Modification of PP by Blending with PS and Reactive Polymers

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SUMMARY: In this paper a polypropylene (PP) resin with controlled rheology was selected as polymer matrix and modified by melt mixing with polystyrene (PS) which has certain processing compatibility with PP. The effect of the addition of polyperoxide (PPX), peroxide modified PS particles (PS-PPX), and maleic anhydride (MAH) to the PP/PS blend during melt mixing on the rheological behavior and morphology of the PP/PS blends has been carefully studied.

Introduction

Generally, a desirable performance of a new material can be achieved by proper selection of blend ingredients, followed by control of morphology via appropriate methods of compatibilization, compounding and processing[1-4]. In the last decade, isotactic polypropylene (PP) blends with polyethylene (PE), with ethylene-propylene copolymer (EPR) or terpolymer (EPDM) (containing a non-conjugated diene), and with polyamide (PA) have been studied and discussed in detail[5].

Blends of PP with PS are primarily of academic interest[6-7]. They are nearly ideal for studying the effects of numerous variables on the blend morphology. The practical use of two-component PP-PS blends is based on flow segregation causing migration of the PP phase to the surface, thus allowing for higher temperature applications and grease-resistance[8]. Blends of PP with high impact PS (HIPS) and styrene-butadiene-styrene tri-block copolymer (SBS) show good mechanical properties and large strain at break[9-10].

In our previous work, we have prepared a series of PS samples, which were polymerized under different conditions, and studied the effect of the addition of PS with different molecular weight and morphology (such as the particle size and shape) on the rheological behavior, crystallinity and structure of the PP/PS blends[11-13].

In this paper a PP resin with controlled rheology (MI=35, test conditions see Tab.1) was

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selected as polymer matrix, and the PS with certain rheological properties and surface characteristics which matched best to the flow behavior of the matrix PP among those previously studied PS samples was used as polymer modifier. The third additives like MAH, PPX or PS-PPX were melt mixed with PP and PS by means of a DACA Micro Compounder. The effect of the addition of MAH, PPX or PS-PPX on the flow properties, micro-morphology and macro-morphology of the PP/PS blend system has been studied.

Materials and methods

Polypropylene (PP), MI=35, was supplied by the pilot modification PP plant of Donghua University. Polystyrene (PS) particles were synthesized by suspension polymerization with polyvinyl alcohol (PVA) as the dispersing agent, benzoyle peroxide (BPO) as the initiator, and $Na_2S_2O_3$ water solution as the termination agent. The polymerization was conducted in a water bath first at 90 °C for 6 hours, and then cured at 95°C for about 3 hours. The synthesis conditions and characteristics of the PS products are shown in Tab.1.

Table 1: The preparation conditions and characteristics of PS

Sample	PVA (g/100g monomer)	BPO (g/100g monomer)	Feed composition	Particle size (mm)	MI * (g/min)
PS	1.25	0.75	1:2	2~3	0.124

* MI is the melt index (g/min) of samples through a capillary with 9.525 mm length and L/D=50 at 230°C, 2.16 kg.

PPX (see Fig. 1, n=15~20) was synthesized using BPO as initiator by radical copolymerization in acetone at 60°C. The structure was characterized by Raman spectroscopy in our earlier work[12]. PS-PPX nanoospheres were made by modification of PS particles (syntheisized by emulsion polymerization[12]) with PPX. The reaction conditions and the related properties of the PS-PPX latex are shown in Tab. 2 and 3. Before the latex was added to PP/PS blend as a modifier, it was solidified by freeze-drying. The powder size is up to about 150 nm[12].

Table 2: Recipe for modification of PS latex by PPX

PS latex	PPX by wt%	NaOH	DI water	T	pH	Reaction time
120g	15	5g	0.5g	90°C	11	9 h

Table 3: Properties of PS-PPX

Sample	Solid content (%)	pH value	Surface tension (mN/m)	Particle size D (nm)
PS-PPX	10	11.9	43.5	53.5

The detailed recipes of the blend systems are shown in Table 4. The mechanical mixing of the blend components was done using a Micro Compounder (DACA) with 4.5 cc maximal filling and co-rotating with 100 rpm at 190 °C for 10 min. The rheological behavior of the blends was investigated by an ARES Rheometer (Rheometrics) with a plate-plate geometry (diameter 25 mm, gap about 1.5 mm) in nitrogen atmosphere. The zero-shear viscosity was fitted by the Carreau model.

