

Mechanical Properties and Morphology of ER/PS Blends.

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ABSTRACT

Thermoplastic elastomeric blends of Polystyrene (PS) and Exudated Resin (ER) with different compositions have been prepared by solution casting method. The mechanical performance of this system has been studied in detail. Stress-stain behavior, tensile strength, elongation at break and young's modulus was determined. The effect of blend ratio on the mechanical properties and surface hardness has been analyzed. By the addition of ER reduces the plasticity of polystyrene. The blend with 60/40 PS/ER combination exhibited comparatively better mechanical properties. 60/40 PS/ER blend ratio shows higher compatibility between the phases among the series of the blends studied. It is explained on the basis of the morphology of the blend. Various theoretical models such as series, Parallel and Halpin-Tsai have been used to fit the experimental mechanical data. Scanning Electron Microscopy was employed to analyze the surface morphology of the blend.

INTRODUCTION

The technology of polymer blends has been one of the major areas of research and development in polymer science in the past four decades. It has been well established that polymer blends offer a promising solution in solving emerging application requirements. The ability to combine existing polymers into new compositions with commercializable properties offers the advantage of reduced research and development expense compared to the development of new monomers and polymers to yield a similar property profile [1,2,3]. The additivity of the main properties of two polymers results only when these form a multiphase system, whereas only an average value of properties is obtained by homogeneous blends [4,5,6]. A series of extensive studies on cross-linked blends have been carried out by many researchers for various blends [7-14]. The formation of two phase systems is not necessarily an unfavorable event since many useful properties, characteristic of a single phase, may be preserved in the blend while other properties may be averaged according to the blend composition [5]. In an attempt to obtain high performance materials, after an extensive literature survey, exudated resin (ER) from *Ailanthus Malabaricum* tree and polystyrene (PS) have been selected as materials for the present investigation. The elastomeric nature of ER can be used as rubber for some applications and it is too flexible. The stiffness of PS can be easily reduced by blending with ER. As an elastomer of natural origin, ER has many useful features such as biodegradability and elastomeric properties. To the best of our knowledge, no attempt has been made to study ER/PS system so far and is a new system for investigation. If the two phases are sufficiently cross-linked, then the physical and chemical properties of the blend are generally improved. In this paper efforts are made to investigate the morphology and mechanical properties of ER-PS blends. The blend morphology has been correlated with mechanical properties. The influence of blend composition on morphology and mechanical properties has been analyzed. Finally, various theoretical models have been used to compare the experimental results.

MATERIALS AND METHODS

Materials

Polystyrene used in this study was purchased from PolyChem, Ltd. (Bombay, India). It has a solubility parameter of $8.56 \text{ (cal/cm}^3)^{1/2}$, number average molecular weight 3.51×10^5 and density 1.04 g/cm^3 . The Exudated resin was collected from the *Ailanthus Malabaricum* trees cultivated around Sagara, Shivamogga District, Karnataka. Dicumyl Peroxide, Divinyl benzene and Benzene were purchased from HiMedia Laboratories Pvt. Ltd. Mumbai, India.

Preparation of ER/PS blends

Exudated resin was first dissolved in benzene at room temperature and filtered the solution to remove the impurities. The solution was then kept for 6 hours to settle down the polymer part at the bottom of the beaker. After that the top portion was removed from the beaker and bottom part kept in oven at $50 \text{ }^\circ\text{C}$ for 12 hours to evaporate the benzene. The dried sample was used to prepare the blends. Polystyrene and resin were dissolved in benzene and mixed with suitable blend proportions by using a magnetic stirrer. 2 % (w/w) Dicumyl peroxide, the crosslinking agent for elastomer and Divinyl benzene, the crosslinking agent for polystyrene were then weighed and dissolved in benzene. The solution of Dicumyl peroxide and Divinyl benzene were then slowly added to the blend solution and stirred well for 2 hours. Then the solution was transferred to the Petri dish and kept in oven at $70 \text{ }^\circ\text{C}$ for 24 hours. These dried materials were peeled out and compression molded using an electrically heated hydraulic press at $140 \text{ }^\circ\text{C}$ for 20 minutes. The film thickness is reduced to 2 to 2.5 mm. Then the samples were introduced to conduct swelling measurements.

