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Study, mechanical characterization and mathematical modeling of compatible SEBS blends for industrial applications in orthopedics

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Abstract

In this work, a system of compatible blends based on two commercial grades of a thermoplastic elastomer, styrene-ethylene/butylene-styrene (SEBS), with extreme Shore A hardness values (5 and 90), was studied in order to obtain a range of different performance blends for orthopedic and childcare applications, where usually liquid silicone rubber is used depending on the pathology. Mechanical properties of different blends were obtained by tensile and hardness tests. Equivalent box model (EBM) was used for the prediction of the mechanical behavior of SEBS blends. The results show good agreement between the theoretical model and experimental data. This research validates the results obtained from the mathematical models that simulate the behavior of new blends of SEBS, thus allowing the full range of hardness available and necessary for orthopedic industry.

1. Introduction.

Silicone plastics are characterized by high chemical inertness and stability at high temperatures, so that they find a wide variety of applications at industrial level such as lubricants, adhesives, chemical barrier and in medical devices such as breast implants, prosthetic heart valves. Liquid silicone rubber (SLR) shows interesting uses in applications characterized by high resistance to light exposure, chemical resistance and excellent physiological performance. So that, it is possible to find liquid silicone rubber in technical uses such as automotive industry (protective housing of spark plug covers, rain sensors and headlights' isolation) and electronics (connecting panels, anode covering and electrical connectors)[1-3]. Also, due to its high chemical inertness, liquid silicone rubber is widely used in medical engineering applications such as cardiac catheter, dummies, contact lens and artificial breath masks [4-6]. Nevertheless, processing of LSR requires a previous mixing of two reactive components in a mixing unit, subjected to pressure to achieve crosslinking[7-9]; furthermore it requires the use of specific injection molding machines and accessories which are not applicable to commodity plastics.

For this reason it is interesting to evaluate new materials as candidates for potential substitution of LSR in applications such as footwear and childcare products. These candidate materials must possess similar properties to silicone plastics and additionally, they could be processed by conventional injection molding. Furthermore as recycling of silicone is difficult due to the crosslinked structure, it is interesting that these new candidates show easy recycling and/or upgrading.

Among the wide variety of thermoplastics, which are useful in many industrial applications, thermoplastic elastomers are characterized by excellent balance between

processability (typical of commodity plastics) and excellent physical properties (typical of vulcanized elastomers). In addition thermoplastic elastomers are used in automotive and medical applications as LSR[10-14]. Styrene-ethylene/butylene-styrene (SEBS) polymers are obtained by hydrogenation of styrene-butadiene-styrene (SBS) polymers; this process allows to remove the unsaturation, typical of the butadiene components (carbon-carbon double bonds are saturated with hydrogen) and this has a positive effect on environmental, thermal and UV radiation resistance maintaining, thermoplastic behavior. Thus, SEBS is useful in applications in which the use of SBS is restricted due to its sensitiveness to degradation[15,16]. The excellent aging resistance of SEBS polymers is due to the absence of carbon-carbon double bonds. By varying the relative ratio of the components (styrene, ethylene and butylene) on SEBS formulations, it is possible to obtain a wide range of elastic modulus and hardness values, which allow to increase its use in the industry. Also, SEBS polymers successfully combine elastomeric properties with low processing costs typical of commodity plastics and they are available in white color or even in transparency grades. In addition, SEBS polymers can be processed at relatively low temperatures and shows excellent resistance to high temperatures.

Thus, in this paper we propose to use SEBS as materials for applications in orthopedic and childcare sector with the advantage of processing by conventional injection molding. With this aim, two SEBS with extreme hardness have been analyzed relating to mechanical performance. In addition Equivalent box model (EBM) has been used in order to predict mechanical behavior of SEBS blends.

2. Experimental.

2.1. Materials.

SEBS blends were made using two transparent SEBS commercial grades with extreme hardness values: Megol TA-5 and Megol TA-90 with ShoreA hardness of 5 and 90 respectively, supplied by ApplicazioniPlasticheIndustriali (API). Generic properties of all SEBSMegol TA provided by the manufacturer are shown in Table 1.

