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POLYURETHANE-EPOXY MALEATE OF BISPHENOL A BLENDS

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ABSTRACT

Blends of polyurethane with epoxy maleate of Bisphenol A were synthesized and their miscibility, the physico-mechanical properties, as well as the thermal behavior were studied. Differential scanning calorimetry (DSC) measurements showed a single composition-dependent glass transition temperature (T_g), and is evidence for a good miscibility of the studied systems. The variation of T_g's of the blends versus composition (Fox, Gordon-Taylor, and Schneider equations) showed the presence of some physical interactions between polyurethane and epoxy maleate polymers. Generally, the physico-mechanical properties of the blends are lower as than those of polyurethane. This suggests that epoxy maleate of Bisphenol A operates in a mixture with polyurethane only as a plasticizer. The thermal behavior of the studied blends showed no large differences to that of polyurethane.

Key Words: Polyurethane; Epoxy maleate; Blends; Miscibility

INTRODUCTION

Polyurethane (PU) is among the most versatile material, which is widely used in many technical applications for its high tensile strength, processability and mechanical properties. It is generally inappropiate for structural applications due to its low rigidity and high thermal expansion coefficient [1]. Blending of PU with

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other polymers is carried out for developing new materials with some characteristic useful properties. The chemical and physical combination of PU with dissimilar polymers is produced to facilitate processing, to modify the mechanical properties, to improve the chemical resistance, weatherability, and other properties [2]. However, most combinations of polymer pairs are immiscible and show poor physical or mechanical properties vs. their components.

In recent decades, a wide variety of blends based on PU have been synthesized and studied regarding compatibilization [3-5], miscibility [6], morphology [7], microphase separation [8], rheological and dynamic mechanical properties [9], as well as the gel formation [10]. Presently, a growing interest is given to the interpenetrating polymer networks (IPNs), a novel type of polymer blend composed of crosslinked polymers. Several papers on IPNs have already described the preparation and the study of PU-based compositions [11-17].

Two component IPNs from PU and epoxy were investigated [7, 18-20]. In our previous work, [21] some semi-IPNs (SIPNs) were obtained starting from PU and epoxy maleate of Bisphenol A (EMBA). The network synthesized showed a good miscibility and excellent mechanical properties. In this work, we report the miscibility of PU with EMBA in the blends obtained by their physical combination. The miscibility of the two polymers was established by the presence of a single glass transition temperature (T_g) using differential scanning calorimetry (DSC) technique. Additionally physico-mechanical properties were determined and discussed in relation with morphology of the blends, respectively with the EMBA content in the blends. The thermal behavior of the synthesized blends was also discussed.

EXPERIMENTAL

Synthesis of PU

The thermoplastic PU was synthesized using a mixture constituted from poly(ethyleneadipate)diol (PEA) and poly(ethylenediethyleneadipate)diol (PEDA) in reaction with 4,4'-diphenyl-methane diisocianate (MDI), as was previously reported [21, 22]. The number average molecular weight of the synthesized PU, determined from gel permation chromatography (GPC), was $\overline{M}_n$ = 56.000.

Synthesis of EMBA

EMBA was synthesized starting from maleic anhydride (1 mol) and Dinox epoxy resin (1 mol), in the presence of water (1 mol). Dinox resin was a commercial product obtained from Bisphenol A and epichlorohydrin. It was supplied by Sintofarm-Bucharest, Romania. The mixture was heated at 80°C, by stirring under nitrogen, for a duration of 1 hour. The polymer obtained was cast on a teflon plated surface dried overnight in air, and manually granulated. The granules were washed with water up to neutral pH, dried at the ambient medium temperature for 24 hours, and exposed to vacuum at 60-70°C, for at least 8 hours, to remove any unsaturated compound. The synthesized EMBA polymer had a number-average molecular weight $\overline{M}_n$ = 53.000.

Preparation of PU-EMBA Blends

Mixtures of PU and EMBA polymers in dimethylformamide (DMF) were prepared by dissolving PU and EMBA both separately, at room temperature, to form 20% by weight solutions. The two solutions were then mixed in the desired proportions, and a number of blends were obtained with the compositions shown in Table 1. The same Table 1 lists T_g values of both the crude polymers and the synthesized blends.

