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Polypropylene + Polystyrene Blends with a Compatibilizer. Part I. Morphology and Thermophysical Properties

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Abstract: Various concentrations of polypropylene (PP) and polystyrene (PS) blends were prepared with styrene-ethylene/butylene-styrene block copolymer (SEBS) added as a compatibilizer between the two main polymers. We have investigated the effect of SEBS on processing, morphology and thermophysical properties of the blends. The compatibilizing agent improves the blend morphology since smaller particles of the dispersed PS phase in the PP matrix blends are obtained; adding more than 5 % SEBS has no further effect on the blends. The presence of SEBS lowers the crystallinity of the PP-rich phase - as reflected in the enthalpy of fusion and also in the enthalpy of crystallization.

Keywords: polymer blends, compatibilization, polypropylene, polystyrene, polymer crystallization

1. Introduction

The use of polymer-based materials (PBMs) is rapidly increasing. The industries of today are increasingly searching to replace metal parts with PBMs because of lower densities, easy maintenance and inexpensive prices [1].

Among a large variety of PBMs [2], those based on polypropylene (PP) [3 - 18] and on polystyrene (PS) [19 - 22] belong to the most important ones. Inexpensive PP + PS blends are also in use. These blends are suitable for low performance parts in manufacturing (i.e. dashboards, computer cases). However, they cannot be used instead of metals in industries - such as automotive and aviation - which require high performance parts. Specifically, PP + PS blends exhibit relatively low impact strengths, low wear resistance, high friction - all properties undesirable for the demanding service conditions. Several of the major problems with PP + PS blends may be caused by poor compatibility of the components. This feature can be improved by using compatibilizers [23]. As discussed by several authors [24 - 28] and reviewed by Kopczynska and Ehrenstein [29], interfacial tensions have decisive effect on properties of multiphase systems. Zaichenko and his colleagues [30] explain how desired properties can be achieved by creation of block polymers. A block copolymer SEBS (styreneethylene/butylene-styrene) contains in each segment two styrene units – which are of course miscible with polystyrene while ethylene-butylene blocks are miscible with polypropylene. Therefore, the block copolymer should create two microphases instead of macrophases: a polystyrene-styrene microphase and a polypropyleneethylene/butylene microphase. This should lead to a reduction in the size of the particles in the matrix of the blend.

We have formulated and studied several uncompatibilized and compatibilized compositions of PP and PS. In the present paper we report effects of the addition of the SEBS block copolymer on morphology, processing and thermophysical properties. A weak side of most polymers is their poor scratch and wear resistance – and much work is needed in this area [31]. We report the effects of compatibilization on tribological and mechanical properties in the following paper [32].

2. Processing behavior

Torque TQ results versus content of PS in the blends obtained during the blend preparation in the extruder are shown in Figure 1. We know that the torque measured during processing is directly related to rheological behavior of the blend at given conditions. The results show higher values of torque for a given PS content in all compatibilized blends. Apparently the presence of the compatibilizer increases the viscosity of polymer melt.



Fig. 1. Torque value TQ of PP + PS blends.

We also see that there is no change of torque with increasing concentration of SEBS block copolymer. While 5 wt. % SEBS produces an effect, adding 2 % more makes practically no difference.

3. Thermal Analysis

Figure 2 shows the crystallization exothermic DSC curves for uncompatibilized blends. Addition of polystyrene to polypropylene reduces the intensity and the width of the crystallization peaks due to higher contents of the amorphous phase. Crystallization peak is significantly displaced to lower temperatures only in the 20/80 blend; this can be explained by a disruption of the supramolecular structure of PP.



Fig. 2. Crystallization peaks of exothermic DSC curves of uncompatibilized PP + PS blends.



Fig. 3. Fusion peaks of binary PP + PS blends as a function of PS content.

Both enthalpy of crystallization (obtained by peak integration) and the degree of crystallinity of the blends decrease with higher content of amorphous PS (Table 1).

Enthalpy of fusion results also indicate a reduction of the polypropylene crystallinity by addition of PS (Figure 3, Table 1). The addition of SEBS to the blends further reduces the enthalpy of crystallization and degree of crystallinity compared to the uncompatilized blends in all investigated compositions (Figure 4).

Tab. 1. Results of DSC analysis; fusion enthalpy ΔH_m , crystallization enthalpy ΔH_c and degree of crystallinity χ of PP homopolymer and PP + PS blends.