Table 1.

2.2. Preparation of blends.

The blends were carried out using a injection molding machine Meteor 270/75 by Mateu& Sole (Mateu& Sole, Barcelona, Spain) with different amounts of Megol TA-5 and Megol TA-90. Blends proposed for the analysis of miscibility and mechanical properties characterization, are shown in Table 2.

Table 2.

Samples for tensile tests were prepared by injection molding after the blending process, with the dimensions according to ISO 527-2. Blending and injection molding conditions used are shown in Table 3.

Table 3.

2.3. Rheological characterization.

The rheological analysis was carried out using a capillary rheometer Thermo Haake Rheoflizer MT (Thermo Fisher Scientific Inc, Newington, USA). A temperature of 185 °C was used for rheological characterization following the injection temperature

recommend by the provider. The rheometer is equipped with three different capillaries, each 1 mm in diameter, but with a coefficient L/D of 10, 20 and 30 (length /diameter). The shear rate used was 100 1/s. The rheological tests were performed according to ISO 11443.

2.4. Mechanical characterization.

The tensile tests were carried out using a universal tensile test machine ELIB 30 (S.A.E. Ibertest, Madrid, Spain) following ISO 527. A 50 mm min⁻¹ crosshead speed was used to determine tensile strength, elongation at break and elastic modulus starting from the tensile graph. All specimens were tested at room temperature. A minimum of 10 samples was analyzed in order to obtain every result. The hardness of SEBS blends was tested using a Shore Adurometer, at a sample thickness of 4 mm.

2.5. Equivalent Box Model (EBM) modeling

In order to model the mechanical characterization of SEBS blends we have used the Equivalent Box Model (EBM). This model combines the parallel and series coupling of components, so it considers that some fractions of the material contribute to the mechanical properties in series, whereas other fractions contribute in parallel, as can be observed in Figure 1. When the adhesion at the material interface is weak, the coupling in series does not contribute to the tensile strength of the blend, and hence this can only be defined by the in parallel contribution (equation 1).

$$\sigma_{R(\min)} = \sigma_1 \cdot v_{1p} + \sigma_2 \cdot v_{2p} + A \cdot \min(\sigma_1, \sigma_2) \cdot v_s \quad (1)$$

where σ_b is the tensile strength of the blend; σ_1 and σ_2 is the tensile strength of each of the components; v_{1p} and v_{2p} is the volume fraction in parallel (co-continuous) of component 1 and 2 respectively; $\sigma_{b \min}$ is the minimum tensile strength of the

components considered; v_s is the total volume fraction in series and A is a term related to the interfacial adhesion between the phases of the different components. Thus, values of A parameter close to 0 are representative of low interfacial adhesion; on the contrary values of A parameter close to 1 are representative of high interfacial adhesion between the different phases of the blend.

Regarding to elastic modulus, the equation 2 shows the elastic modulus determination by EBM.

$$E_b = (E_1 \cdot v_{1p} + E_2 \cdot v_{2p}) + \frac{v_s^2}{\left[\left(\frac{v_{1s}}{E_1} \right) + \left(\frac{v_{2s}}{E_2} \right) \right]} \quad (2)$$

Where E_b is the elastic modulus of the blend; E_1 and E_2 is the elastic modulus of each of the components; v_{1p} and v_{2p} is the volume fraction in parallel (co-continuous) of component 1 and 2 respectively; v_{1s} and v_{2s} is the volume fraction in series of component 1 and 2 respectively, and v_s is the total volume fraction in series.

