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Mechanical properties and morphology of low density polyethylene/polydimethylsiloxane immiscible blends: modeling and influence of curing agent

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Abstract: The tensile behavior of low density polyethylene/polydimethylsiloxane immiscible blends was investigated with respect to morphological variation of the blends. Experimental data of elastic modulus was compared with theoretical predictions of parallel model (mixing rule), as the upper bound of modulus, Halpin-Tsai model, and a two-parameter equivalent mechanical model proposed by Kolarik, which takes into account the continuity of minor phase. As the predictions of these models were not in good quantitative agreement with experiment, some modifications were made to the Kolarik model. Furthermore, a new approach for determining equivalent mechanical model parameters was proposed based on the calculation of phase continuity parameters as a function of composition. Using this approach, the values predicted for elastic modulus were found to be in good agreement with the experimental data. Moreover, the influence of a peroxide curing agent on the tensile properties of the blends was studied. The improvement of the tensile properties of the blends could have resulted from two contributions: the effect of curing reaction on the tensile properties of constituents and the better interfacial adhesion, because of possible interfacial reaction, as indicated by morphological observation.

Introduction

Blending is one of the easiest and most cost-effective ways of preparing new polymeric materials with desirable properties. However, because of the lack of special interactions and low entropy of mixing, most polymer pairs are immiscible and blending leads to heterogeneous materials. The properties of these polymer blends are to a large extent determined by their morphology - i.e. the size, shape and distribution of the components – which in turn is determined by several factors such as composition, interfacial tension, rheological properties of components, and processing conditions.

Mechanical properties are among those properties of immiscible blends which show strong dependency on morphological features. In the case of droplet-matrix morphology, tensile behavior of a blend is mainly determined by the matrix phase, while in the case of fibrous morphology the dispersed phase plays a dominant role in mechanical properties, especially in oriented samples [1]. For the blends with cocontinuous morphology both phases can contribute to mechanical properties in all directions and the interpenetrated networks of phases lead to better stress transfer across the interface. It was shown that cocontinuous morphology can yield higher mechanical properties than that of the dispersed phase morphology, in the same composition range [2-4].

Considering the importance of mechanical properties in engineering applications, several studies have been reported on mechanical modeling in both direct and reverse modes [5-12]. In the direct mode, final properties of a blend are predicted from the knowledge of morphology, composition and characteristics of the pure components. The reverse mechanical modelling, which is proposed more recently, permits the extraction of valuable information about actual characteristics of each phase from application of the model to experimental data. This could be especially useful for estimating the properties of in-situ formed interphase in reactive blends.

The objective of this paper is to investigate and model the tensile behavior of low density polyethylene (LDPE)/polydimethylsiloxane (PDMS) immiscible blends in full range of compositions. Moreover, the influence of a peroxide curing agent on the tensile properties of the blends is studied. Interesting characteristics of PDMS such as maintaining elastomeric behavior in a wide range of temperatures, good insulating properties, and biocompatibility in combination with relatively good electrical and mechanical properties, and low cost of LDPE, could result in a blend with unique properties.

Theory

Using a combination of parallel and series elements is a well-known method for modelling the mechanical response of a two-phase system [9, 10, 13]. The so-called equivalent mechanical models furnish a convenient framework for phenomenological description of immiscible blends behavior [14]. In the simplest form components are assumed to be coupled in a single parallel or series elements [15];

Series model: $$E_b = v_1 E_1 + v_2 E_2 \tag{1}$$

Parallel model: $$E_b^{-1} = v_1 E_1^{-1} + v_2 E_2^{-1} \tag{2}$$

in which E_b is the blend modulus and E_i and v_i are modulus and the volume fraction of phase i, respectively.

In generalized scheme, combination of a parallel and a series element is exploited, where the parallel element represents the continuous fraction of phases and the series element represents the dispersed fractions. The scheme shown in Figure 1 is a two parameter model; of the four volume fractions v_{ij} only two are independent.

Therefore, in order to use this model in direct mode, parameters need to be calculated as a function of blend composition. It should be noted that the volume fraction of each phase in the parallel element is proportional to its degree of continuity, c_i.

$$\begin{gathered} v_{2s} = v_2 - v_{2p} \quad ; \quad v_{1s} = v_1 - v_{1p} \\ v_p = v_{1p} + v_{2p} \quad ; \quad v_s = v_{1s} + v_{2s} \\ v_{2p} = c_2 v_2 \quad ; \quad v_{1p} = c_1 v_1 \end{gathered} \tag{3}$$

To calculate model parameters, Kolarik [9, 10] has derived the following equations based on percolation theory [16, 17];

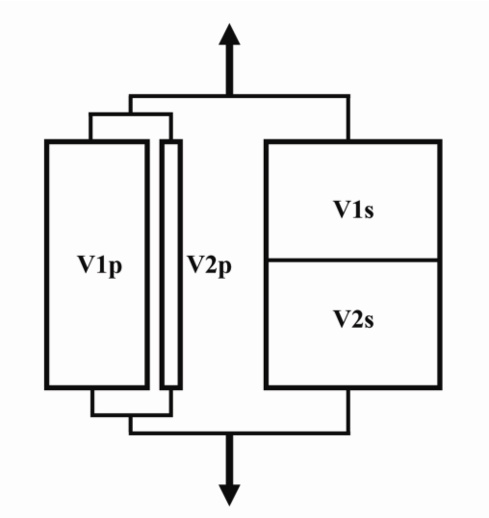

Fig. 1. Schematic representation of an equivalent model for a binary blend.

$$v_{1p} = [(v_1 - v_{1cr})/(1 - v_{1cr})]^{\tau} \quad (4)$$

$$v_{2p} = [(v_2 - v_{2cr})/(1 - v_{2cr})]^{\tau} \quad (5)$$

where v_{1cr} and v_{2cr} are percolation threshold of the components. The percolation threshold volume fraction which is highly sensitive to the aspect ratio of dispersed phase domains was calculated as $v_{cr} = 0.156$ for a dispersion of spherical particles with the same size [17]. Most experimental values of exponent τ are located in the interval 1.7 to 1.9. As the contribution of minor phase in the parallel element has been considered, this model can account for partial continuity above percolation threshold.