Mechanical Properties

Before the mechanical testing, the test specimens were vacuum dried at $70 \text{ }^\circ\text{C}$ for 3 h to remove the moisture. Tensile testing of the samples was performed at $25 \pm 2 \text{ }^\circ\text{C}$ according to ASTM D412 test method using dumb-bell shaped test specimens at a crosshead speed of 500 mm/min using a Universal testing machine (UTM, SHIMADZU AGI). Hardness (Shore A) was measured according to ASTM D 2240 method using a hardness tester (Shore A durometer). All the values reported are obtained from at least four test results.

Morphology

To investigate the morphology of the blends Scanning Electron Microscopy (SEM) was performed with a JEOL JSM 5800LV instrument. The accelerating voltage is typically in the range of 1-40 kV and current is 20 micro amperes. Samples require surface conductivity, thus a thin layer ($\sim 10\text{nm}$) of a conductive metal (gold or platinum) is sputtered onto the surface.

RESULTS AND DISCUSSION

Mechanical properties

To gain some knowledge about the mechanical properties of thermoplastic elastomeric blends prepared from ER/PS system, the stress-strain behavior was examined for different compositions. The stress-strain plots for various blend ratios are given in Fig. 1. There is a considerable change in the deformation behavior of blends compared to the pure component. As the fraction of ER in the blend increases, stress-strain behavior of the blend is deviated from plastic to rubbery nature. The toughness of the Polystyrene material decreases with the incorporation of elastomeric ER. For blends, the cross-linked structure reduces the chain mobility or freely motion of molecules and the toughness increased. The deformation nature of a given material under an applied load can be understood from the stress-strain curves.

The curve for polystyrene exhibits a typical plastic nature and the initial slope of the curve is higher for polystyrene. With the addition of elastomeric resin into polystyrene gradually reduces the initial slope of the curves. As the ER content increases the initial modulus as well as the yielding tendency decreases. Above 30 % of ER in the blend the curves exhibit elastomeric behavior. On further increasing the ER content, the yield point disappears. Pure elastomeric resin shows a typical elastomeric stress-strain behavior.

The variation of tensile strength with the amount of ER in the blend is shown figure 2. The tensile properties are mainly dependent on the crystallinity of the polymer. A reduction in crystallinity by the addition of elastomers in polystyrene is also expected. As a result, the tensile properties must be decreased by the incorporation of ER in the blend. A drastic reduction in tensile strength is observed with increase in the amount of ER into PS phase. Above the maximum tensile strength the blend sample gets ruptured. It depends completely on

the interaction between the two polymer phases in the blend. A sudden increase in tensile strength is observed for the blends when the amount of PS crosses 50 percent.