The percolation theory has been used to determine the fractions of each component, which work in parallel. This theory has supplied satisfactory results in polymer blends systems[1, 2], where the critical volume fraction has been established, within which co-continuity between the phases is possible. Thus, v_{1p} and v_{2p} can be calculated according to equations (3) and (4):

$$v_{1p} = \left[\frac{v_1 - v_{1crit}}{1 - v_{1crit}} \right]^{T_1} \quad (3)$$

$$v_{2p} = \left[\frac{v_2 - v_{2crit}}{1 - v_{2crit}} \right]^{T_2} \quad (4)$$

where v_{cr} is the percolation threshold representing the critical value of the volume fraction, and T is the critical exponent[3].

The relation between the tensile strength value obtained experimentally and those obtained according to the EBM allows the value of A to be established, thereby offering the best adjustment. This value of A is related with the adhesion between the phases and to a certain degree, of the compatibility between the constituents of the blend [6].

3. Results and discussion.

3.1. Blend viscosity.

The viscosity study of the two SEBS materials studied and their blends system allow to determine the behavior relating to processability. Figure 2 shows the evolution of viscosity of TA-5 and TA-90 SEBS and their blends as a function of SEBS TA-90 amount. It can be observed a high difference of viscosity between the two studied polymers. SEBS TA-5 shows a low viscosity close to 40 Pa·s, meanwhile TA-90 rises to 130 Pa·s, this represents an increase of 325%. In addition as it can be expected the viscosity of SEBS blends increase with the amount of polymer with higher viscosity (SEBS TA-90).

Figure 2

3.2. Mechanical characterization.

Figure 3 shows the variation of tensile strength as a function of composition of SEBS blends of Megol TA-5 and TA-90. As it can be observed, the tensile strength of Megol TA-5 is strongly lower than TA-90, rising from 0.76 to 6.35 MPa for TA-5 and TA-90 respectively. In addition, in SEBS blends, the tensile strength increases with the

amount TA-90. Also, the increase of tensile strength is lower for low content of TA-90 and for higher contents the tensile strength increase abruptly. So for a blend with 30 and 50 wt% of TA-90, the tensile strength results 1.23 and 1.66 MPa respectively, meanwhile for SEBS blend with 70 wt% the tensile strength is nearly 2.9 MPa.

Figure 3

With regard to the elongation at break, it is foreseeable that the incorporation of a SEBS with higher hardness (TA-90), characterized by a lower capacity of deformation than TA-5, may cause a decrease in the elongation at break in the blend. As Figure 4 shows, a decrease on elongation at break occurs with the TA-90 amount. Moreover, it can be observed that there are minimum values of elongation at break with values lower than SEBS-TA-90 for blends in the range 10-40 wt% of TA-5.

Figure 4

Figure 5 shows the variation of tensile modulus as a function of SEBS blend composition. As it can be observed, the incorporation SEBS TA-90 to blend, induces a higher increase in the tensile modulus, ranging the tensile modulus values from 0.11 to 5.48 MPa. It should be emphasized that the elastic modulus of SEBS reach much lower values compared with traditional thermoplastic. These values are typical of SEBS due to elastomeric nature of this polymer.

Figure 5

On the other hand Figure 6 shows the stress-strain plots for SEBS blends with different compositions. The tensile test curves shows a clear tendency on both increase tensile strength-elastic modulus and decrease on elongation at break with the SEBS TA-90 amount. The values of tensile strength for 100% of elongation at break, range from 0.11 to 5.48 MPa for TA-5 and TA-90 respectively. Thus, it can be found a wide range of mechanical performance: a higher mechanical resistance is shown in those blends with high content in SEBS with highest hardness (TA-90) and otherwise a higher ductile properties are obtained in those blends with high content in SEBS with lowest hardness (TA-5). By this way, the SEBS blend composition determines the mechanical behavior in order to achieve the suitable application.

Figure 6

With regard to hardness, Shore A hardness has been analyzed for over the whole concentration range in SEBS blends system. Figure 7 shows the variation of Shore A hardness as a function of SEBS blend composition. In the system SEBS TA-5/TA-90 and increase in the hardness, proportional to the concentration of SEBS TA-90 is produced. The results obtained for all the blends indicate a linear correspondence between the hardness and the composition of the blend.