Another group of models that have been applied to the problem of predicting and analyzing the mechanical behaviour of immiscible blends, especially those with dispersed phase morphology, are the so-called "self-consistent" models. This group of models, such as the ones proposed by Kerner [18] or Halpin and Tsai [19, 20] do not have any parameter which needs to be calculated in advance. Therefore, the self-consistent approximation can be used independently in a predictive manner. The Halpin-Tsai model gives the following equations for elastic modulus;

$$E = E_1(1 + ABv_2)/(1 - Bv_2)$$

$$B = (\frac{E_2}{E_1} - 1)/(\frac{E_2}{E_1} + A) \qquad \& \qquad A = \frac{2L}{D} \quad (6)$$

where E_1 and E_2 are the elastic modulus of matrix and dispersed phase respectively, and $\frac{L}{D}$ is the length to diameter ratio of dispersed phase domains.

Results and discussion

Morphology

SEM micrographs of the uncured and cured blends are shown in Figures 2 and 3, respectively. Development of continuity in minor phase could be easily observed as the concentration of the dispersed phase is increased. At 20 wt% of both components, the minor phase is dispersed as separate domains in the matrix of the major component (see Figures 2a and 2c). As can be seen in Figure 2b, the extent of continuity has been increased with concentration of the minor phase until cocontinuous morphology is formed at 50/50 composition.

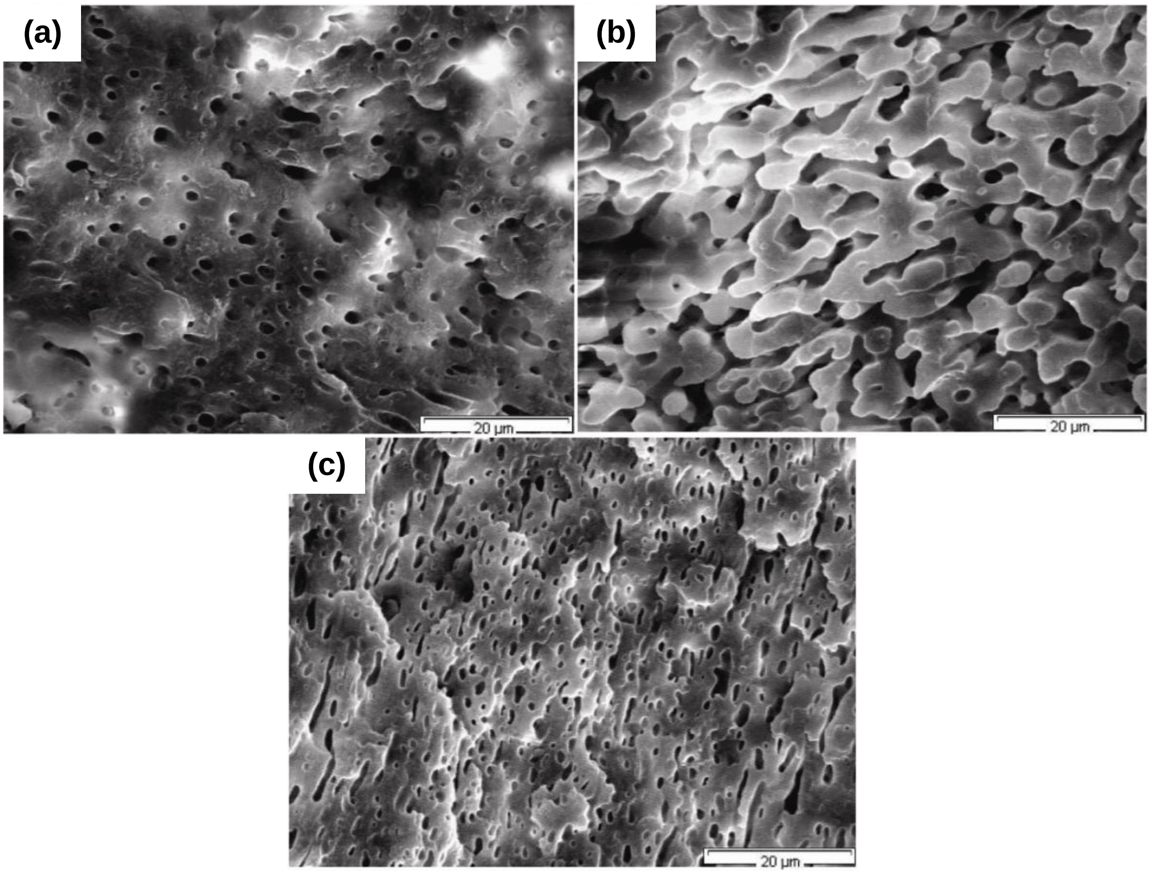

Fig. 2. SEM micrographs of uncured blends, a) LP2080; b) LP5050; c) LP8020.