Approximately 25 cm^3 clear solutions of PU-EMBA mixture in DMF were cast as films on a glass slide by means of a doctor blading with a slit of 0.8 mm. After degassing in a vacuum oven at 60°C for 24 hours up to constant weight, the films were thermally treated at 120°C for 2 hours. Then, the films were air cooled and detached from the glass surface to be used for experiments. The transparent films had no trace of solvents, as was proved by IR spectroscopy.

Characterization

The synthesized PU-EMBA blends were characterized the DSC technique, using a Mettler 12E instrument, in a temperature range between -20 up to + 40°C, at a heating rate of 10°C/min, in a nitrogen atmosphere.

The physico-mechanical measurements were carried out at room temperature, using a TIRA-TEST 2161 machine (Germany), at a speed of 100 mm·min^{-1}. The reported data are the average of 5 measurements.

The density evaluation was made by means of a picnometer at 25°C, in methanol.

Table 1. Composition and Tg of the Blends Synthesized from PU and EMBA

Sample	PU (%)	EMBA (%)	Tg (°C)
PU	100	—	−19
B-1	91.0	9.0	−8
B-2	83.3	16.7	−6
B-3	77.0	23.0	−2
B-4	71.4	28.6	0
B-5	66.7	33.3	2
B-6	62.5	37.5	3
B-7	58.8	41.2	6
EM	—	100.0	32

The thermal behavior of the blends was studied using a MOM-Budapest derivatograph, under the following operational conditions: sample weight 50 mg, heating rate 12°C·min^{-1}, in atmospheric air and reference material α-Al_2O_3.

RESULTS AND DISCUSSION

T_g Measurements

T_g is one of the most important characteristics of the polymeric materials. In this study, the DSC technique was used to examine the miscibility of PU with EMBA polymers. The miscibility of two polymers is generally established by the presence of a single T_g [23, 24]. Figure 1 shows the DSC traces for the synthesized PU-EMBA blends, including both the PU and EMBA crude polymers.

As can be seen, the studied blends show a single composition-dependent T_g, which varies smoothly from that of pure PU to that of pure EMBA crude polymer.

