Compatibilizing effect of EPM-g-MA in Sorona®/EPDM incompatible Blends

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Abstract

The morphology and properties of immiscible and highly incompatible blends of Sorona® [poly (trimethylene terephthalate)] and EPDM blends has been studied with and without the addition of a compatibilizer precursor EPM-g-MA. These incompatible blends are characterized by a two-phase morphology, narrow interphase, and poor physical and chemical interactions across the phase boundaries. Therefore a reactive route was employed to compatibilize these blends by the addition of maleic anhydride grafted ethylene propylene rubber (EPM-g-MA). The influence of EPM-g-MA on the phase morphology was studied quantitatively by scanning electron microscopy (SEM). It was found that the addition of EPM-g-MA reduces the domain size of the dispersed phase followed by a leveling off at higher concentrations of the compatibilizer. This is an indication of interfacial saturation. The experimental compatibilization results were compared with theoretical predictions. Free volume measurements using positron annihilation lifetime spectroscopy (PALS) were done to analyze the interaction of blends. In the case of uncompatibilized blends the free volume values tend to increase by the addition of EPDM phase showing high level of incompatibility. Addition of EPM-g-MA to the blends tends to decrease the free volume showing its compatibilizing effect.

Key words: Sorona®, Morphology, Compatibilizer, Scanning electron microscopy (SEM), Positron annihilation lifetime spectroscopy (PALS).

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1. Introduction

Blending has now emerged as a major tool to obtain new polymeric materials with desirable properties. Rubber-plastic blends have been commercialized as rubber-toughened plastics or as thermoplastic elastomers (TPEs) [1-2]. However, most of the thermoplastic/rubber blends are immiscible and incompatible. In general, the physical, mechanical and rheological properties of immiscible polymer blends depend not only on the constituent polymers but also on the morphologies of the blends Due to the deformable nature of the minor phase in immiscible polymer blends a wide range of morphologies can be obtained during melt processing. Thermoplastic elastomers from the blends of polyesters and rubbers have gained a lot of interest in recent years.

Sorona® is the trade name for a new generation of polymer from Du Pont. The polymer is basically poly (trimethylene terephthalate) made by the condensation polymerization of 1, 3-propanediol and terephthalic acid or dimethyl terephthalate. The new polymer, Sorona®, has exceptional properties like softness, stretch with recovery, resilience, stain resistance, easy dyeablity for fibers and high air impermeability.

Blends of Sorona® and EPDM are a new class of TPEs that combine the excellent engineering properties of Sorona® and the elastic and ozone resistant properties of EPDM rubber. However, these blends are highly immiscible and incompatible due to the high polarity difference between the component polymers.

The main objectives of the present study are to analyze the phase morphology of the compatibilized and uncompatibilized blends of Sorona® with EPDM as a function of blend composition and concentration of compatibilizer added.

2. Experimental

2.1 **Materials**

Sorona® was supplied by DuPont, USA and EPDM was supplied by DSM, Netherlands (Keltan® 720). EPM-g-MA was supplied by Exxon Chemical Company.

2.2 *Melt Blending*

The blending was carried out in Haake Rheocord mixer at a temperature of 235 ^{0}C and a rotor speed of 60 rpm with a mixing time of 4 minutes.

2.3 *Phase Morphology Studies*

For phase morphology analysis, the samples were cryogenically fractured using liquid nitrogen. SEM photographs of the fractured surfaces were taken after preferential extraction of the minor phase. The dispersed phase size analysis was done using an automatic image analyzing technique.

2.3 *Free Volume Studies*

The free volume studies to evaluate the compatibility of the blends were done using Positron annihilation lifetime spectroscopy (PALS) [3-5]. In PALS studies two parameters are measured mainly o-Ps life time (τ_3) and o-Ps intensity I_3. τ_3 is a measure of the number of free volume sites in the polymer matrix. Using τ_3, the radius of free volume sites R in the blend matrix is computed and then its volume V_{13} .The fractional free volume is given by

$$F_v = C\, I_3\, V_{13} \qquad (1)$$

3. Results and Discussion

3.1 *Morphology of the uncompatibilized blends*

The morphology of the Sorona®/EPDM blends over the entire range of composition can be understood from the SEM micrographs. Figure1(a) and 1(b) shows the SEM of the fracture surface of 90/10 and 70/30 blends. The holes in the figures indicate the EPDM phase that has been preferentially extracted by the solvent. The blend viscosities are in between those of the component homopolymers. In the present study, viscosity ratio was found to be 5.794, when EPDM form the dispersed phase. Since the Sorona matrix viscosity is low, the EPDM coarsening is highly favored. The phase coarsening of Sorona®, when it was the dispersed phase (viscosiy ratio = 0.1726), is marginal compared to that of EPDM phase. This is associated with the high viscosity of EPDM.

