

Thermal & Morphological Evaluation of Linear and Radial SEBS-polypropylene Blends

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Abstract: Blending of two or even more immiscible polymers is a very useful method to obtain new polymeric materials with ordered and tailored properties. Thermoplastic elastomers (TPE's) are interesting materials for various applications, including the automotive industry, due to their excellent balance between processability and physical properties, especially using hydrogenated styrene-butadiene copolymer. In the present work, two structures of styrene-ethylene/buthylene-styrene (SEBS) triblock copolymer (linear and radial) were blended with polypropylene (PP) using a process aid oil. Three different SEBS-PP ratios were evaluated. Phase behavior was studied by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and Scanning electron microscopy (SEM), which confirmed the formation of a single phase material. PP crystallinity was affected by SEBS structure causing a lamellar thinning of crystals. The SEM analysis shows that radial and linear structures of SEBS have different morphology.

Keywords: *Thermoplastic elastomer, morphology, SEBS, crystallinity.*

Introduction

Thermoplastic elastomers (TPE's) are materials that combine rubber elastic properties with the thermoplastic polymers processability. Important classes of these materials are olefinic thermoplastic elastomers (OTPE's). Most of OTPE's are from isotactic polypropylene (PP) with ethylene-propylene-diene (EPDM), also named thermoplastic vulcanizated (TPV). TPV's are prepared by curing and blending simultaneously EPDM and PP, resulting of a blend that consists of elastomeric particles dispersed on PP matrix. An alternative for competition of TPV is a blend of copolymer poly (styrene-*b*-butylene-*co*-ethylene-*b*-styrene) triblock copolymer (SEBS) with PP. SEBS has an excellent thermal stability at high temperature and combined with PP results into a stiff and high processability compound.

A Blend of two or more immiscible polymers is a well known path to obtain new polymeric materials with ordered and tailored properties. The final size and shape of minor phase in polymer blend are related to factors such as composition, viscosity ratio, interfacial tension, shear rate, elasticity and processing conditions. In most cases, a blend of polymers without a compatibilizer cannot allow to improve the final product properties^[1].

PP has been a widely studied polymer in blends with elastomeric materials^[2-4] and the most evaluated variables like crystallinity and processability conditions.

Among the variety of thermoplastics with several industrial applications, TPE's are characterized by its excellent balance between processability (typical for commodities) with excellent physical properties (typical of elastomers). SEBS polymers combine successfully elastomeric properties with low processing costs. Excellent aging resistance of SEBS is due to absence of

double bonding C-C. SEBS polymers are commercially available and show an excellent intermediate temperature resistance^[5].

An important factor for TPE's blended with PP is polyolefin stereochemistry. Factors affecting the morphology of PP-TPE blends are size and hydrogenation of olefinic components in copolymer as well as processing conditions. In some reports the mechanical properties of isotactic PP blend were related to SEBS content and crystallization behavior of blends were studied. The morphology of PP blends is affected by olefinic component size and hydrogenation in rubbery copolymer^[6].

The compatibility of materials is a key factor to obtain a good blend with excellent homogeneity. In some cases it is necessary to add a compatibilizer to improve the compatibility among polymers.

It is well known that SEBS is used as an impact modifier for polyolefins, especially PP. The addition of a nucleant agent has been studied to improve the mechanical properties in a PP/SEBS proportion close to 50%^[7].

An important issue in SEBS-PP blends is the processing conditions (temperature profile, screw and feeding speed), due to mechanical properties on phase dispersion can vary according to the conditions. For instance, it has been reported that the impact resistance can be improved increasing rotor's speed and feeding in twin screw extruder, while an increase on temperature profile produces a diminish in this property^[8]. Interfacial interaction between PP and elastomeric can be improved by addition of compatibilizer, often a grafted block copolymer is used^[9]. PP and PS block is an incompatible

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blend, however and the path to improve performance and morphology is by using commercial triblock copolymers as SBS and SEBS^[10].