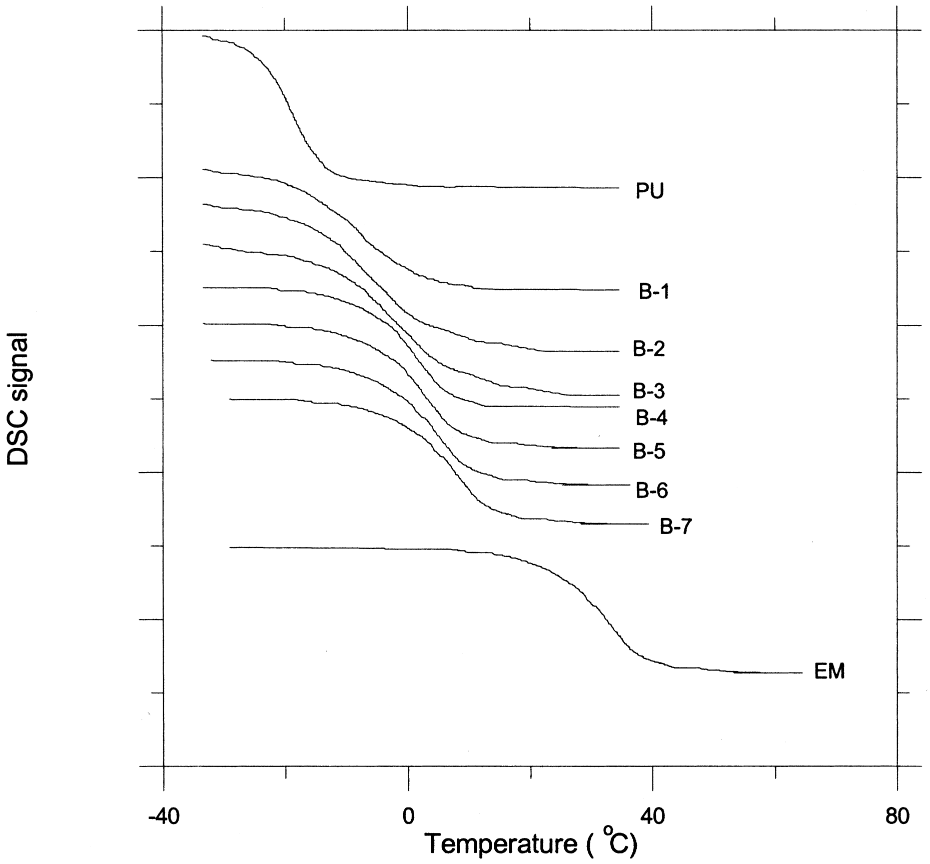

Figure 1. DSC curves of PU, EMBA, and PU-EMBA blends at a heating rate of 12°C/min.

The variation of T_gs of the blends vs. composition (EMBA wt%) was carried out using the Fox Equation 1 [25].

$$\frac{1}{Tg} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2} \tag{1}$$

where w_1 and w_2 are the weight fractions, and T_{g1} and T_{g2} are T_gs of the two starting polymers.

The results obtained using both the experimental data and the Fox equation are shown in Figure 2.

The positive deviation of T_g values from the Fox equation, as can be observed in Figure 2, is evidence for the presence of some specific interactions between the two polymers in the studied blends [26, 27].

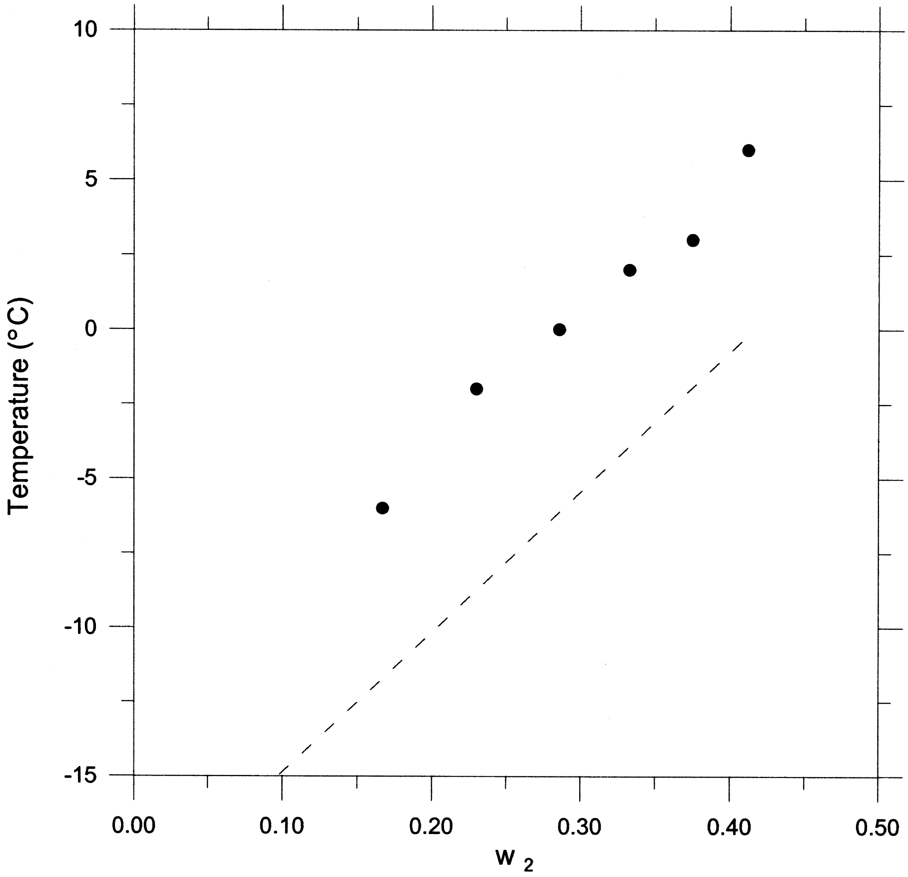

Figure 2. Plot of T_g against composition for PU-EMBA blends: (●) experimental T_g values; the dotted line is a theoretical plot based on the Fox equation.