Figure 7

3.3. Mechanical characterization modeling

Data obtained for tensile strength and elastic modulus from tensile test can be fitted to the Equivalent Box Model (EBM) described previously. So experimental

data from elastic modulus and tensile strength are confronted to values derived from EBM in order to validate the model and allow to predict the mechanical behavior of SEBS blends system for a given composition.

We have considered $T_1 = T_2 = 1.8$ value in between 1.7 and 1.9, the interval where most experimental values are located. Regarding to percolation threshold, we have established $v_{cr1} = 0.15$ $v_{cr2} = 0.18$. The difference of percolation threshold values is justified by the difference of viscosities of two components of the blends [4, 5]. So, the component with lower viscosity in the blend melt (SEBSTA-5) preserves higher phase continuity than the other component (SEBSTA-90). This means that the volume fraction necessary for a co-continuous phase of SEBS TA-5 is 15% and for SEBS TA-90 component is 18%.

Figure 8 shows the comparison of experimental data of elastic modulus with predicted values based on the EBM as a function of blend composition. As it can be observed the curve fits quite accurately in position and shape with the data obtained from EBM. This agreement between experimental and EBM data validates the EBM application in SEBS blends for determining the elastic modulus.

Figure 8

With regard to tensile strength, in figure 9 can be observed the experimental data of tensile strength versus data obtained from EBM. The relation between the tensile strength values obtained from tensile test and those obtained according to the EBM allows to establish the value of A parameter, thereby offering the best adjustment. This value of A is related with the adhesion between the phases and to a certain degree of the compatibility between the components of the blend. In analyzed SEBS blends, the value

of A, which provides the best adjustment with respect the experimental values, is around 0.2. This indicates a lower interfacial adhesion of the existing phases in SEBS blends, mainly due to great difference of viscosity between the two SEBS TA-5 and TA-90 as was explained previously.

Figure 9

Regarding to Shore A hardness, it is possible to establish an empirical relation capable of predicting the hardness of a specific composition. This relation is according to the linear mixing rules for miscible binary polymer blends as equation (5) shows:

$$H_B = H_A \times v_A + H_B \times v_B \quad (5)$$

Where H_B is the hardness in the blend, H_A is the hardness of the SEBS TA-5, and v_A is the fraction in volume of the incorporated SEBS TA-5, H_B is the hardness of the SEBS TA-90, and v_B is the fraction in volume of the incorporated SEBS TA-90.

In Figure 10 can be observed a comparison of experimental Shore A hardness with predicted values based on the mixing rule for different SEBS blend composition. This fact can be attributed to the special nature of the hardness with regard to other mechanical properties, such as tensile strength, more sensitive to compatibility levels of the components in the blend.

4. Conclusions.

The mechanical characterization of polymer blends based on two SEBS blends with very high hardness differences, reveal a clear tendency on increase tensile strength and elastic modulus, opposite to a decrease on elongation at break with the amount of SEBS

high hardness. By this way, the SEBS blend composition determines the mechanical behavior in order to achieve the suitable application.

Data obtained from equivalent box model (EBM) shows a reasonable agreement with the experimental data obtained from tensile test, so the EBM application has been validated. In addition, the adjustment of the tensile strength value using the EBM allows to quantify the interfacial adhesion of the existing phases in SEBS blends. The low result obtained is due to great difference of viscosity between the two SEBS TA-5 and TA-9, which prevents the correct compatibility of the components that form the blend.

In contrast, the hardness evolution for SEBS blends are similar to linear mixing rules typical of miscible binary polymer blends due to the hardness is not so influenced by low levels of compatibility and high viscosity differences.

The use of SEBS blends represents an interesting solution in the orthopedic industry where the mechanical properties required are variable according to customer needs. By this way, the study of SEBS blends developed in this work, has allowed to validate a model for predicting the mechanical performance, which will assist in the choice of the most suitable blend as a function of its application.