As it can be seen for the cured 50/50 blends, regardless of how the DCP is added, curing reaction results in the breakdown of cocontinuous structure to finer dispersed phase morphology and therefore significantly increases the interfacial area compared with the uncured blends (Figures 3a and 3b). On the other hand, for LPD8205 sample, where curing agent was added to both phases, a noticeable decrease in dispersed phase domain size was observed compared to the uncured blend (Figure 3c). However, in the case of LPR8205 sample only a negligible difference was found between the particle sizes of this blend compared to that of the uncured blend with the same composition (Figure 3d). Average particle size of the dispersed phase domains for LP2080, LP8020, LPD8205 and LPR8205 are also given in Table 1.

The observed morphological changes caused by the addition of the DCP might be attributed to the cure induced interfacial modification. With the progress of curing reaction during melt mixing, presence of the chains having free radicals on their backbone at the interface are more probable and this can result in an interfacial reaction and formation of graft copolymers. These in-situ formed copolymers can reduce the interfacial tension, suppress particles coalescence and consequently decrease the dispersed phase particle size.

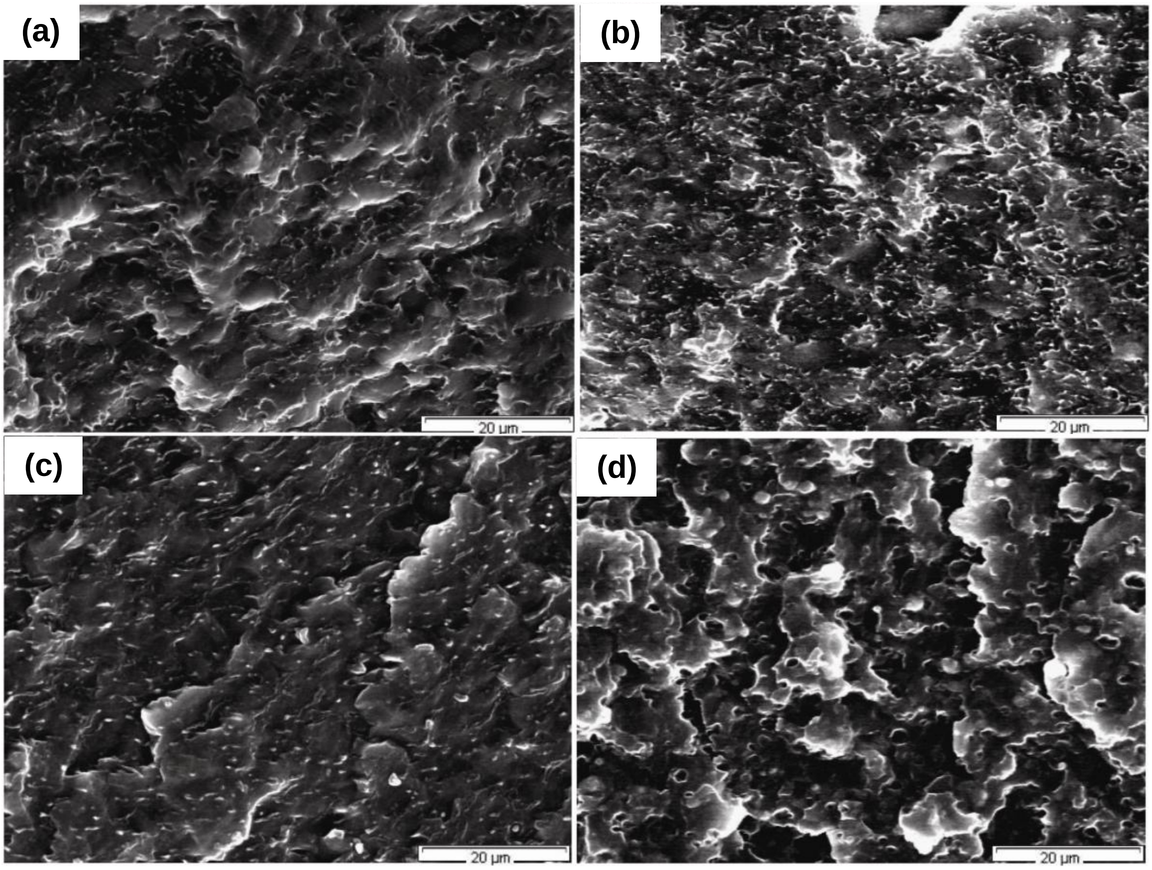

Fig. 3. SEM micrographs of cured blends, a) LPD5505; b) LPR5505; c) LPD8205; d) LPR8205.

Tab. 1. Average particle radius of the dispersed phase in LDPE/PDMS blends.

Sample	LP2080	LP8020	LPD8205	LPR8205
Average radius of particles in µm	1.05	0.97	0.73	1.09

Mechanical properties of uncured blends

Considering the structural dissimilarity and lack of any specific interaction between LDPE and PDMS chains, the two polymers are immiscible and one can expect rather low adhesion at the interface of the materials. In addition, uncured PDMS has poor mechanical properties and except for those blends containing high concentration of LDPE, in which this component plays the dominant role in determining the properties, the other blends show low tensile properties. The variations of elastic modulus and also stress and strain at break with composition for uncured blends are shown in Figures 4 and 5, respectively. As could be perceived from the figures, variations of the properties clearly reflect the changes in morphology with increasing LDPE concentration. Up to 20 wt% LDPE, where little or no contact exists between LDPE dispersed domains, only a slight increase can be seen in the properties. Further increase of LDPE concentration to 30 wt% makes a noticeable improvement in tensile properties, which could be attributed to the development of partial continuity in this phase. At higher concentration of LDPE, 70 wt% for strain at break and 80 wt% for modulus and stress at break, a further increase in slopes of the curves can be observed in association with the disappearance of partial continuity in PDMS.