An appreciation of the strength of the interaction between PU and EMBA polymers was performed using the Gordon-Taylor Equation 2 [28].

$$Tg_1 - Tg_2 = \frac{Kw_1(Tg - Tg_2)}{w_2} \tag{2}$$

where K is the ratio of the difference of the of expansion coefficients, being a constant which indicates the strength of the interactions in the studied blends.

Figure 3 shows the plot T_g -T_{g1} vs. w_2 (T_{g2}-T_g)/w_1.

The plot in Figure 3 is a typical characteristic S-shaped curve showing negative and positive deviations from the Gordon-Taylor equation. Using the Gordon-Taylor equation a straight line was obtained, with a slope value of K = 1 ± 0.03.

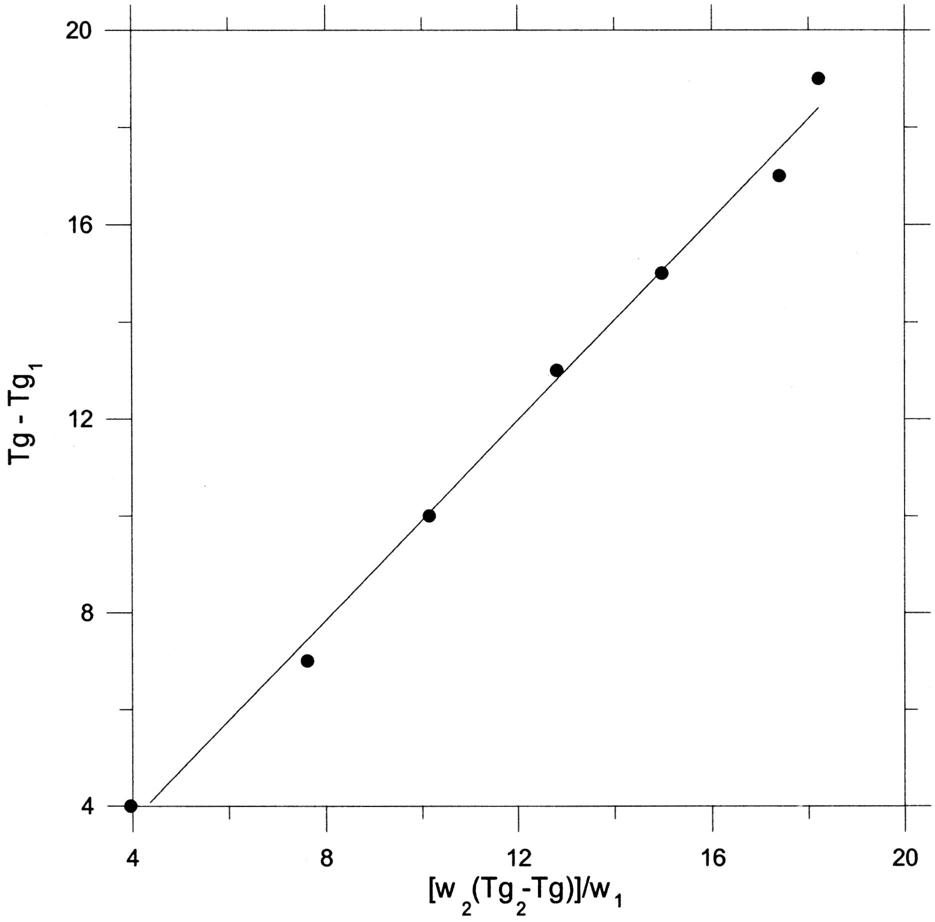

Figure 3. Plot (T_g-T_{g1}) vs. w_2(T_{g2}-T_g)/w_1 (Gordon-Taylor equation) for PU-EMBA blends: (●) experimental T_g values; (——) Gordon-Taylor equation.

This value around unity suggests that the interactions between the two studied polymers are not very strong.

The PU-EMBA blend miscibility and the presence of the interactions between the two blend components were also evident using the third-power Equation 3, which is based on the assumption that the contact between the two polymers influences both conformation and “free volume distribution” [29] in the polymer blends.

$$\frac{Tg - Tg_1}{Tg_2 - Tg_1} = (1 + K_1)\cdot w_{2c} - (K_1 + K_2)\cdot w_{2c}^2 + K_2 \cdot w_{2c}^3 \tag{3}$$

where $w_{2c} = Kw_2/(w_1+Kw_2)$ represents the corrected weight fraction of the component with the higher T_g, and K is given by $K = K'(T_{g1}/T_{g2})$. Her,e K’ is related to the ratio of the densities of the two crude polymers.