Figure 1: Stress-strain plots of ER/PS blends for different blend compositions

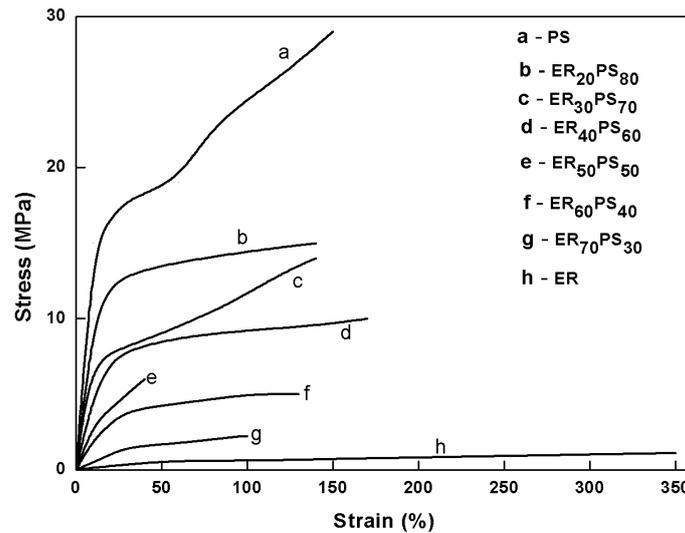


Figure 2: Variation of tensile strength with the amount of PS

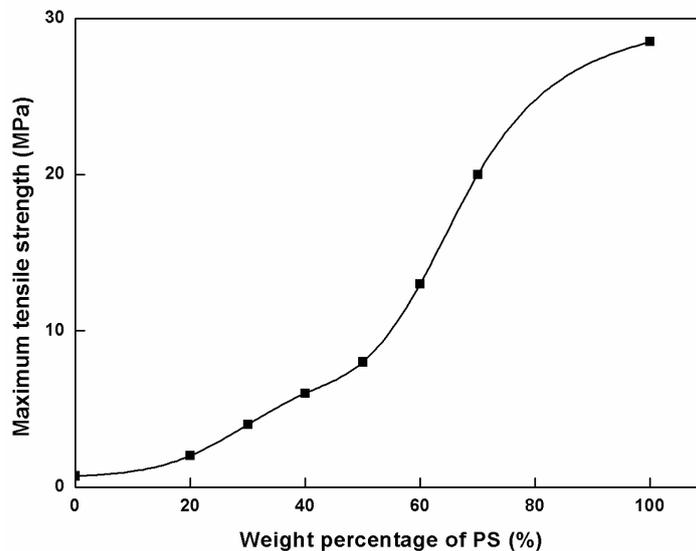


Figure 3 depicts the variation of Young's modulus of the blend system for different compositions. The plot shows a drastic reduction in their values as the ER content in the blend increases. A sharp increase in Young's modulus is observed on exceeding the percentage of PS above 40 % in the blend. The remarkable increase in modulus is due to the presence of high modulus polystyrene as continuous phase. This clearly indicates the enhancement in toughness by the addition of PS into the elastomer. By suitably selecting the appropriate composition of the independent polymer constituents it is possible to obtain the required properties.

Figure 4 shows the effect of percentage of polystyrene on elongation at break. The elongation at break is higher for pure ER. In the case of pure ER, it will relax completely under stress by a flow mechanism. The addition of polystyrene into the elastomeric resin reduces the elongation at break by restricting the free movement of elastomeric chains in the blend. The value decreases as the polystyrene content increases, and is found to be comparatively better for 60/40 blend composition. Further the elongation at break is found to be decreased. A minimum value is observed for the blend with 50 % PS. The low value of the elongation at break can be explained on the basis of the poor adhesion between the two phases in the blend.

The effect of blend ratio on hardness of the blend is shown in Figure 5. The hardness decreases as the elastomer content increases. Polystyrene is crystalline and ER is an amorphous material of poor strength. Therefore as the elastomer content increases the hardness decreases. This is due to the decrease in crystallinity caused by the incorporation of elastomer phases. The enhancement in hardness by the addition of polystyrene is a clear evidence for the significant improvement of plasticity in ER/PS blend system.