Although the dispersion of elastomeric domains in thermoplastic matrix mostly results in the improvement of strain at break for blend systems [21, 22], in the case of uncured LDPE/PDMS blends, because of very low tensile properties of PDMS, the domains of this phase would undergo rupture at small strains and consequently decreases the tensile deformability of the blends.

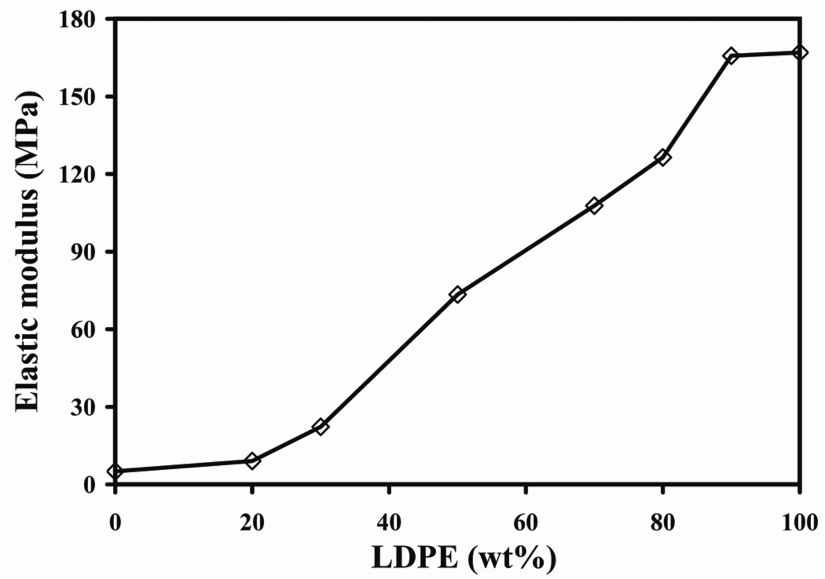

Fig. 4. Variation of elastic modulus as a function of composition for uncured blends.

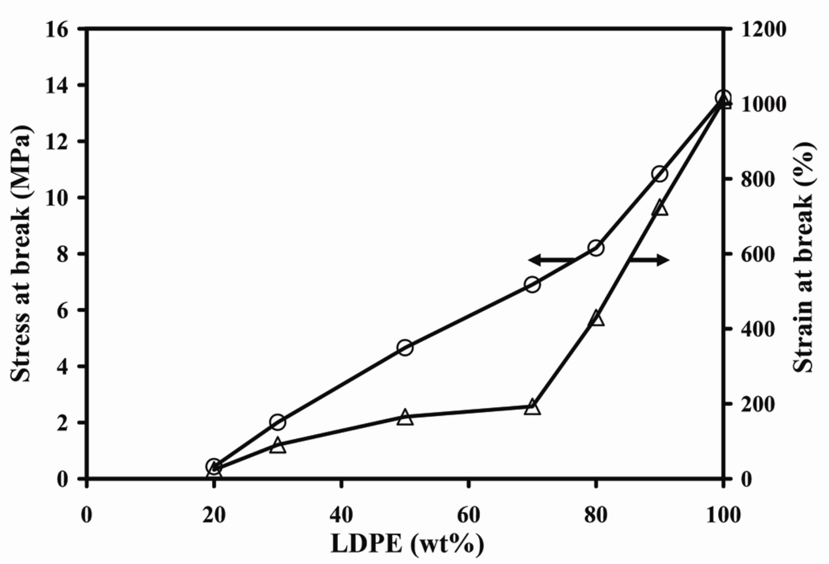

Fig. 5. Variation of stress and strain at break as a function of composition for uncured blends.

Modelling

Prediction of parallel model (mixing rule), which is usually assumed as upper bound of modulus, in comparison with experimental values of tensile modulus is shown in Figure 6. In the region of cocontinuity, the modulus of the blend is close to the values predicted by the parallel model. This could be related to the formation of an interpenetrated network structure of phases which promotes stress transfer across the interface. For LP9010 blend the measured elastic modulus is higher than that of the value calculated by the parallel model. In this composition, PDMS practically has very little or no contribution to the mechanical properties. However, parallel model suggests that each component contributes to the blend modulus proportional to its volume fraction. This may be the reason for the lower value predicted by the model.

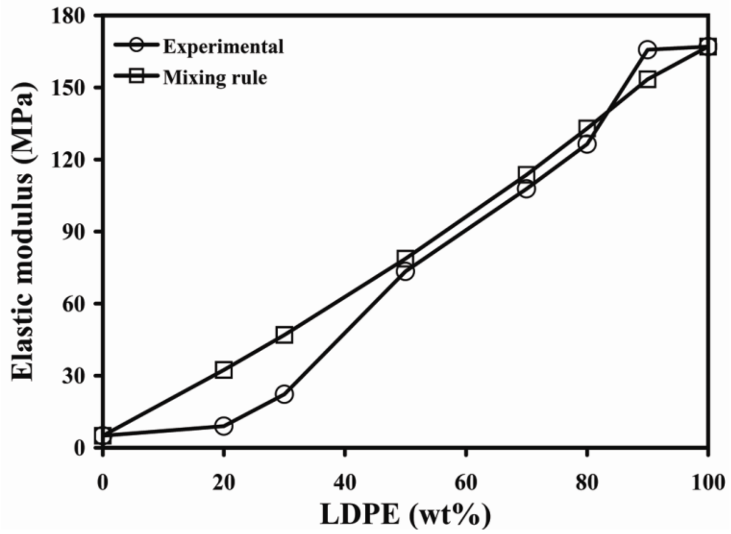

Fig. 6. Prediction of parallel model in comparison with the experimental data.