For volume addition, $K_1 = 0$ and $K_2 = 0$, and Equation 3 is reduced to Equation 4.

$$\frac{(\mathrm{Tg} - \mathrm{Tg}_1)}{(\mathrm{Tg}_2 - \mathrm{Tg}_1)\cdot \mathrm{w}_{2c}} = 1 \tag{4}$$

In this situation, the plot $(T_g\text{-}T_{g1})/(T_{g2}\text{-}Tg_1)\cdot w_{2c}$ vs. w_{2c} is a horizontal straight line with plot K_1 about 1.

The presence of the specific real interactions between the blend components leads to an inclined straight line of slope K_1 ($K_2 = 0$), or a curved line ($K_2 \neq 0$). For the studied blends in this work, the plot $(T_g\text{-}T_{g1})/(T_{g2}\text{-}T_{g1})\cdot w_{2c}$ was an inclined straight line (Figure 4) of slope $K_1 = 1.2$.

Density Measurements

The miscibility of the studied PU-EMBA blends is indicated and by the density measurements [13]. The density of PU-EMBA blends was compared to that predicted by the law of mixtures Equation 5.

$$d = w_1 \cdot d_1 + w_2 \cdot d_2 \tag{5}$$

where d is the density of the blend, d_1 and d_2 are the component density, and w_1 and w_2 are the corresponding weight fractions.

Figure 5 shows that the density of the blends decreases with increase of the EMBA content in the blends. Simultaneously, there are no large differences

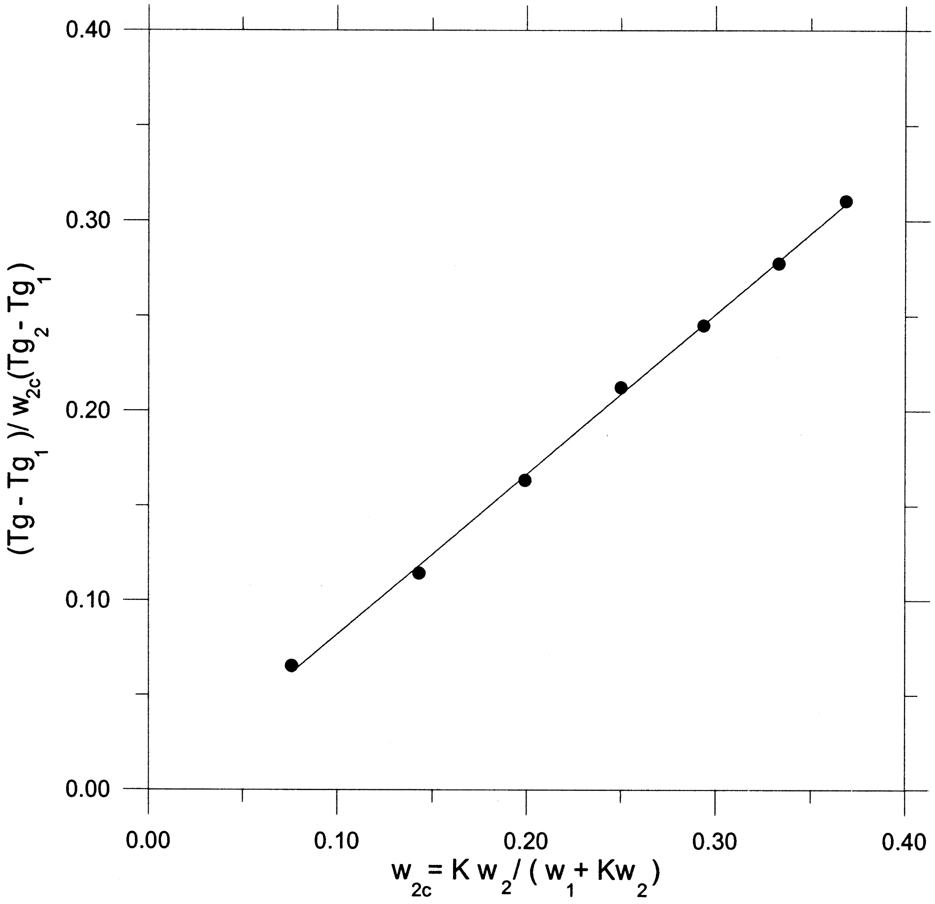

Figure 4. Plot $(Tg\text{-}Tg_1)/(Tg_2\text{-}Tg_1)\cdot w_{2c}$ vs. w_{2c} (Schneider equation) for PU-EMBA blends.

between the experimental and the theoretical values obtained using the Equation 5.