Figure 3: Variation of Young's modulus of ER-PS blends with the amount of PS

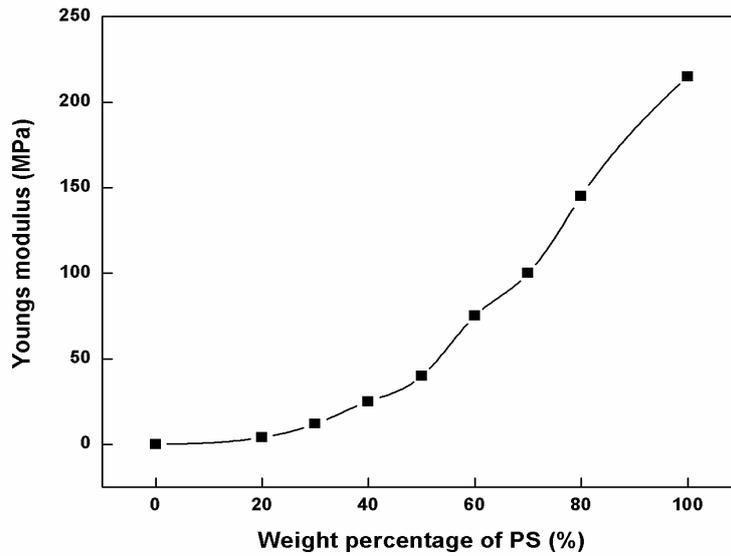


Figure 4: Effect of blend composition on elongation at break of ER-PS blends

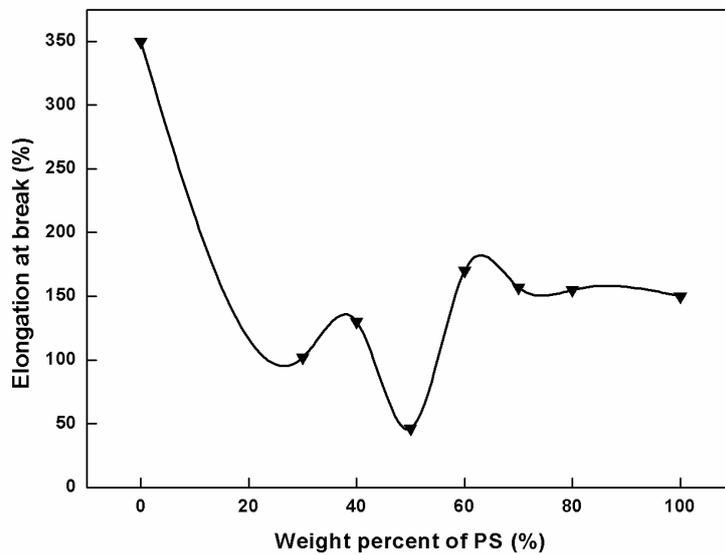
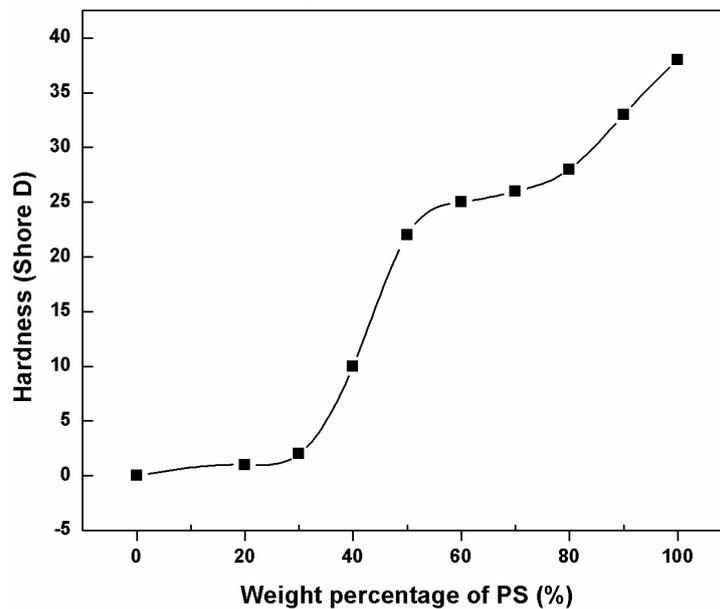