Figure 7 shows the elastic modulus calculated by the Halpin-Tsai model in comparison with the data obtained experimentally. For using the model, the value of $\frac{L}{D}$ was taken to be 1.5.

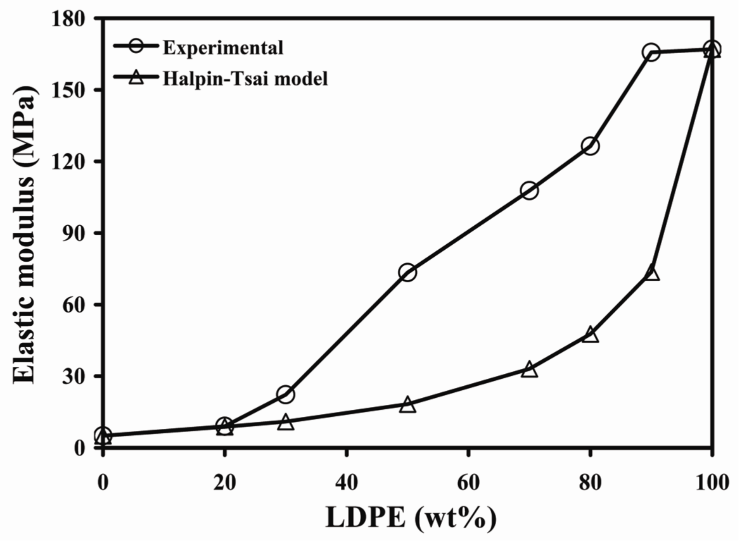

Fig. 7. Prediction of Halpin-Tsai model in comparison with the experimental data.

This value was obtained by analyzing the SEM micrographs of LP8020 and LP2080 blends. Except for LP2080 blends where LDPE, the more rigid component, is dispersed as separate domains in PDMS phase, at other compositions the calculated values show substantial negative deviation from the experimental data. This is because, the Halpin-Tsai model was originally proposed for the case where a more rigid component was dispersed as filler inside a relatively weak matrix. In addition, it is impossible to assign a reasonable value to $\frac{L}{D}$ for concentrations higher than that of the percolation threshold. Therefore, this model cannot account for continuity.

The equivalent mechanical model used in this study is a combination of one parallel and one series elements (Figure 1). For this arrangement of elements the elastic modulus is given by the following equation [10];

$$E_b = (E_1 v_{1p} + E_2 v_{2p}) + v_s^2 /(v_{1s} / E_1 + v_{2s} / E_2) \tag{7}$$

The most important factor determining the agreement between model predictions and experimental data is based on the accurate calculation of adjustable parameters. Figure 8 shows the estimated values of elastic modulus when the model parameters are calculated with percolation theory. As it can be seen, this model gives better predictions than the Halpin-Tsai model. However, there is still a significant deviation from the experimental values. This discrepancy is originated from the inaccurate calculation of model parameters with percolation theory.

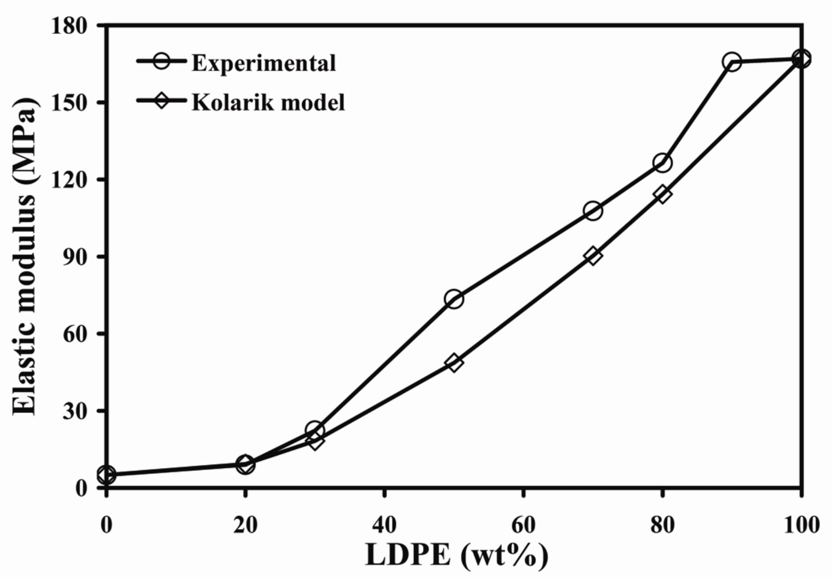

Fig. 8. Prediction of Kolarik model in comparison with the experimental data.

To investigate possibility of improving the method proposed by Kolarik, modified form of percolation theory could be exploited instead of its original form. In the modified form, the contribution of matrix phase is added to the exponential expression such that [23];

$$E_b = E_1 + E_0 (v - v_{cr})^{\tau} \tag{8}$$

Furthermore in Kolarik model v_{1p} is calculated using the assumption $E_1 >> E_2$ and then v_{2p} is calculated assuming $E_2 >> E_1$, at the same concentration. Certainly using both of these assumptions simultaneously would be erroneous. To avoid possible errors caused by this assumption, by knowing $E_1 >> E_2$ (1: LDPE and 2: PDMS), v_{1p} can be calculated for all compositions using the following equation;

$$v_{1p} = E_2 / E_1 + (1 - E_2 / E_1) \times [(v_1 - v_{cr}) / (1 - v_{cr})]^{\tau} \tag{9}$$

By calculating v_{1p} at any specific volume fraction, continuity degree of component 1 can be determined as a function of volume fraction from eq. (3); i.e.

$$c_1 = \frac{v_{1P}}{v_1} \tag{10}$$

Supposing that in an immiscible blend continuity degree of the components are equal at the same compositions, for instance $c_1\big|_{30vol\%} = c_2\big|_{30vol\%}$, the second unknown parameter , v_{2p}, can be calculated by using the values of c_2 such that;

$$v_{2p} = v_2 \times c_2 \tag{11}$$

In spite of the applied modifications only a slight increase in predicted values of modulus (up to 6 MPa) is observed. It is to be noted that the great difference in mechanical properties of uncured LDPE with PDMS is possibly the main reason for negative deviation of modified Kolarik model from experimental data.

