixing of carboxylic terminated PP and oxazoline terminated PS we observed a similar strong effect of the viscosity ratio on the morphology (Fig. 5).[7] At unfavourable viscosity ratios, $\lambda$ higher than 1, the effect of the reactivity is clearly visible while at favourable viscosity ratios, $\lambda$ near 1, the reactive system has only a slight 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.

PP1-COOH/PS, $\lambda$= 1.6 PP1-COOH/PS-Ox, $\lambda$ = 2.2



PP2-COOH/PS, $\lambda$ = 0.6 PP2-COOH/PS-Ox , $\lambda$ = 0.9

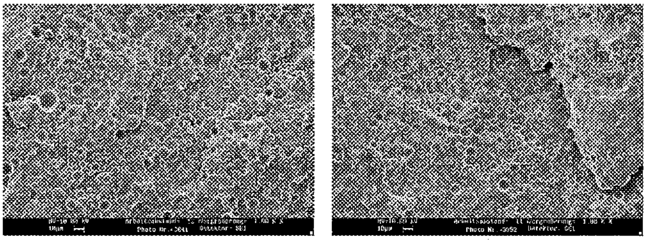
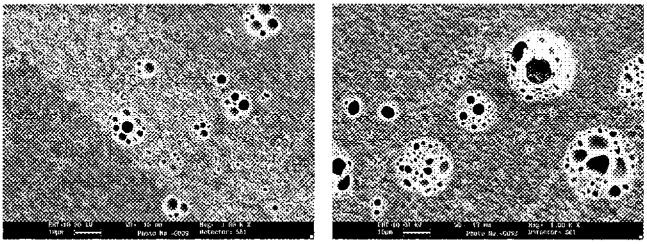


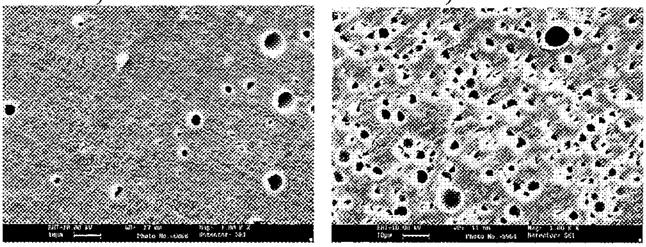
Fig. 5. Influence of the reactivity and viscosity on the morphology of PP/PS = 70/30 blends, SEM of cryofractures [7] (frame size 310x220 μm).

When 5 % HBP are added to the PP/PS blends (Fig. 4), the HBP distributes in a different manner as compared to PP-Ox/PS-Ox blends. In the samples etched with THF a bimodal distribution of the hole sizes resulting from the etching process is visible, in the reactive as well as in the non-reactive blend. When dissolving only the HBP phase by etching with aqueous NaOH it is clearly visible that the big holes in the PP/PS blend are formed from the HBP phase. However, even for the very big HBP particles there seems to be a PS layer around the HBP, visible as a bright shadow. Some other PS particles contain small drops of HBP but there are also unfilled PS drops. There is no HBP particle observable, which is in direct contact to PP. In PP-Ox/PS-Ox blends the HBP locates also mainly within the PS-Ox particles resulting in bimodal size distribution of the PS-Ox phase: small particles without entrapped HBP and large PS-Ox particles containing rather fine distributed HBP. The difference to the nonreactive blend consists in the existence of more than one (up to 15) very finely dispersed HBP drops in one PS-Ox particle, whereas the nonreactive blend always contains only one HBP particle in PS. Therefore, in both blends, only a very small part of the HBP is located at the interphase between the two main components as it would be necessary for acting as interfacial active compatibilizer.

The tendency of the HBP to locate within the PS-Ox particles increases with increasing mixing time. Fig. 6 gives examples of big PS-Ox particles containing a large number of HBP particles. The size of the PS-Ox particles filled with the HBP increases while the size of the unfilled PS-Ox particles (visible only as shadow) remains very fine. In order to proof if it is possible to locate the HBP at the PP-Ox/PS-Ox interphase, a mixture of HBP in PP-Ox was prepared initially by melt mixing for 30 min. After that the PS-Ox was added and the blend was melt mixed for further 5 min. In this case the "phase in phase" morphology is not visible. The HBP is distributed in the PP-Ox matrix as big particles and the PS-Ox exists as finely distributed particle.



a) 5 min mixed b) 30 min mixed



c) subsequent mixing (see text) d)

Fig. 6. Morphology of ternary systems PP-Ox/PS-Ox + HBP (2/1 + 5 wt%) in dependence on the preparation conditions, a) and b) simultaneous mixing, c) and d) subsequent mixing; a)-c)surfaces etched with NaOH, d) surface etched with THF (frame size 116x86 μm).