Figure 5: Effect of blend composition on the hardness of ER-PS blends



Theoretical modeling

The mechanical properties of two-phase composites made up of a continuous polymer phase and particulate filler phase have been studied in great detail. As a result, a variety of models are available to describe the modulus, tensile strength, and elongation at break as a function of filler weight fraction. Different models like parallel, series and Halpin-Tsai models have been used to predict the mechanical properties of these blends [15]. The highest-upper bound parallel model is given by the rule of mixtures,

$$M = M_1 \phi_1 + M_2 \phi_2 \quad (1)$$

where M is any mechanical property of the blend. M_1 and M_2 are the mechanical properties of the components 1 and 2 respectively, and ϕ_1 and ϕ_2 are their corresponding weight fractions. In the lowest-bound series model the equation is given as follows,

$$\frac{1}{M} = \frac{\phi_1}{M_1} + \frac{\phi_2}{M_2} \quad (2)$$

Parameters M , M_1 , M_2 , ϕ_1 and ϕ_2 are the same as in the upper limit model.

According to Halpin-Tsai equation,

$$\frac{M_1}{M} = \frac{[1 + A_i B_i \phi_2]}{[1 - B_i \phi_2]} \quad (3)$$

where

$$B_i = \frac{\left(\frac{M_1}{M_2}\right) - 1}{\left(\frac{M_1}{M_2}\right) + A_i} \quad (4)$$

In these models subscripts 1 and 2 correspond to the continuous and dispersed phases respectively. The constant $A_i = 0.66$ when elastomers forms the dispersed phase in continuous hard matrix. On the other hand, if the hard material forms the dispersed phase in a continuous elastomer matrix, then $A_i = 1.5$. In the case of incompatible blends, generally the experimental value is between the parallel upper bound (M_U) and the series lower bound (M_L) values [16].

Figures 6 and 7 show the experimental and theoretical curves of tensile strength and Young's modulus as a function of soft phase volume fraction. This result is almost consistent with our experimental results from morphology and mechanical properties studies. From the various models used for predicting the mechanical properties, it is observed that there is significant adhesion between the phases in the blend. Halpin-Tsai model is highly comparable with the experimental results. This may be due to the interfacial interaction in the blend by cross-linking both the phases. The interfacial interaction is further confirmed from the morphology studies.

Scanning Electron Microscopy of the blends

Scanning electron microscopy is performed to study the surface morphology of the prepared samples. Figure 8 shows the SEM photographs of pure polystyrene and its blend with various ER percentages. Pure polystyrene exhibits a porous nature in the photograph. Micro-scale morphology is a powerful tool to determine the properties of polymer blends. The addition of fillers and elastomers decides the morphology of the blend [17]. By the addition of elastomer into polystyrene reduces the porosity of polystyrene as observed in figure. A better surface morphology is achieved for the blend with 40 percent of ER. The thermoplastic elastomers are phase-separated systems in which one phase is hard and solid while the other phase is rubbery at room temperature. The tensile properties normally depend on the amount of hard phase present. The elastomeric phase interpenetrated into the thermoplastic phase by blending. Consequently the morphology of the blend shows a comparatively better non

porous manner. A fine dispersion of ER in to PS phase is seen in the blend ratio ER₄₀PS₆₀. The elastomer phase controls the stability and physical properties of the resulting products.