Physico-mechanical Properties

Data on the physico-mechanical characteristics of the studied blends in comparison with the crude PU showed that EMBA plays the role of "solvent" for urethane-urethane structure.

Figure 6 shows the experimental curves obtained plotting the stress against the strain for the studied blends. It can be observed that the stress used for the strain of the same unit of length for blends is lower as compared to that evoluated for PU. With only one inversion (sample B-6 against B-5) the stress decreases along with increase of the EMBA content in the blends.

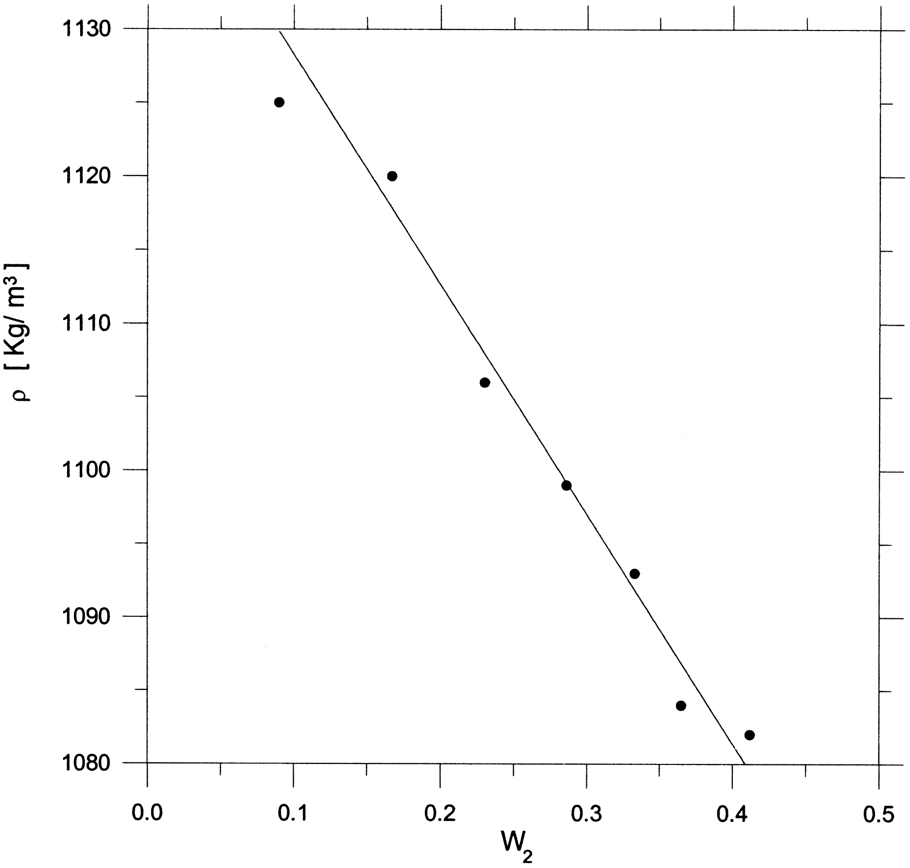

Figure 5. The density of the synthesized PU-EMBA blends vs. composition: (●) experimental data; (——) law of mixture.

The other mechanical properties evoluated for the PU-EMBA blends, namely the unitary stress, the elastic resilience, the resistance and the strain at the break, respectively the initial modulus, are listed in Table 2.

As can be noted, the increase of the EMBA in the blends up to a percentage of 16.7 wt% leads to a slight decrease of the strain at the limit of elasticity from 17.423 wt% (PU) to 15.828 wt% (sample B-2), then an increase to 43.120 wt% (sample B-4), followed by a gradual decrease up to 21.233 wt% (sample B-7).