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Figure captions

Figure 1. Equivalent box model for a binary blend.

Figure 2. Variation of viscosity as a function of SEBS blend composition

Figure 3. Variation of tensile strength as a function of SEBS blend composition.

Figure 4. Variation of elongation at break as a function of SEBS blend composition.

Figure 5. Variation of elastic modulus as a function of SEBS blend composition.

Figure 6. Comparison of stress-strain plots for SEBS blends with different compositions.

Figure 7. Variation of Shore A hardness as a function of SEBS blend composition.

Figure 8. Comparison of experimental data of elastic modulus with predicted values based on the EBM for different SEBS blend composition. Percolation parameters: $v_{cr1}=0.15$; $v_{cr2}=0.18$ and $T_1=T_2=1.8$.

Figure 9. Variation of tensile strength as a function of SEBS blend composition when compared with predicted values based on the EBM for different A parameters values. Percolation parameters: $v_{cr1}=0.15$; $v_{cr2}=0.18$ and $T_1=T_2=1.8$.

Figure 10. Comparison of experimental Shore A hardness with predicted values based on the mixing rule for different SEBS blend composition

Table 1.Main properties of SEBSMegol TA.

Shore hardness range	5-90 A
Compatibility	PP-PE-EVA
Ageing resistance Ozone (72h - 40°C - 200ppcm)	Excellent
Weathering	Excellent
Density (g/cm ³)	0.88-0.89
Tear strength w.n. (KN/m)	22-44
Tensile modulus 100% elongation (MPa)	1.1-4.2
Tensile modulus 300% elongation (MPa)	1.9-5
Tensile strength (MPa)	6-7.2
Elongation at break (%)	700-550

Table 2. Blends composition used for analysis of miscibility and mechanical characterization.

Blend ID	SEBS TA-90wt%	SEBS TA-5wt%
B01:0-100	0	100
B02:10-90	10	90
B03:20-80	20	80
B04:30-70	30	70
B05:40-60	40	60
B06:50-50	50	50
B07:60-40	60	40
B08:70-30	70	30
B09:80-20	80	20
B10:90-10	90	10
B11:100-0	100	0

Table 3. Blending and injection molding conditions used for preparing samples for tensile test.

Injection rate	35%
Injection distance	294 dmm
Injection shot	150 dmm
Filling	144 dmm
Holding pressure	15%
Holding time	10 s
Charge distance	294 dmm
Suction distance	0 dmm
Mold temperature	40 °C
Cooling time	11 s
Clamp pressure	54 Tm

Figure 1. Equivalent box model for a binary blend

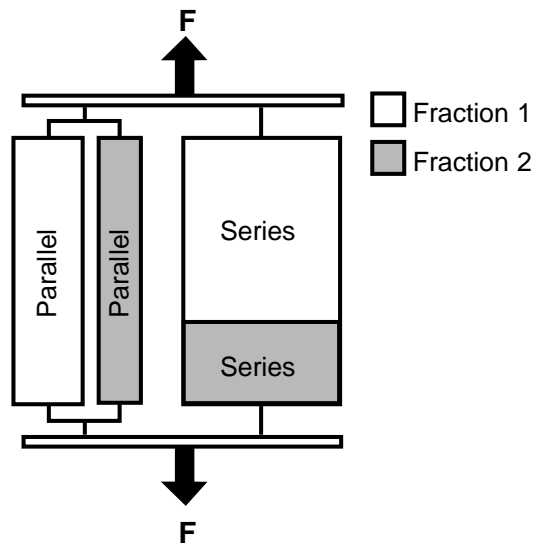


Figure 2. Variation of viscosity as a function of SEBS blend composition.