For light microscopy microtomed thin sections (3 µm) were investigated using a phase contrast light microscope (BH2, Olympus). Scanning electron microscopy was carried out using a SEM LEO (Zeiss). An acceleration voltage of 10 kV was used. The preparation of strands for SEM was performed by chemical etching of microtomed surfaces. Samples were etched in xylene at room temperature for 3 hours and then washed in freshly xylene and acetone. Then the samples were dried overnight. The samples were sputtered with gold.

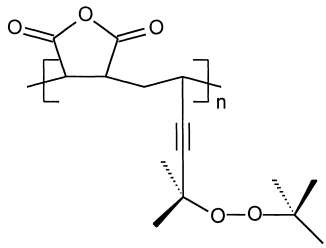

Fig. 1: Chemical structure of PPX

Table 4: Blend composition

Sample No.	PP	PS	PS-PPX	PPX	MAH
S0	100	0	0	0	0
S1	80	20	0	0	0
S2	80	20	5	0	0
S3	80	20	0	2	0
S4	80	20	0	2	5
S5	100	0	2	0	0

Results and discussion

Flow behavior

For most polymer blends, the Huggins-Flory binary thermodynamic interaction parameter is large, $\chi>0$, engendering low degree of molecular entanglement in the interfacial region. As a result, the interfacial adhesion in both molten and solid state is usually poor. For example, the value of the interphase viscosity was estimated to be about 100 times smaller than that of the neat resin[5]. For uncompatibilized blends, the solid state properties versus composition usually show a strong negative deviation from additivity. In this paper, the PP80/PS20 system was constant and the blends were varied by the use of different third additives such as MAH, PPX and PS-PPX.

Fig. 2 demonstrates the influence of modifiers on PP/PS blends measured by ARES rheometer. The blends PP/PS without third modifier show a higher viscosity than the neat PP at measuring condition. The zero-shear viscosity increases sharply from 272 Pa s to 451 Pa s.

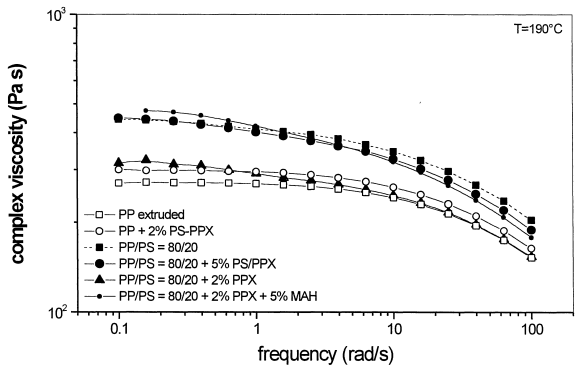

Fig. 2: Influence of modification of PP/PS=80/20 blends by PS-PPX, PPX and MAH on melt viscosity

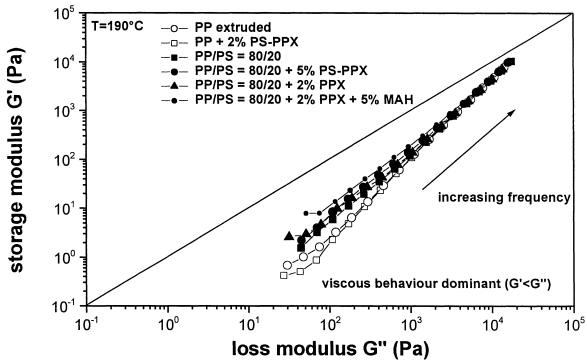

Fig. 3: Relation between viscous part and elastic part for different samples

The addition of 5 % PS-PPX to PP/PS blend does not lead to a significant change in melt viscosity. The shape of the viscosity-frequency dependence is slightly changed. The addition of 2 % PPX to PP/PS sample reduces the viscosity. There is a decrease in zero-shear viscosity from 450 Pa s to 330 Pa s, indicating a partial degradation of the PP matrix caused from the peroxy groups of PPX. The addition of 2 % PPX and 5 % MAH to PP/PS sample leads to an obvious change in the shape of the viscosity-frequency dependence. The melt viscosity of it is higher than that of all the other related samples at lower frequency (zero-shear viscosity increases up to 520 Pa s), but sharp decrease with frequency leads to lower viscosity at higher frequency.