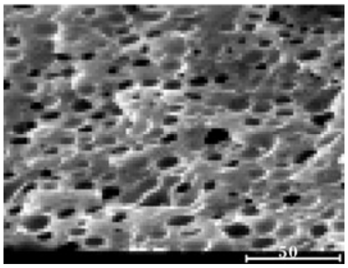


Figure 1 (a)

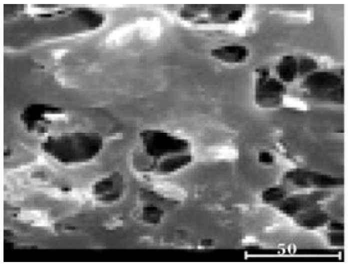
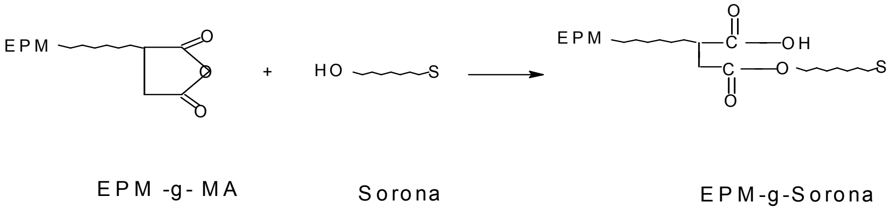


Figure 1 (b)

3.2 *Morphology of Compatibilized Blends*

3.2.1 *Compatibilization strategy*

The present compatibilization strategy involves the compatibilization of Sorona $^{®}$ with a second immiscible phase (EPDM) by the introduction of a compatibilizer precursor (EPM-g-MA) which is physically miscible with the EPDM phase but has chemical functionality (maleic anhydride group) which can react with the hydroxyl end group of Sorona$^{®}$ to form a graft copolymer at the interface as shown in reaction scheme 1.



The formation of graft copolymer, EPM-g-Sorona, at the interface is evident from the torque measurements. The equilibrium torque measured for uncompatibilised Sorona/EPDM (30/70) blend was found to be 5.8 Nm and for the blend compatibilised with 5 wt% EPM-g-MA was 6.7 Nm. The torque increase is due to the grafting reaction at the interface, which in turn brings down the interfacial tension and greatly promotes intermixing, which normally leads to increased viscosity.

3.2.2 *Effect of EPM-g-MA on the morphology of the blends*

Figure 2(a) and 2(b) shows the morphology of the 70/30 Sorona$^{®}$/EPDM blends containing 1 and 5 wt % EPM-g-MA respectively. It can be seen that the size of the dispersed EPDM phase decreases with the addition of a few percentage of EPM-g-MA followed by a leveling off at higher concentration. A similar behavior was observed for all other blend compositions. The reduction in particle size with the addition of the functionalized EPM is due to the stabilization of the blend morphology by the graft copolymer (EPM-g-MA) formed during melt mixing. The formed graft copolymer reduces the interfacial tension and suppresses the coalescence behavior. In addition, the presence of the graft copolymer at the blend interface broadens the interfacial region through the penetration of the copolymer chain segments into the corresponding adjacent phases

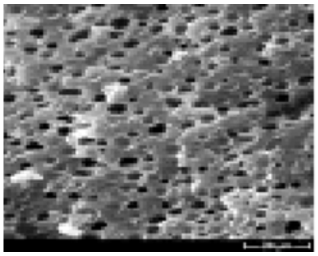


Figure 2 (a)

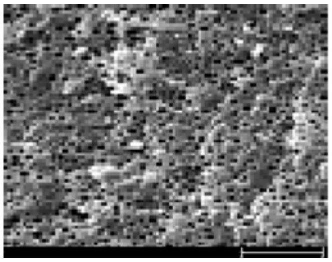


Figure 2 (b)

The variation of polydispersity index (D_w/D_n) as a function of EPM-g-MA is represented in Figure 3. It is seen that the polydispersity index decreases with increasing concentration of EPM-g-MA followed by a leveling of at higher concentration.

The interfacial area per unit volume of the blend has been estimated using the equation

$$a = 3\varphi_A/R \qquad (2)$$

where φ_A is the volume fraction of the dispersed phase and R radius of the dispersed phase. The interfacial area per unit volume of the blend as a function of weight percentage of EPM-g-MA is presented in Figure 4. It was found that the interfacial area per unit volume increases with the addition of a few weight percentage of EPM-g-MA followed by leveling off. This also indicates interfacial saturation.