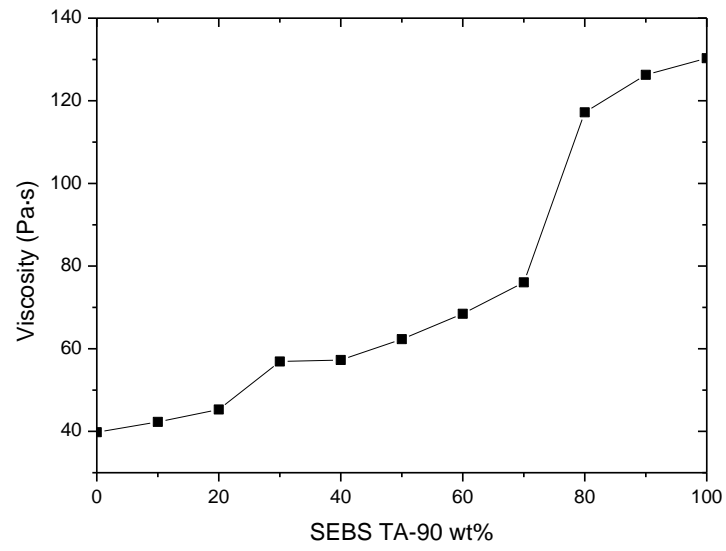


Figure 3. Variation of tensile strength as a function of SEBS blend composition.

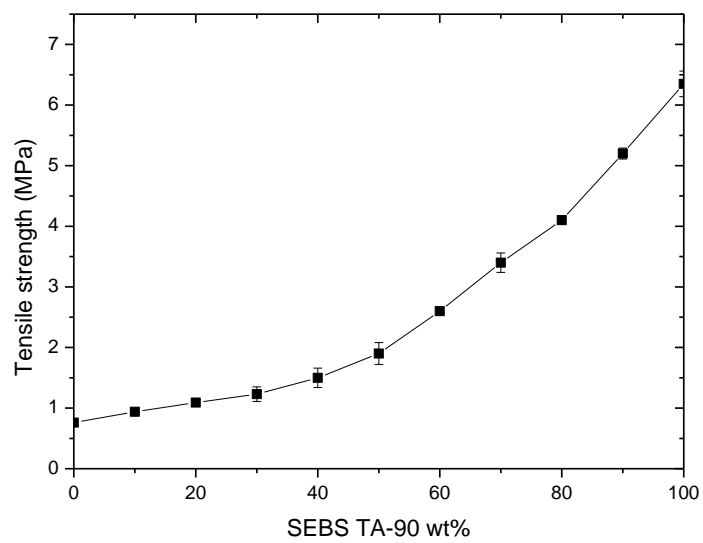


Figure 3. Variation of elongation at break as a function of SEBS blend composition.

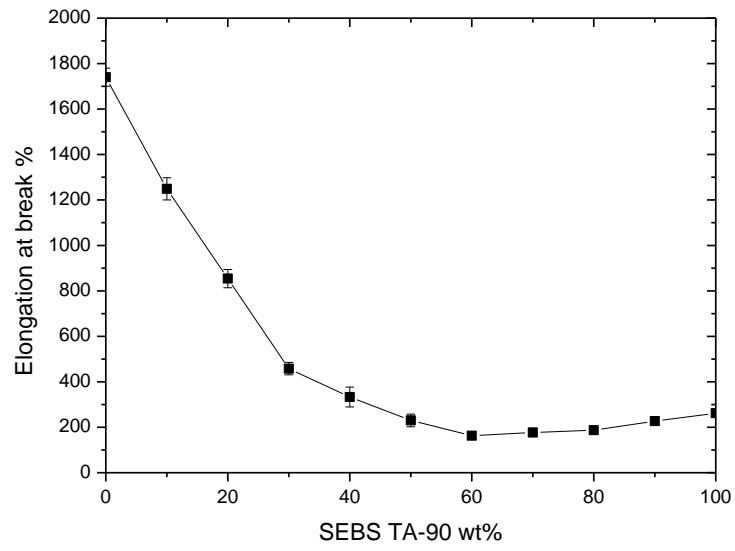


Figure 3. Variation of elastic modulus as a function of SEBS blend composition.