Fig. 3 shows the relation between viscous part (loss modulus G") and elastic part (storage modulus G') of the complex viscosity for different samples. No significant change has been found when 2 % PS-PPX were added to pure PP, but small increase in elastic part after modification of pure PP and PP/PS blends with PS-PPX, PPX, and MAH has been observed. That reveals some chemically or physically interaction between matrix and disperse phase as well as the influence of the modifiers. Overall the viscous behaviour remains dominant in the blends compared to their elastic behaviour.

Morphology

The properties of polymer blends can be controlled by morphology (which in turn depends on the molecular parameters of the blend components) and composition, as well as by the compounding and processing conditions. In the case of amorphous blends, the size and shape of the two phases, their distribution and orientation, define

the morphology.

Fig. 4 and Figs. 5-6 show light micrographs and scanning electron micrographs, respectively, of selected blends. From Fig. 4a it can be seen that PS-PPX particles are dispersed homogeneously in the PP matrix in the size of about 0.5-3 μm, much larger than the original size of the added PS-PPX powder (<0.15 μm), which accounts for PS-PPX agglomeration or coalescence during the blending process. Larger disperse PS particle size (2-8 μm) was observed in PP/PS/PS-PPX (80/20/5) blends than in PP/PS (80/20) blends (1-5 μm, Fig. 4b,c and Fig.5). In addition, the PP spherulite shape and size have been affected strongly by blending with PS.

Fig. 6 shows the influence of MAH addition on the morphology in PP/PS = 80/20 blends. It can be seen clearly that the addition of 2 % PPX by weight to PP/PS=80/20 blends improves the homogeneity of the particle size and distribution. More round particles were found in S3 (PP/PS/PPX = 80/20/2) sample which means that coalescence between dispersed particles is reduced. The particle size itself is not very much influenced. Adding MAH to the PP/PS/PPX system the particle size is reduced significantly. All particles are smaller than 2 μm which indicates that MAH in combination with PPX acts as a reactive compatibilizer.

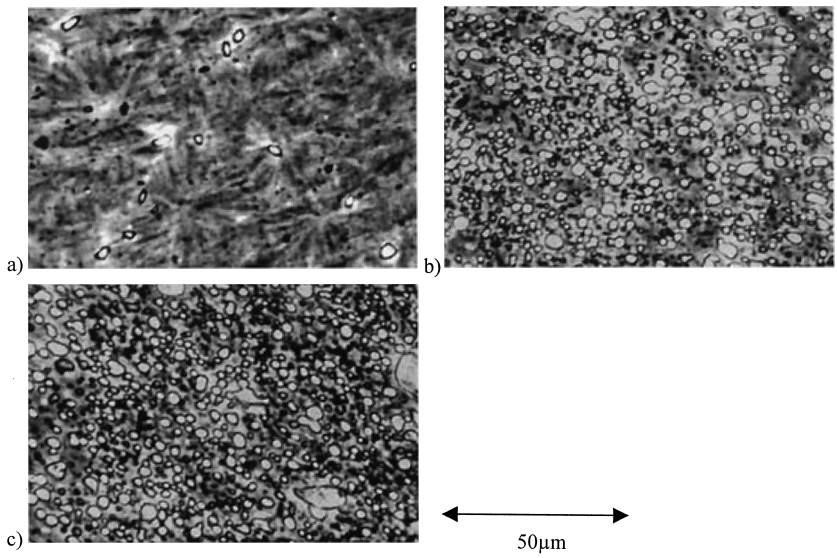

Fig. 4: Light micrographs of: a) S5 (100 PP / 2 PS-PPX); b) S1 (80PP/20PS);
c) S2 (80PP/20PS/5PS-PPX)

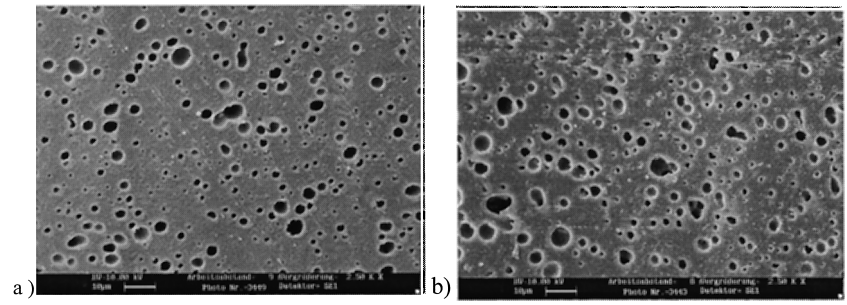

Fig. 5: SEM micrographs of: a) S1 (80PP/20PS); b) S2 (80PP/20PS/5PS-PPX)