SAMPLE	∆H _m (J/g)	∆H _c (J/g)	X (%)
PP	86.4	94.3	56.5
PP/PS 90/10	84.8	94.0	56.5
PP/SEBS/PS 90/10/5	68.9	75.5	45.2
PP/PS/SEBS 90/10/7	64.0	70.1	42.0
PP/PS 80/20	75.7	83.0	49.7
PP/PS/SEBS 80/20/5	65.7	72.4	43.4
PP/PS/SEBS 80/20/7	63.7	70.4	42.2
PP/PS 50/50	45.3	50.1	30.0
PP/PS/SEBS 50/50/5	43.2	47.5	28.5
PP/PS/SEBS 50/50/7	41.6	45.9	27.5
PP/PS 20/80	15.6	7.2	/
PP/PS/SEBS 20/80/5	14.6	9.3 1.7	/
PP/PS/SEBS 20/80/7	13.7	1.5 2.0	1

The reduction of crystallinity is more pronounced by adding 7 % of SEBS (Table 1). Effects of the presence of the SEBS block copolymer on melting behavior of our blends are presented in Figure 5.



Fig. 4. Crystallization peaks of PP + PS blends compatibilized with 7 wt. % SEBS .





4. Morphological study

Figure 6a shows the image of the uncompatibilized PP/PS 90/10 blend. We see a two-phase morphology with PS particles dispersed in the PP matrix, a result of high

interfacial tension between the components. Also, we can observe holes formed during streching on the fractured specimen. The addition of SEBS to binary blends changes their morphology. The block copolymer is located at the interface between PP and PS (Figure 6b, 6c). The size of the dispersed PS particles is reduced at both compositions, namely 5 % and 7 % of the added compatibilizer; the effect is more pronounced at 5 % of SEBS (Figure 6b). A better adhesion of the dispersed phase in the matrix can be recognized – along with a decrease in the number of holes when the copolymer is present.



Fig. 6. SEM microphotographs of a) PP + PS 90/10, b) PP + PS+SEBS 90/10/5, c) PP + PS + SEBS 90/10/7.



Fig. 7. SEM microphotographs of a) PP + PS 80/20, b) PP + PS + SEBS 80/20/5, c) PP + PS + SEBS 80/20/7.

As shown in Figure 7, the addition of the compatibilizer to 80/20 blend leads to a reduction in size of the dispersed PS particles, but not as effectively as in the 90/10 blend.



Fig. 8. SEM microphotographs of a) PP + PS 20/80 and b) PP + PS + SEBS 20/80/7; PS extracted with xylene.

The influence of the compatibilizer in producing a more uniform structure is also visible in the case of the PP + PS 20/80 blend (Figure 8).

5. General discussion

Although there is a slight increase in torque during extrusion of the PP + PS + SEBS blends, it is not enough to change drastically the processability of the material. It is clear that the higher the amount of semicrystalline PP in the blends, the higher enthalpy of crystallization results. However, as we add SEBS to the system, there is an amorphization effect that can be seen if we compare both enthalpy of crystallization and enthalpy of fusion of the compatibilized blends against the uncompatibilized ones.

The microstructure of the system is also changed by adding SEBS. The SEM micrographs show a reduction in particle size of the dispersed phase in the blends with compatibilizer - what suggests a reduction in interfacial tension between PP and PS. The concentration of 5 % of SEBS in the system was found to be optimal. We recall how interfacial tension reduction by a fluoropolymer in a commercial epoxy results in lowering of friction [34] and improvement of scratch resistance [35]. These results have been connected to surface tension of the blends [36]. We also note that PS exhbits low tenacity (low internal cohesion) [37] and is much more brittle than most polymers [38]. Therefore, smaller PS islands in the PP matrix are desirable. As noted in the beginning, we shall report how the structure changes due to compatibility affect tribological and mechanical properties [32].

6. Experimental

Materials

Polypropylene was supplied by Basell Polyolefins under the name Moplen HP 500N. Polystyrene E-678 was acquired from DIOKI in Zagreb, Croatia. SEBS block copolymer, also called Kraton G 1650, was provided by Kraton Polymers of Germany.

Processing

Specimens were prepared in a Haake Record 90 twin extruder according to the desired weight composition of the blends. Weight compositions used include PP + PS 90/10, 80/20, 50/50, and 20/80. SEBS block copolymer was added to the blends to be compatibilized at 5 and 7 wt. %. The extruder was set at the temperature range 170 - 210 °C and the frequency of rotation 60 rpm. Torque TQ was recorded during the processing in the twin extruder.

Thermal Characterization

The thermal behavior of the PP + PS blends was analyzed in a TA Differential Scanning Calorimeter (DSC) model 2910. Samples were heated from room temperature to 190 °C, kept at this temperature for 10 minutes, and then cooled to room temperature at 10 K/minute. They were then reheated to 190 °C at the same heating rate. Parameters of crystallization and melting were taken from the second run curves. Sample crystallinity content was calculated using a PP fusion enthalpy reference value of 167 J/g [33].

Scanning electron microscopy

Scanning electron microscopy (SEM) was used to examine the samples after fracture in liquid nitrogen. The specimens were first coated with gold by means of vapor deposition using vacuum sputtering in order to avoid excessive charging during imaging. They were then investigated and photographed with a JEOL 5800 scanning electron microscope.

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