Figure 6. Applicability of various models on the tensile strength of the blends

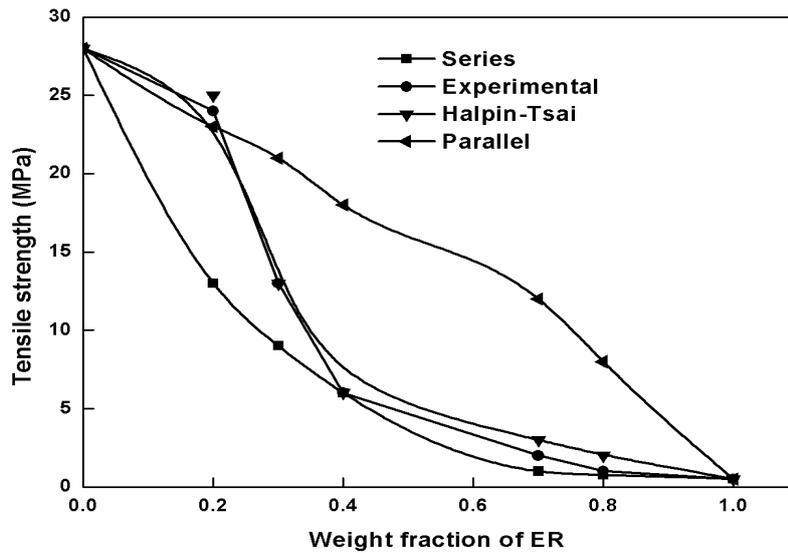
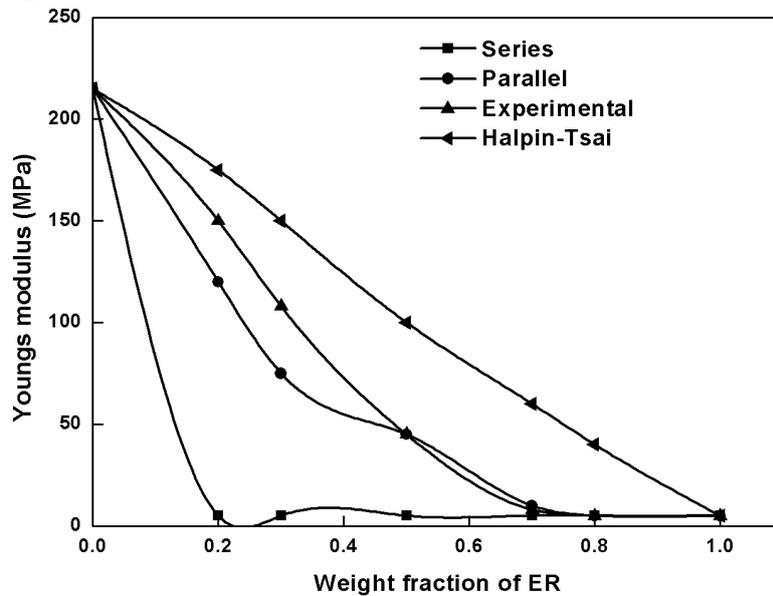
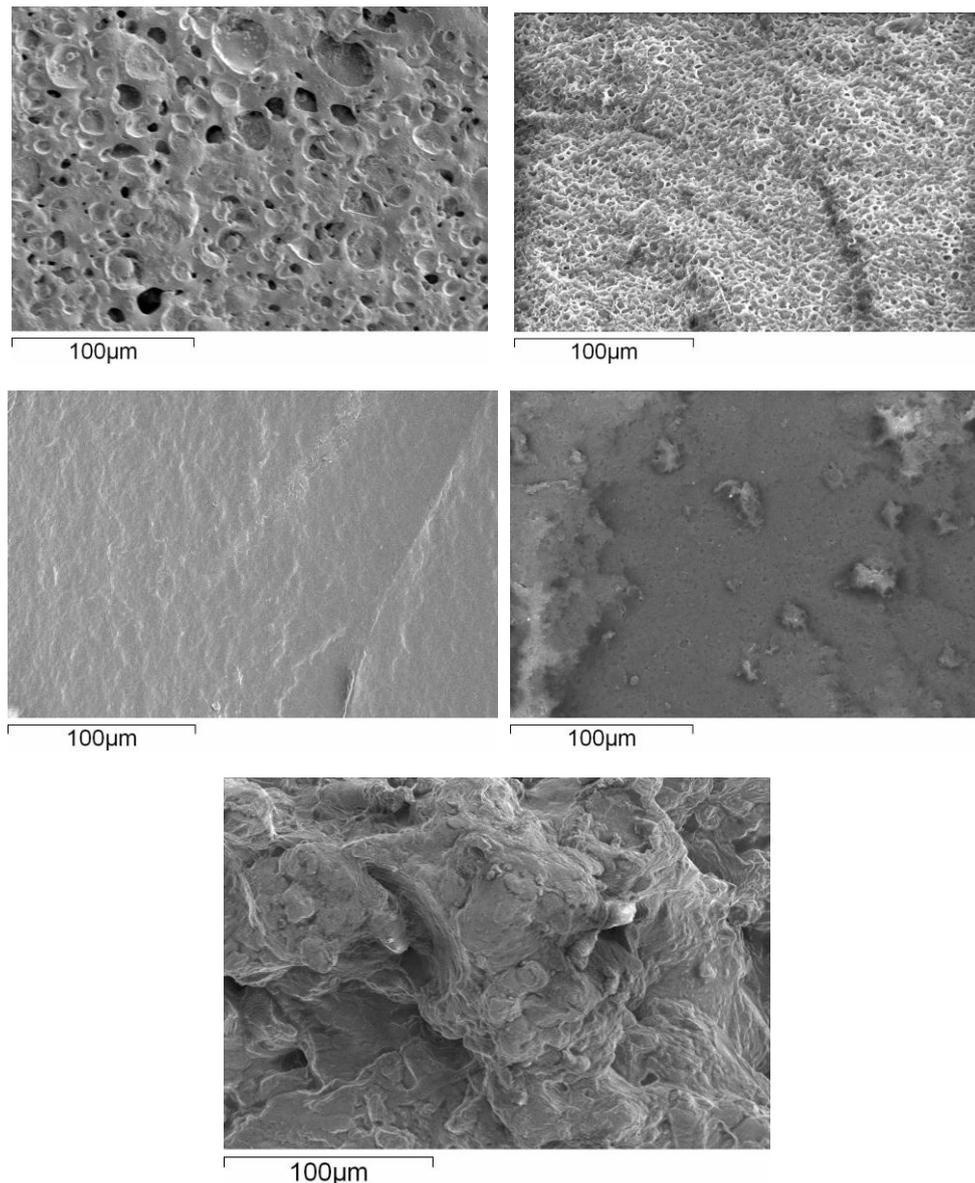