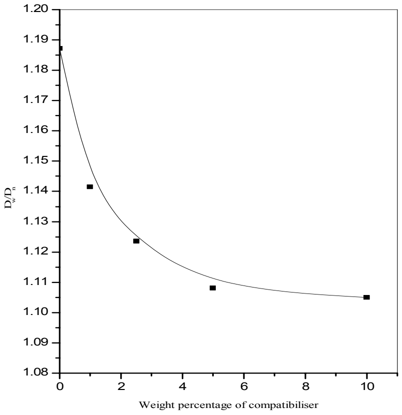


Figure 3

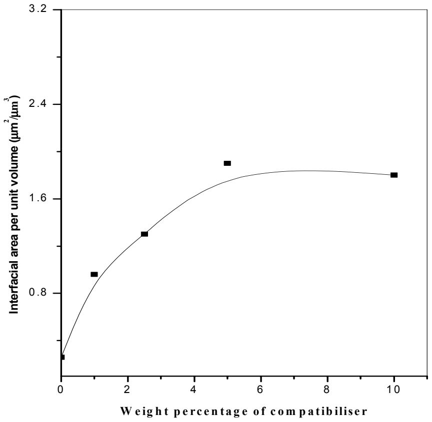


Figure 4

According to Tang and Huang [6] the change in the interfacial tension with the concentration of compatibilizer is directly proportional to the interfacial tension difference.

$$\text{ie} \qquad -d\gamma / dc = K (\gamma - \gamma_s) \tag{3}$$

where γ is the interfacial tension at a compatibilizer concentration C, γ_s is the inter facial tension at the saturation concentration and K is the rate constant for the change in interfacial tension with concentration of the compatibiliser. The K value is expected to increase with the level of compatibilization and decrease with the degree of self-association in the blend [6-7].

Average radius (R) of the dispersed phase is given by [6]

$$R = (Ro - Rs)\, e^{-KC} + Rs \tag{4}$$

where Ro and Rs are the average radii of dispersed domains at compatibilizer concentration zero and at saturation respectively and C is the concentration of compatibilizer. The changes of average radius of domains with compatiblizer concentration were fitted to Equation (4). The fitted parameters for R_n and K values are given in Table 1. Here K value increases up to about 5-wt% of compatibilizer and then decrease with further increase in compatibilizer concentration depicting the micelle formation.

Table 1

Wt % of compatibilizer.	Radius (R) (µm)	K – Value
0	4.062	0
1.0	2.700	23.802
2.5	1.915	25.21
5.0	1.553	30.04
10	1.596	15.134

3.2.3 Comparison of the experimental compatibilization data with theory

Noolandi and Hong proposed a general theory for two immiscible homopolymers A and B diluted with a solvent in the presence of a diblock copolymer [8-10]. The interfacial tension in these systems was evaluated from free energy considerations. Their model was based on the assumption that part of the copolymer that does not localize at the interface will be randomly distributed in the bulk of the homopolymers phase as micelles. Localization of the copolymer however results in a decrease in the entropy and ultimately limits the amount of copolymer at the interface. The separation of the blocks and the consequent stretching of the blocks into the corresponding homopolymers also causes a decrease in entropy. However the main contribution to the reduction in interfacial tension is the entropy loss of the copolymer that localizes at the interface. An analytical expression for the interfacial tension reduction was derived by Noolandi and Hong neglecting the conformational entropy. According to their equation

$$\Delta\gamma = d\phi_c [(1/2\chi\phi_p+1/Z_c)-1/Z_c \exp (Z_c\chi\phi_p/2)] \tag{5}$$

where d is the width at half-height of the copolymer profile reduced by the Kuhn statistical segment length, ϕ_c the bulk copolymer volume fraction of the copolymer, ϕ_p the bulk volume fraction of the polymer A or B, Z_c is the degree of polymerization of the copolymer and is the Flory-Huggins interaction parameter between A and B segments. Noolandi and Hong [8] further suggested that both copolymer molecular weight and concentration are equally important in reducing the interfacial tension. They noted that the interfacial tension surface is bounded by a critical micelle concentration curve, as blocks of large molecular weight tend to form micelles in the bulk of the homopolymers phases. Therefore the theoretical treatment of Noolandi and Hong is valid only for concentrations below CMC. For concentrations below CMC, the interfacial tension is expected to decrease linearly with copolymer concentration, whereas for concentrations above CMC a leveling off is expected. Noolandi further suggested that in the absence of a solvent the equation (5) reduced to

$$\Delta\gamma = d\phi_c [(1/2\chi+1/Z_c)-1/Z_c \exp (Z_c\chi/2)] \tag{6}$$

As the interfacial tension reduction is directly proportional to the particle size reduction at low volume fraction of the dispersed phase, as suggested by Wu, it can be argued that

$$\Delta D = K\, d\phi_c [1/2\chi+1/Z_c \exp (Z_c\chi/2)] \tag{7}$$

where K is proportionality constant.