The aim of this present paper is to evaluate effect of elastomeric structure in SEBS-PP blends. The main objective of this work is related to obtain a SEBS-PP blend that can be an option to automotive application materials. The PP-SEBS ratio was evaluated in order to find an adequate behavior. The radial and linear SEBS structure was also studied. Dynamic Mechanical Analysis (DMA) and Scanning Electron Microscopy (SEM) were used to determine phase behavior and Differential Scanning Calorimetry (DSC) which allows to find crystallization behavior of the blends.

Experimental

Materials

PP homopolymer (PP homopolymer with MFI 2.2 dg/10 min at 230 °C and 2.16 kg) was obtained from Repsol Química®, styrene-ethylene/buthylene-styrene SEBS triblock copolymer with linear (Mn=185,000-195,000) and radial (Mn=100,000-150,000) structure and styrene content 30% were provided by Dynasol Elastomers®, Primol 352 a paraffinic oil purchased by Exxon Mobil was used as processing oil.

Blends preparation

Blends preparation was carried out in a co-rotative twin-screw Century extruder model CX-65, using a temperature profile of 175, 180 and 190 °C, and a screw speed of 63 rpm, three levels of SEBS-PP ratio were studied for linear and radial SEBS (1.0, 1.25 and 1.5). The amount of oil was constant in polymer-resin-oil ratio 100-80-150. Table 1 shows relation of prepared blends.

Characterization

The melting and crystallization properties of blends were evaluated by Differential Scanning Calorimetry (DSC), using a Perkin Elmer DSC8000 equipment with cooling accessory under a nitrogen atmosphere in a 25 mL/min flow. The sample (10 ± 2 mg) was heated from 40 to 150 °C at 20 °C/min, cooled back to -100 °C at 20 °C/min, and held at -100°C for 5 minutes, and then the second heating to 200 °C.

Dynamic mechanical measurements were carried out on a TA Instruments DMA2980 to evaluate viscoelastic properties. The experiment was performed in a mode of multifrequency with a dual cantilever clamp in a

temperature range from -100 to 150 °C, with 1 Hz frequency and a heating ramp of 3°C/min.

Scanning electron Microscopy (SEM) was carried out with a 3 nm resolution (high vacuum mode) and 4 nm (variable pressure), with an acceleration voltage of 0.5 KV-30KV, variable pressure range from 1 to 270 Pa, using a secondary electron and retrodispersive detector in a Jeol JSM 6390 equipment.

Results

Differential Scanning Calorimetry (DSC)

Crystallization behavior of PP in SEBS-PP blends was analyzed as a function of nature and content of the elastomeric component by DSC. Various methods to determine miscibility between polymers have been described^[11], being the method of melting-point depression one of most used. DSC thermogram of PP, showed a fusion peak at 178 °C, indicative of a more stable thermodynamically phase. Know the crystalline phase in blends SEBS/PP is very important due is related with blends performance. According to studies^[12] the melting point for PP is reported at 165 °C attributed to α phase and a small shoulder close to 159 °C from β phase of PP, a thermodynamically instable phase. The melting temperatures and ΔH of fusion peak are displayed in Table 2. It can be observed that there is a significant decrease on ΔH values from PP structure in blends which is indicative of a decrease in crystalline phase; this is caused because SEBS trends to spread in PP matrix preventing access PP chains to an ordered structure. The ΔH value for crystalline PP has been reported around 209 J/g^[13] and 190 J/g^[12], in this case a value of 71 J/g was found for PP.

Decrease on fusion peak is a result of lamellar thinning of PP crystals in blends with SEBS, linear structure have more affectation on this property than radial, according with ΔH values. Similar behavior of decreasing of Tm value in blends SEBS-PP has been reported before^[12].

In the other hand, it can observe that SEBS presence causes a slight decrease in melting temperature when SEBS amount increase in blends, being more significant for linear than radial SEBS, indicative that PP crystalline phase is changing due the presence of processing oil added. There are reports that SBS and SEBS have a nucleating effect in blends with isotactic PP and nylon 6, which it is not observed in present work^[7].