The adjustable parameters of equivalent mechanical model presented in Figure 1 can be calculated directly from the estimated values of continuity parameter. The continuity parameter depends on many factors such as composition, processing conditions, rheological properties of constituents, and the nature of interface. Among these, the composition of components is one of the most important factors. Here an exponential relation has been assumed between continuity parameter and volume fraction such that;

$$c = kv^a \tag{12}$$

In order to determine k and a -which are adjustable parameters and dependant on the factors influencing continuity parameter - it is required to know the value of continuity parameter at two different concentrations. Certainly perfect continuity can be assumed to be at $v = 1$;

If $v_1 = 1 \Rightarrow c_1 = 1$ (13)

On the other hand, at percolation threshold of the component with higher modulus (v_{1cr}), self-consistent models such as Halpin-Tsai model can yield a satisfactory approximation for the modulus of blends. Thus, by neglecting small contribution of series element, blend modulus, E_b, at v_{1cr} is given by;

$$E_b\big|v_{1cr} = E_1 v_{1cr} c_{1cr} + E_2(1 - v_{1cr})c_2 \quad \text{where} \quad v_{1cr} = 0.156 \tag{14}$$

To obtain c_{1cr} from the above equation, c_2 value at $(1 - v_{1cr})$ is required. It can roughly be assumed that at the percolation threshold of component 1, component 2 has perfect continuity, i.e. $c_2 = 1$, then;

$$E_b\big|v_{1cr} = E_1 v_{1cr} c_{1cr} + E_2(1 - v_{1cr}) \tag{15}$$

By rearranging eq. (15), c_{1cr} could be calculated at v_{1cr} as follows;

$$c_{1cr} = \frac{E_b \left| v_{1cr} - E_2(1-v_{1cr}) \right.}{E_1 v_{1cr}} \tag{16}$$

With this method, the continuity parameter is known at two different volume fractions – ($c_1 = 1$ at $v_1 = 1$) and ($c_1 = c_{1cr}$ at $v_1 = v_{1cr}$) – and therefore it is possible to calculate the unknown parameters of a and k from eq. (12). The value of v_{ip} can then be calculated by using eq. (3) and subsequently E_b can be predicted from eq. (7).

The values predicted by this model are compared with the experimental data in Figure 9. The calculated modulus, especially in cocontinuity region and where the concentration of LDPE is high, is in good agreement with the experimental data. This model, like Kolarik model, is valid only for $v_{1cr} \leq v \leq v_{2cr}$.

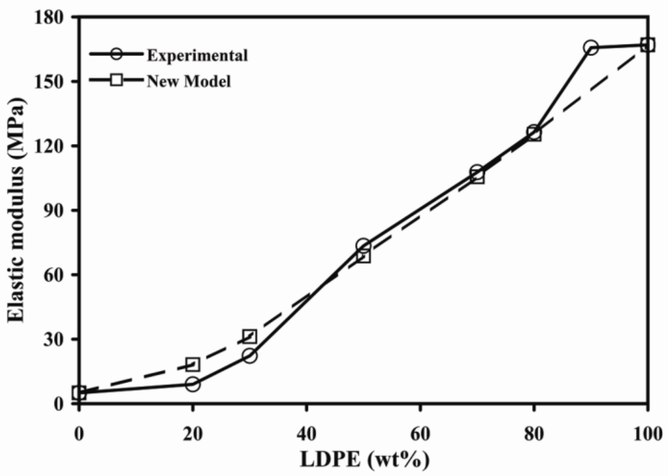

Fig. 9. Prediction of the proposed model in comparison with the experimental data.

Tensile properties of cured blends

The addition of DCP to one or both components could have strong effects on the factors determining tensile behavior of the blends, such as morphology, mechanical properties of the components, and the nature of interface.

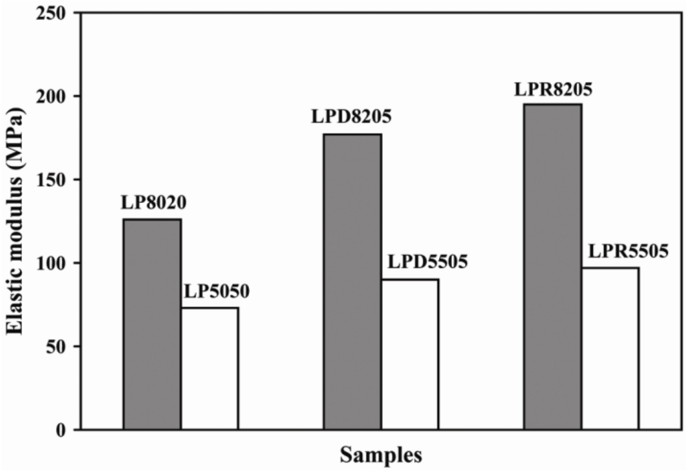

Fig. 10. The effect of curing on elastic modulus.