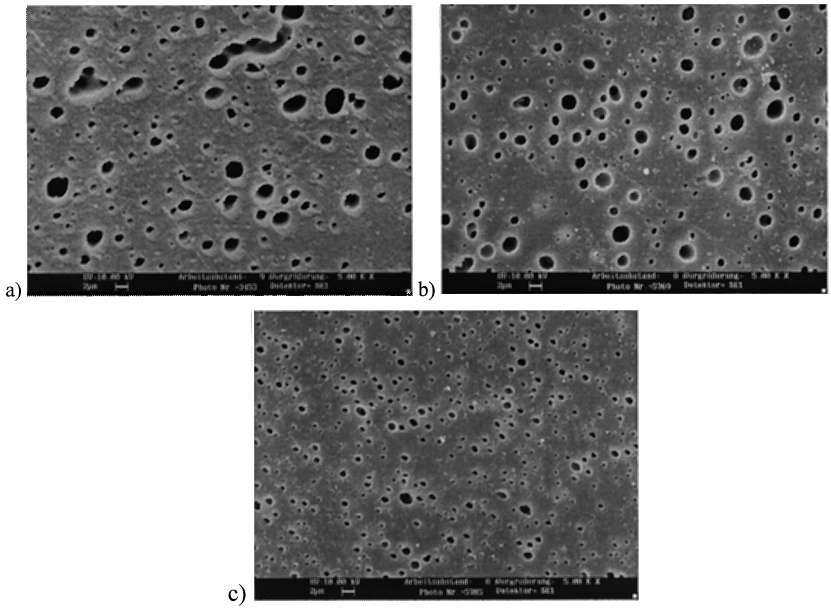

Fig. 6: Influence of MAH addition on the morphology in PP/PS = 80/20 blends (SEM): a) S1 (80PP/20PS), b) S3 (80PP/20PS/2PPX), c) S4 (80PP/20PS/2PPX/5MAH)

Conclusion

Reactive polymeric additives like PPX and PS-PPX are useful modifiers for PP/PS blends. Their addition during the blending process results in changes in the rheological properties of the blends and in special interactions at their interface. These interactions suppress the coalescence tendency resulting in finer and more homogeneous morphologies by use of PPX. The biggest influence was observed when PPX was used as modifier in combination with MAH.

PS-PPX which was added as nanospheres (up to 150 nm) to the blend agglomerates to bigger particles (0.5-3 μm) during mixing into PP. It does not improve the blend morphology in PP/PS = 80/20 blends.

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1. L.A. Utracki, Melt flow of polyethylene blends, in: *Multiphase Polymers: Blends and Ionomers*, Vol.395, L.A. Utracki (Ed.), American Chemical Society, Washington DC 1989, pp.153-210

2. M. Zhu, X. Wang, Y. Zhang, Y. Chen, *China Synthetic Fiber Industry*, **20**, 13 (1997)

3. X. Huang, M. Zhu, Y. Zhang, Y. Chen, *Synthetic Fiber in China*, **27**, 18 (1998)

4. Y. Lu, M. Zhu, X. Huang, Y. Zhang, Y. Chen, *Petrochemical Technology & Application*, **17**, 138 (1999)

5. I.J. Karger, in: *Polypropylene 2: Copolymer and Blends*, J. Karger-Kocsis (Ed.) CHAPMAN & HALL, London 1995, pp.51-78

6. V.B. Gupta, Y.C. Bhuvanesh, *J. Appl. Polym. Sci.*, **60**, 1951(1996)

7. P. Pötschke, H. Malz, J. Pionteck, *Macromol. Symp.*, **149**, 231 (2000)

8. Mobil Oil Corp., *US Patent* 4 673 711, 1987

9. Montefine SA, *European Patent Application* 0 060 524, 1982

10. Tokyo Jidosha KK , *European Patent Application* 0 376 081, 1990

11. Y. Chen, Y. Lu, M. Zhu, *PPS-16 (THE POLYMER PROCESSING SOCIETY Sixteenth Annual Meeting)*, Shanghai, 2000, pp.614-615

12. M. Zhu: *Study on functional PS-based polymers and their application* (PhD Thesis), Donghua University, Shanghai, 1999

13. M. Zhu,Y. Lu, Y. Chen, World Polymer Congress IUPAC 2000 *38th Macromolecular IUPAC Symposium*, Warsaw, 2000, p.1159