Table 1. Relation of blends SEBS-PP and identification code.

SEBS structure	SEBS/PP ratio	ID
Linear	1.0	D1
Linear	1.25	D2
Linear	1.5	D3
Radial	1.0	D4
Radial	1.25	D5
Radial	1.5	D6

Table 2. Tm and ΔH fusion values for SEBS-PP blends.

ID	Tm, °C	ΔH , J/g
PP	178.7	71.1
D1	160.1	23.87
D2	157.4	14.92
D3	156.8	9.31
D4	156.7	20.10
D5	157.4	19.92
D6	156.6	14.97

Dynamic Mechanical Analysis (DMA)

DMA has been used before in polyolefins-elastomers blends to identify phase behavior, as well as evaluate presence of crosslinking in styrene-butadiene materials^[14]. Also can be evaluated plasticizer effect of processing oil in SEBS-PP blends, although some problems to identify PP Tg can be present due overlap with elastomers phase region.

Figure 1 shows DMA thermogram for PP, tan delta curve shows a transition around 16 °C and other around 178 °C, the first one is associated with Tg and the second one to softening before fusion. In Figure 2 (left) shows the temperature dependence of storage modulus of linear SEBS-PP blends for 3 ratios 1.0, 1.25 and 1.5. It

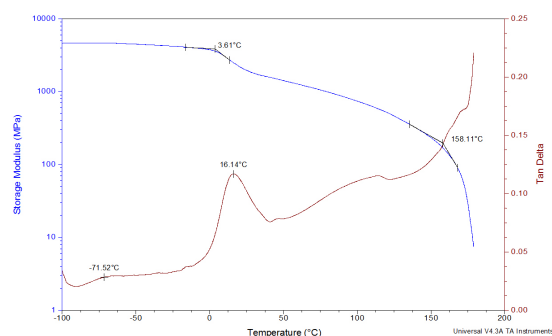


Figure 1. DMA thermogram for PP.

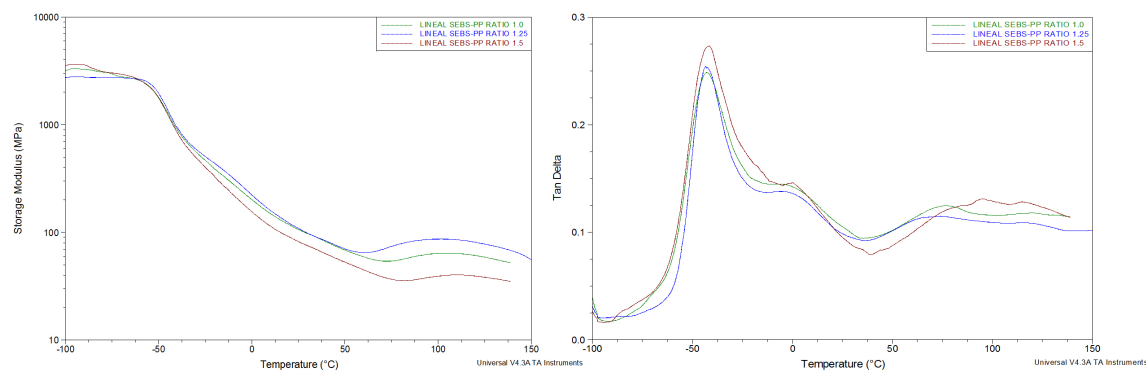


Figure 2. Dependence of storage modulus (left) and tan delta (right) on temperature for linear SEBS-PP blends in 1.0, 1.25 and 1.5 SEBS-PP ratio.