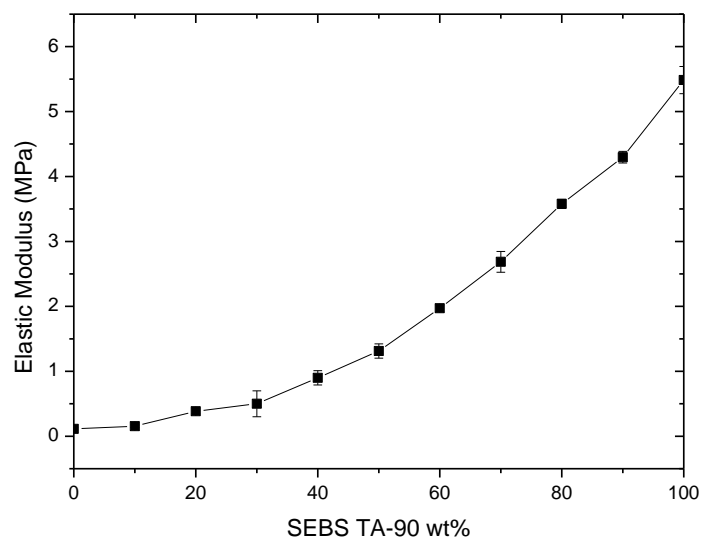


Figure 5. Comparison of stress-strain plots for SEBS blends with different compositions.

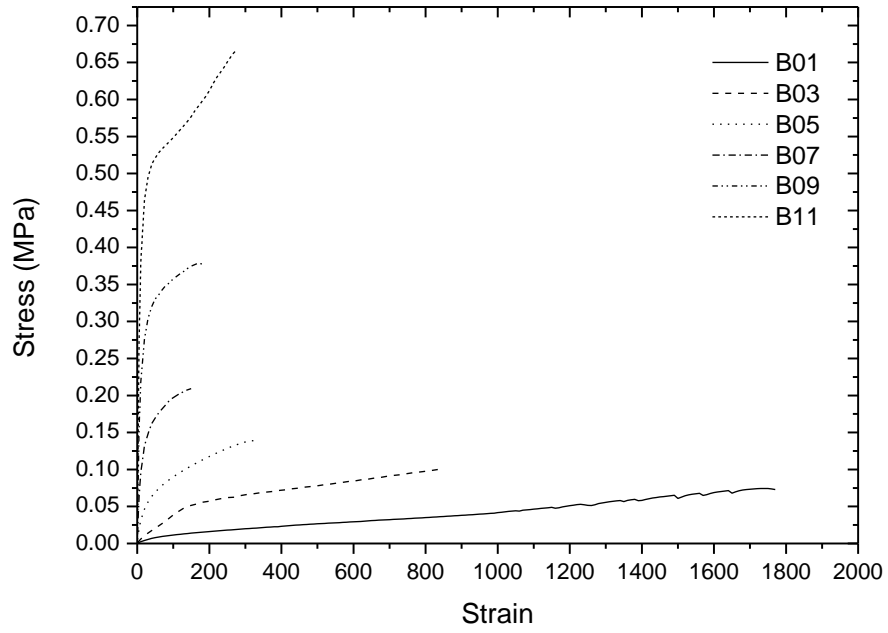


Figure 6. Variation of Shore A hardness as a function of SEBS blend composition.