As it is expected, the most dominant influence of curing agent is the alteration of mechanical properties of components, which is more noticeable for PDMS because of its very low tensile properties in uncured state. Introduction of DCP to LDPE could affect both its crystalline and amorphous regions. It has been reported that the addition of a small amount of DCP (lower than 1 wt %), increases stress and strain at break values and decreases elastic modulus of LDPE [24]. Furthermore, as suggested earlier, formation of graft copolymers at the interface of the two polymers can also improve interfacial adhesion and increases stress transfer across the interface in the blends containing DCP. Therefore, the observed increase in tensile properties of the cured blends can be attributed to the modification of mechanical properties of the components and also the improvement of interfacial adhesion between the two phases. The tensile properties of LPD and LPR blends with those of uncured blends are compared in Figures 10 to 12. It can be seen that the trend of variations of tensile properties are similar for the uncured and cured blends containing 80 wt% and 50 wt% of LDPE. The improved tensile properties of the blends containing DCP is in complete agreement with the aforementioned effects of curing reaction.

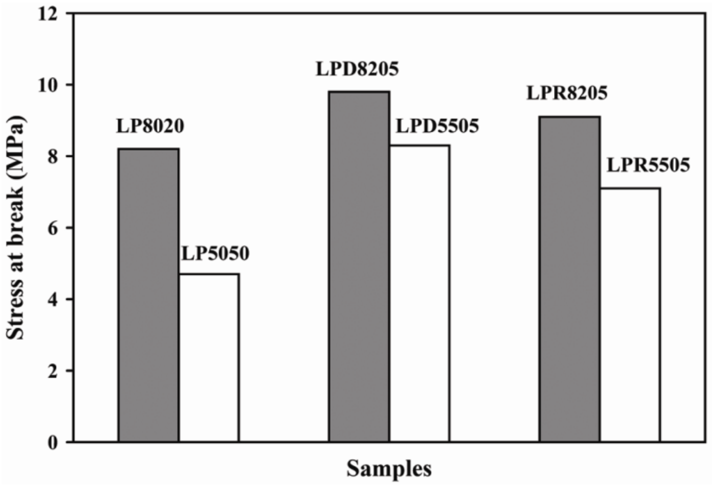

Fig. 11. The effect of curing on stress at break.

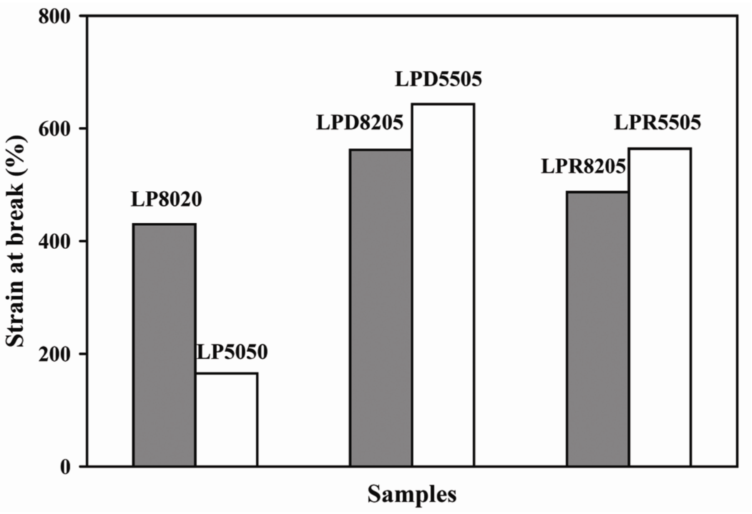

Fig. 12. The effect of curing on strain at break.

Higher modulus and lower stress and strain at break of LPR blends comparing to LPD series, could also be related to the fact that in LPD blends DCP was also added to LDPE phase and therefore curing would have a pronounced effect on LDPE properties by lowering its crystallinity and making cross-links between the chains in amorphous regions.

Conclusions

In this study the morphology and tensile behaviour of uncured and cured LDPE/PDMS blends of different compositions were investigated. Changes in morphology and tensile properties of the blends indicated that the addition of curing agent, besides modifying the properties of components, could induce an interfacial reaction which resulted in an improved interfacial adhesion. For the case of uncured blends, experimentally measured elastic modulus was compared to the values predicted by parallel model, Halpin-Tsai model and Kolarik model. In the cocontinuity region, the experimental data was close to the values predicted with parallel model because of the formation of interpenetrated network structure of phases. As in Kolarik model, partial continuity in the minor phase was accounted for; this model gave better predictions than Halpin-Tsai model. However, both models showed significant negative deviations from experimental data. Although some modifications were made into Kolarik model, only a slight improvement was obtained in the values predicted. Herewith, a different approach for calculating equivalent mechanical model parameters was proposed. The values of modulus predicted with this method showed satisfactory agreements with experimental data.

Experimental Part

Materials

The raw materials were obtained from commercial sources. PDMS was supplied from Wacker Chemie (Germany) with the trade name of Elastosil R401/60. The Mooney viscosity [ML (1+4) 100 ^{o}C] as measured by Zwick viscometer (model 4309, Germany) was 22±1. The hardness and density of PDMS were 60 shore A and 1.14 g/cm^3, respectively. LDPE was supplied from Bandar Imam Petrochemical Co. (Iran) with the trade name of Poliran LF0200. The melt flow index and density of LDPE were 2 g/10min (190 ^{o}C and 2.16 kg) and 0.92 g/cm^3, respectively. Dicumyl peroxide (DCP 98%; Di-Cup, Hercules Inc.) was also used as a curing agent. All the materials were used without any further treatment.

Blends preparation

The recipes for preparation of all the uncured and cured blends studied are presented in Tables 2 and 3, respectively. The blends were prepared by melt-mixing of the components in an internal mixer (Haake Rheomix; HBI SYS90) with rotor speed of 50 rpm and at 150 °C. In order to prepare uncured blends, LDPE was melted for 3 min. and PDMS was then added into the mixer and mixing continued for another 7 min.