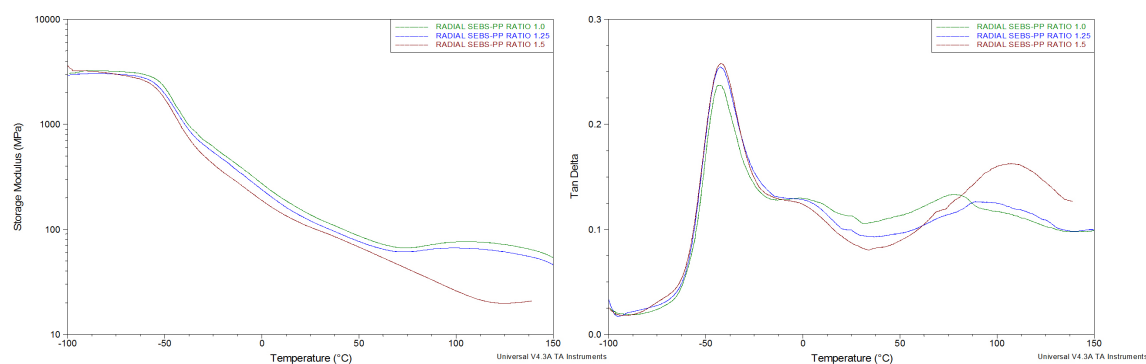


Figure 3. Dependence of storage modulus (left) and tan delta (right) on temperature for radial SEBS-PP blends in 1.0, 1.25 and 1.5 SEBS-PP ratio.

can be observed that at low temperatures there is not a significant variation on storage modulus for 3 blends, but around -35 °C blend with 1.5 SEBS-PP ratio has a lower modulus to 150 °C. The SEBS-PP ratio 1.25 was the higher value material in the storage modulus, indicating the higher stiffness. The phase behavior is evaluated in tan delta curve (Figure 2 right), where there are no significant changes in behavior of the elastomeric phase (predominant phase), due only one peak is observed and a shoulder around 60 °C attributed to a plasticizer effect of processing oil in PP phase, which also is evident in storage modulus curves, mainly for SEBS-PP ratio 1.25 and 1.0. Two Tg values are identified by means of DMA studies in polyolefin-elastomer blends before^[15], and when only one Tg is shown the miscibility is improved. In this study only one Tg can be observed for blends and a shoulder around 60 °C, which was discussed before, indicating a good miscibility between PP and SEBS.

Radial SEBS-PP blends have a similar behavior to the linear SEBS-PP blends (Figure 3), a small difference in modulus values between radial and linear SEBS was observed, being radial SEBS-PP ratio 1.5 which has no plasticizer effect because the more entanglement structure of SEBS which cannot be softened. According to results PP phase is affected more than SEBS phase, which causes a Tg value decrease, attributed to processing oil that is added in blends, PP is semicrystalline and only amorphous parts are accessible for the oil. This behavior has been reported before^[13]. The modification of phase

by the addition of additives, such as processing oil is common in polyolefin-elastomer blends. Some reports^[16] indicate T_g of plastic phase can be modified by an oil and that chains mobility increase due to a higher free volume of polymer. This provides in a greater flexibility in blend products.

Scanning Electron Microscopy (SEM)

The SEM analysis provides an insight interfacial activity of block copolymer blends. The effect of SEBS-PP ratio in linear and radial SEBS structure on morphology was evaluated by SEM micrographs, shown in Figure 4 and 5. Single phase morphology is clearly observed for linear SEBS-PP blends (Figure 4), which is indicative that a good dispersion of materials, with some curved surfaces or plates attributed to SEBS particles, increasing when SEBS-PP ratio increase due to a low interfacial tension and coalescence that provide a good adhesion between phases. Addition of PP to elastomers have no significant effect on the morphology of blends elastomer-polyolefin, this indicated that PP got entrapped inside the elastomeric phase forming particles^[17]. In some cases cryogenic fracture surface is an efficient method to evaluate interactions between phases in blends^[18,19]. Several studies of SEBS-polyolefinic blends report a phase separation between olefinic and elastomeric phases, when PP is in higher amount^[17,20,21].