## Discussion

The morphology of ternary PP/PS + HBP blends depends strongly on the preparation conditions and the reactivity of the system. Due to the polar character of the HBP it is more compatible with PS and therefore tends to migrate preferably into the PS phase. Because of the favourable viscosity ratio between HBP and PS this results in a fine distribution. When a reaction between the PS-Ox and HBP occurs, the HBP phase is fixed in the PS-Ox phase and finally the HBP is embedded as stabilized dispersed particle inside the PS-Ox particles. The growth of the HBP filled PS-Ox particles with mixing time can be explained by coalescence of the PS-Ox particles in the low viscous PP-Ox matrix because the interface is not stabilized. In addition, due to the reaction of the HBP with PS-Ox the viscosity of the HBP filled PS-Ox droplets increases (see below) resulting in worse viscosity ratios for fine droplet formation. However, inside the PS-Ox particles, the HBP particles do not coalesce but remain their small size. In case of PP/PS blends, the PS particles also coalesce but the HBP entrapped inside seems to coalesce within the PS particles, thus leading to the very big HBP particles. When mixing HBP with PS-Ox the viscosity raised with time detectable as an increase in the torque necessary for remaining a constant speed of the screws and as a continous increase in the pressure measured at the bottom of the Micro compounder. This effect could be also checked by measuring the complex viscosity with time of blends melt mixed for 5 min (Fig. 7). Only in case of PS-Ox/HBP the viscosity increased with time while in case of PP-Ox/HBP and PP-Ox/PS-Ox + HBP the viscosity remained constant over 60 min at 200°C. This indicates a reaction between HBP and PS-Ox but no significant reaction of the HBP with PP-Ox. Reasons for this may be the lower degree of functionalization of the PP-Ox and the relatively small PP-Ox/HBP interfacial area in these blends.

Parallel to that we could prove the chemical reaction between PS-Ox and HBP by FTIR. A decrease in the oxazoline absorbance ($\nu_{C=N}$=1654 $cm^{-1}$), an increase in the amid absorbance ($\nu_{CONH}$=1680 $cm^{-1}$), and a shift in the region of carbonyl bands ($\nu_{CO}$=1700-1730 $cm^{-1}$) were found when comparing a PS-Ox/HBP = 95/5 mixture with a blend melt mixed for 30 min at 200°C (Fig. 8).[12]

When mixing HBP first with PP-Ox, the HBP phase becomes a dispersed phase in PP-Ox exhibiting a large particle size caused by the unfavourable viscosity ratio. In addition, the HBP phase is immobilized by the interaction to PP-Ox. This hinders a finer distribution of the HBP particles as well as the thermodynamically preferred transport of the HBP towards the

PP-Ox/PS-Ox-interface and into the PS-Ox particles when the PP-Ox/HBP preblend is finally melt mixed with PS-Ox.

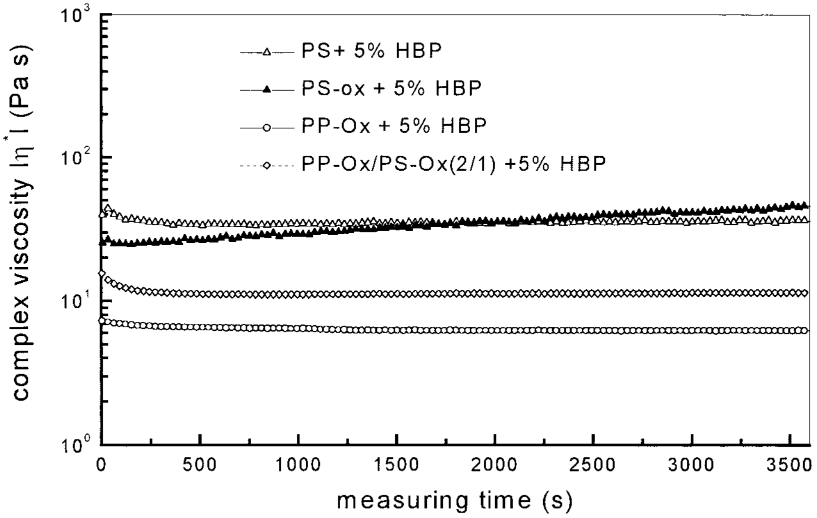


Fig. 7. Time dependence of the complex viscosity at 200°C of blends mixed for 5 minutes in the Micro compounder.

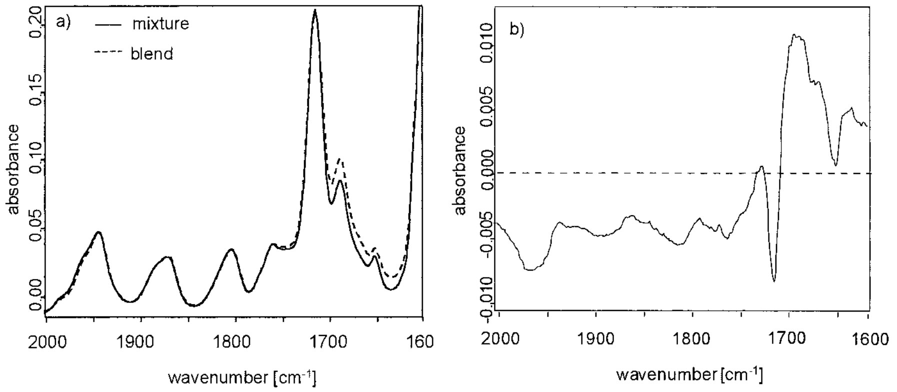


Fig. 8. Transmission IR spectra a) and difference spectrum b) of a PS-Ox/HBP=95/5 mixture and a blend melt mixed for 30 min at 200 °C.

Based on the discussions, it can be concluded that the COOH bearing HBP is not found as a suitable compatibilizer in the studied system of PP-Ox/PS-Ox. By simultaneous mixing of all components in both systems (reactive as well as nonreactive), HBP is not located at the interface. Instead, it resides entirely in the PS or PS-Ox phase (as one particle or many small particles, respectively). However, the mechanism observed offers a new possibility to create phase in phase morphologies that may have interesting properties which has to be studied in future work.

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