The plot of domain size reduction as a function of the volume fraction of the EPM-g-MA for the 30/70 Sorona®/EPDM blend is shown in Figure 5. It can be seen that at low EPM-g-MA concentration (below CMC), ΔD decreases almost linearly with the increase in volume fraction of the graft copolymer whereas at higher concentration (above CMC) a leveling off is observed in agreement with the predictions of Noolandi and Hong.

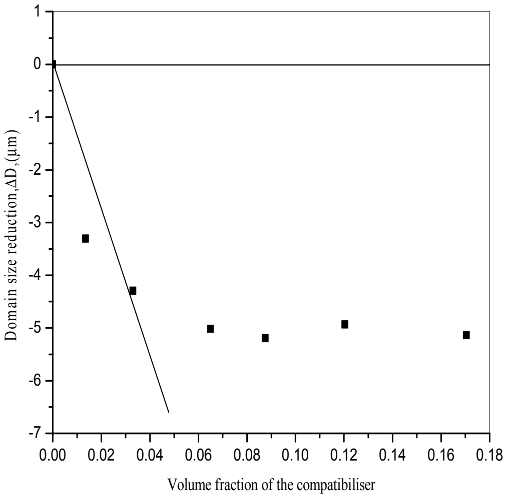


Figure 5

3.3 Free volume measurements of Sorona/EPDM blends.

The free volume measurements was successfully used to study the morphology and compatibility of Sorona®/EPDM blends. In the case of uncompatibilized blends free volume values show a positive deviation. The free volume values increase with addition of EPDM phase because of the very poor physical and chemical interactions across phase boundaries. As a result high extent of void formation can occur. This accounts for the increase in free volume with increase in rubber content. The variation of free volume with weight percentage of EPDM in Sorona/EPDM blends is shown in Fig 6.

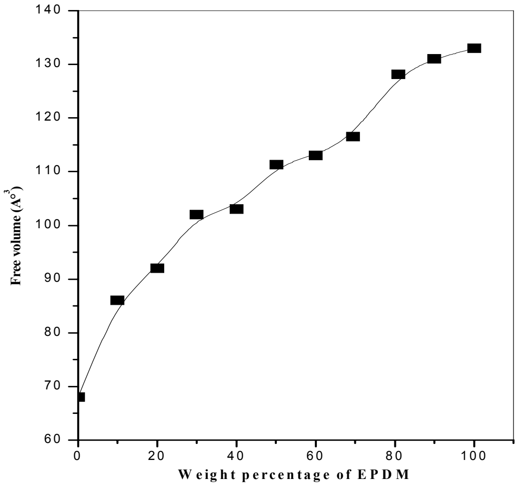


Figure 6

The addition of a compatibilizer (EPM-g-MA) reduces the free volume in Sorona /EPDM blends. The effect of compatibilizer concentration on the free volume of Sorona/EPDM 30/70 blend is shown in figure 7. It was found that a decrease in free volume was noted with the incorporation of EPM-g-MA. This is associated with the high level of interfacial interactions.

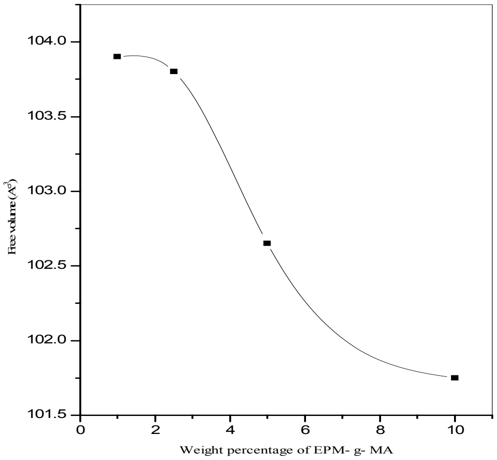


Figure 7

4. Conclusions

The phase morphology of uncompatibilized Sorona®/EPDM blends and blends compatibilized with EPM-g-MA was investigated as a function of composition and compatibilizer concentration. The morphology indicated a two-phase structure. The incompatible blends were compatibilized by the addition of EPM-g-MA. The compatibilzing action of EPM-g-MA was associated with the reaction between the anhydride group of EPM-g-MA with hydroxyl group of Sorona leading to the formation of a graft copolymer at the blend interface. The domain size of the dispersed phase was found to decrease with the increasing concentration of the EPM-g-MA followed by a leveling off at higher concentrations, which is an indication of interfacial saturation. The experimental result was in agreement with the predictions of Noolandi and Hong. The K-value obtained from the equation suggested by Tang and Huang shows that the level of compatibilization increases upto 5wt% of the compatibilizer and then decreases with further increase in compatibilizer concentration showing the aggregation of the compatibilizer or the formation of micelles. Free volume measurements using Positron Annihilation Lifetime spectroscopy shows positive deviation in free volume for the uncompatibilized blends showing poor compatibility. However the addition of EPM-g-MA tends to decrease the free volume depicting its compatibilizing effect.

5. References

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