Figure 7. Applicability of various models on the modulus of the blends



Many researchers have attempted to compare the morphology with the physical properties of the blends [17-19]. Initially the elastomer dispersed polystyrene blend interpenetrated each other and reduces the tensile strength by softening the sample. Upon further adding the elastomeric resin into polystyrene enhances the elastomeric or softness of the blend. The blend ratio ER₄₀PS₆₀ exhibits a comparatively better tensile properties especially elongation at break as a result of the fine surface morphology. This may be due to the enhanced interfacial interaction between the two phases in the blend. Elastomeric agglomeration is observed in the photographs above 40 percent ER in the blend. It clearly indicates that the surface morphology has a strong influence in the mechanical stability of thermoplastic elastomeric blends.

Figure 8. Scanning electron micrographs of (a) PS, (b) ER₃₀PS₇₀, (c) ER₄₀PS₆₀ (d) ER₅₀PS₅₀ and (e) ER₇₀PS₃₀



CONCLUSIONS

Morphology of ER-PS blends indicates a two phase structure in which ER is dispersed as domains in the continuous Polystyrene phase at lower proportions, but as the proportion of the ER increases beyond 40 %, this component also exists as a continuous phase. It is found that the minor component appears as the dispersed phase, and its domain size increases with increase of its concentration. The morphology of the blend is found to have a strong influence on the mechanical properties. The mechanical properties are found to increase rapidly beyond 40 wt % of Polystyrene. This abrupt rise in mechanical properties is associated with the fully continuous nature of the polystyrene matrix. Mechanical properties such as tensile strength, Young's modulus and hardness are higher for blends containing higher proportions of polystyrene. The modulus is also found to be maximum for composition of higher plastic content. Almost all properties are found to decrease with the addition of ER, which is due to the reduced crystallinity of the polystyrene and also due to the poor interfacial interaction at the blend interface. Various theoretical models have been used to predict the tensile strength and Young's modulus of the blends. It is found that the model fit the experimental results.

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