In case of radial SEBS-PP blends (Figure 5) the morphology is quite different due to the presence of channels, rough areas and some SEBS pieces that are not

dispersed on the PP matrix, mainly attributed to radial structure of elastomer that not allows good dispersion between phases. As SEBS-PP ratio increase, the channels are more evident because the radial structure is in a higher concentration, this is according with DMA results that shows phase separation with increasing SEBS proportion in blend. Morphology of elastomers domains dispersed on thermoplastic matrix is very influenced by the nature of elastomers, for instance structure, molecular weight^[9].

Conclusions

DSC analysis shows that PP crystallinity decreases significantly in blends due to the affected olefinic phase by the addition of process oil resulting in a lamellar thinning of PP crystals, and SEBS structure have also influence on crystallinity decreasing for spread in PP phase.

This tendency was validated by DMA, where in addition was identified that SEBS-PP ratio affect blend properties. Also in DMA a plasticizer effect was identified by the increasing of storage modulus value above 60 °C. A phase separation was not identified, only in radial SEBS with SEBS-PP ratio of 1.5. The one phase presence was also confirmed with SEM micrograph that shows a dispersed elastomeric phase on olefinic matrix.

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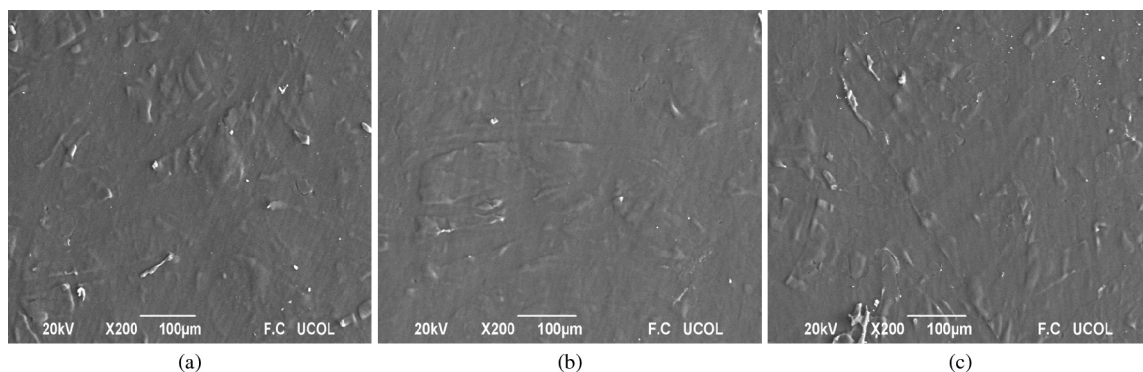


Figure 4. SEM micrographs for linear SEBS-PP ratios a) 1.0, b) 1.25 and c) 1.5.

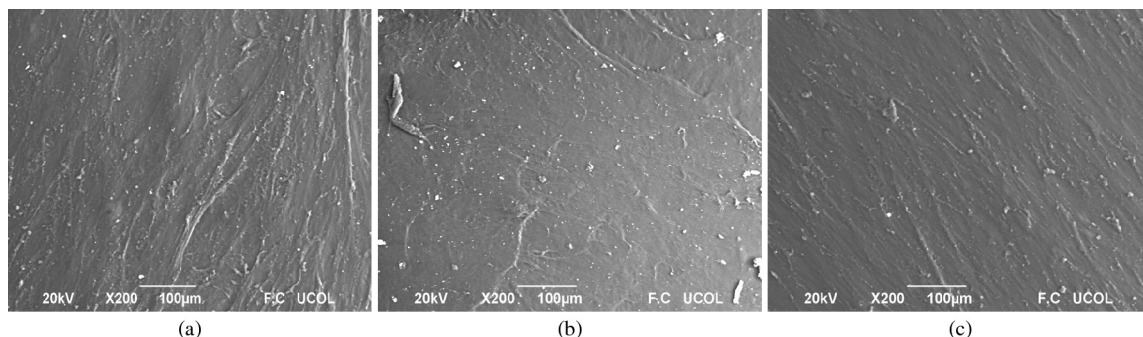


Figure 5. SEM micrographs for radial SEBS-PP in ratios a) 1.0, b) 1.25 and c) 1.5.

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