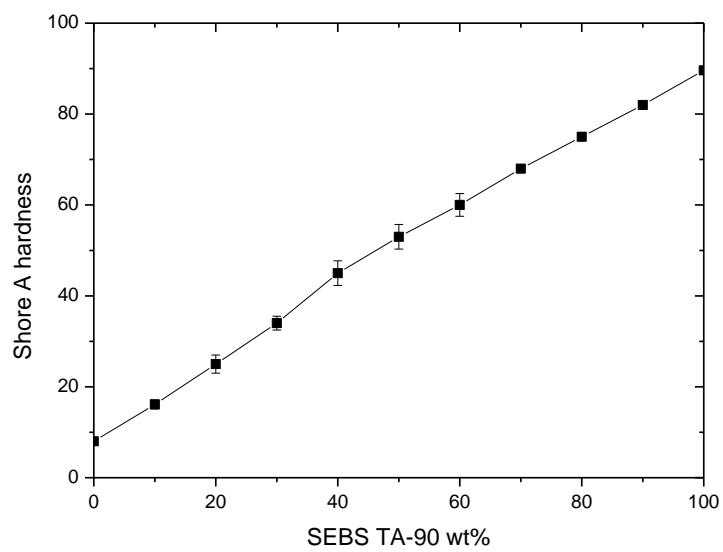


Figure 7. Comparison of experimental data of elastic modulus with predicted values based on the EBM for different SEBS blend composition. Percolation parameters: $v_{cr1} =$

0.15; $v_{cr2} = 0.18$ and $T_1 = T_2 = 1.8$.

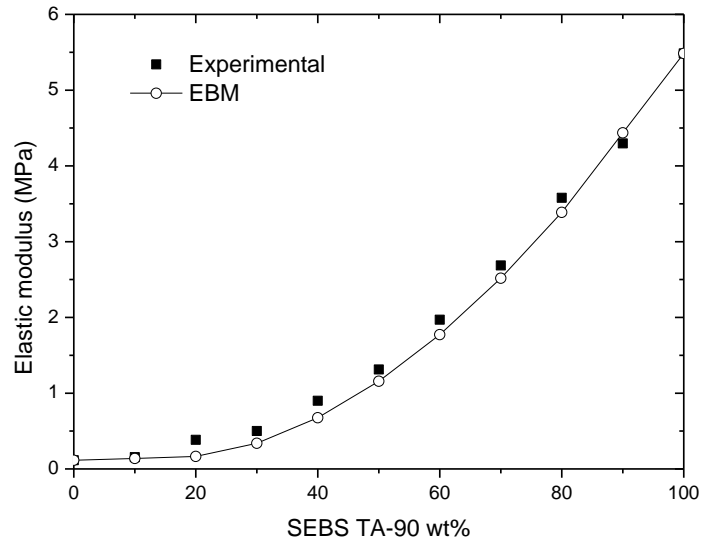


Figure8. Variation of tensile strength as a function of SEBS blend composition when compared with predicted values based on the EBM for different A parameters values.

Percolation parameters: $v_{cr1}=0.15$; $v_{cr2}=0.18$ and $T_1=T_2=1.8$.

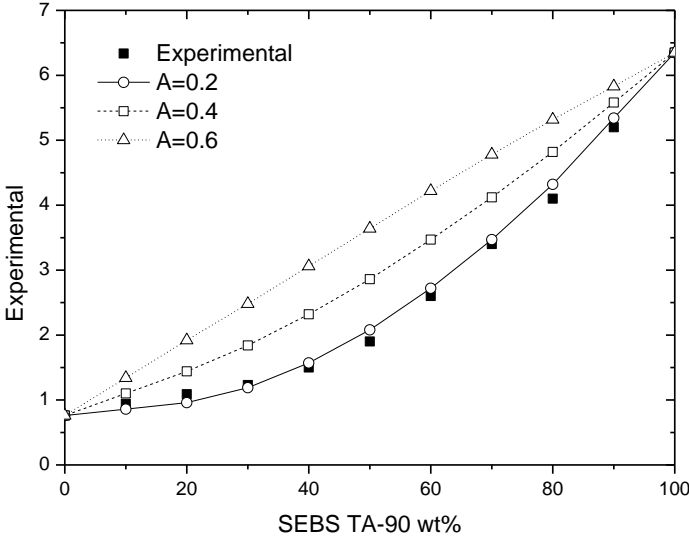


Figure 9. Comparison of experimental Shore A hardness with predicted values based on the mixing rule for different SEBS blend composition