For the blends containing curing agent, mixing was preformed in two different ways. In LPD series, both components were first mixed similar to uncured blends and DCP was then added and mixing was continued for another 4 min. In the case of LPR series, PDMS and DCP were mixed together at 50 °C for 5 min. No sign of curing reaction was observed in this step. This was examined by observing mixing torque-time curve in which no sign of increasing in torque was seen after the addition of DCP into the mixing chamber. PDMS containing curing agent, was then added to LDPE at 150 °C and mixing was performed for further 4 min.

In all cases the blends were compression moulded immediately after mixing was finished. Square plaques (160 mmx160 mmX1 mm) of the blends were prepared in a Toyoseiki Mini Test hydraulic Press (Japan) at 180 °C and 20 MPa for 3 min. The sheets then were quenched to room temperature with water circulating system while the sheets remained under pressure in the press.

Tab. 2. Composition of the uncured LDPE/PDMS blends.

	LP2080	LP3070	LP5050	LP7030	LP8020	LP9010
LDPE*	20	30	50	70	80	90
PDMS*	80	70	50	30	20	10

* Polymers concentrations are in wt%

Tab. 3. Composition of the cured LDPE/PDMS blends.

	LPD5505	LPD8205	LPR5505	LPR8205
LDPE*	50	80	50	80
PDMS*	50	20	50	20
DCP**	1	2.5	1	2.5

* Polymers concentrations are in wt%
**DCP concentration is in phr

Mechanical testing

Dumbbell shaped specimens, having dimensions in accordance with ASTM D638 Type D, were cut out from moulded sheets of the parent polymers and blends. Tensile experiments were carried out on the specimens using a MTS tensile testing machine (model 10/M, USA) with crosshead speed of 50 mm/min at 23 ± 1 ^{o}C. The elastic modulus was determined from the initial slope of stress-strain curve.

Morphology

The morphology of cryogenically fractured surface of the blends, after coating with a thin layer of gold, was investigated with a Cambridge S-360 scanning electron microscope (SEM, England). The fractured surfaces of the blends were also etched in toluene for 48 hours at room temperature. Average particle radii for the blends were also obtained with commercial software called analySIS (Soft Imaging System GmbH, Germany).

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References

[1] Machiels, A.G.C.; Denys, K.F.J.; van Dam, J.; de Boer, A.P. *Polym. Eng. Sci.* **1996**, 36, 2451.

[2] Willemse, R.C.; Speijer, A.; Langeraar, A.E.; de Boer, A.P. *Polymer* **1999**, 40, 6645.
[3] Veenstra, H.; Verkooijen, P.C.J.; van Lent, B.J.J.; van Dam, J.; de Boer, A.P.; Nijhof, A.P.H.J. *Polymer* **2000**, 41, 1817.
[4] Mamat, A.; Vu-Khanh, T.; Cigana, P.; Favis, B.D. *J. Polym. Sci. Part B Polym. Phys.* **1997**, 35, 2583.
[5] Bandyopadhyay, G.G.; Bhagawan, S.S.; Ninan, K.N.; Thomas, S. *J. Appl. Polym. Sci.* **1999**, 72,165.
[6] Joseph, S.; Thomas, S. *J. Polym. Sci. Part B Polym. Phys.* **2002**, 40, 755.
[7] Bandyopadhyay, G.G.; Bhagawan, S.S.; Ninan, K.N.; Thomas, S. *J. Polym. Sci. Part B Polym. Phys.* **2004**, 42, 1417.
[8] Alberola, N.D.; Merla, G.; Benzarti, K. *Polymer* **1999**, 40, 315.
[9] Kolarik, J.; Eur. Polym. J. **1998**, 34, 585.
[10] Kolarik, J. *Polym. Eng. Sci.* **1996**, 36, 2518.
[11] Colombini, D.; Merle, G.; Alberola, N.D. *Macromolecules* **2001**, 34, 5916.
[12] Woo, E.M.; Su, C.C.; Kuo, J.F.; Seferis, J.C. *Macromolecules* **1994**, 27, 5291.
[13] Takayanagi, M.; Imada, K.; Kajiyama, T. *J. Polym. Sci. Part C Polym. Symp.* **1967**, 15, 263.
[14] Paul, D.R.; Newman, S. *Polymer Blends*, Academic press, New York, **1978**.
[15] Nielsen, L.E.; Landel, R.F. *Mechanical Properties of Polymers and Composites,* Marcell Dekker, New York, **1994**.
[16] Hsu, W.Y.; Wu, S. *Polym. Eng. Sci.* **1993**, 33, 293.
[17] Stauffer, D.; Aharony, A. *Introduction to Percolation Theory*, Taylor and Francis, London, **1994**.
[18] Kerner, E.H. *Proc. Phys. Soc. Part B* **1956**, 69, 808.
[19] Dickie, R.A. *J. Appl. Polym. Sci.* **1973**, 17, 45.
[20] Halpin, J.C.; Kardos, J.L. *Polym. Eng. Sci.* **1976**, 16, 344.
[21] George, J.; Joseph, R.; Thomas, S.; Varughese, K.T. *J. Appl. Polym. Sci.* **1995**, 57, 449.
[22] Loyens, W.; Groeninckx, G. *Polymer* **2002**, 43, 5679.
[23] Lyngaae-Jorgensen, J.; Kuta, A.; Sondergaard, K.; Poulsen, K.V. *Polym. Networks Blends* **1993**, 3, 1.
[24] Andreopoulos, A.G.; Kampouris, E.M. *J. Appl. Polym. Sci.* **1986**, 31, 1061.