The decrease of the strain at the limit of elasticity for the samples B-1 and B-2, respectively, as against PU, can be connected with the appearance of a new PU-EMBA matrix, where the new inter and intramolecular bonds established between the two polymers are less resistant to the unitary stress.

On the other hand, the increase of the strain at the limit of elasticity over that of PU for EMBA content is higher than 24.799 wt%, along with the continuous decrease of the unitary stress, suggests that EMBA in PU matrix operates only as a plasticizer.

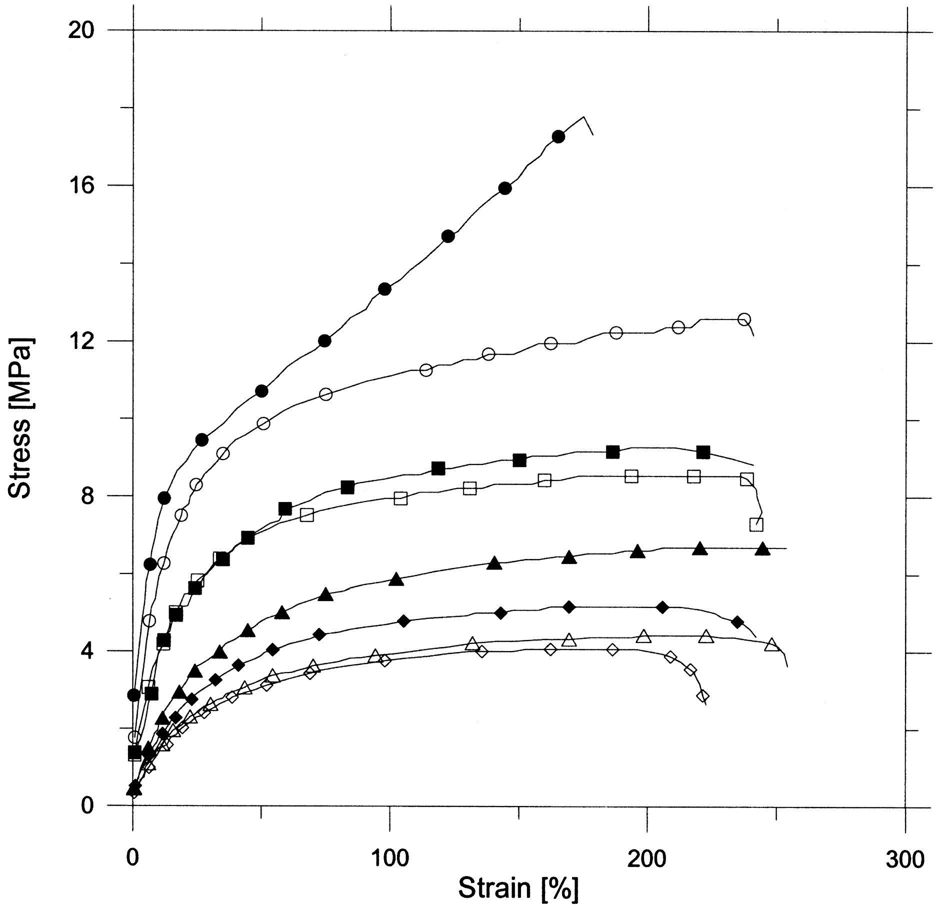

Figure 6. The stress of PU-EMBA blends against the strain (●) PU; (O) B-1; (■) B-2; (□) B-3; (▲) B-4; (△) B-5; (◆) B-6; (◇) B-7.

Important modifications can be seen for the elastic resilience of the blends against PU. Table 2 shows a strong decrease of the elastic resilience in the sample B-1, about 2.26 times vs. PU, then a gentle decrease (samples B-2 up B-4), followed by an accentuated decrease (samples B-5, B-6, and B-7, respectively). In our opinion, this behavior of the elastic resilience shows that the EMBA has an action in the PU matrix only on the morphology of polyesteric chains.

Thermal Decomposition

Thermal behavior of the studied blends was examined by TG analysis. Figure 7 shows the thermograms of both the pure homopolymers and of the PU-EMBA blends recorded at temperatures from ambient up to 600°C.

Table 2. Modification of the Physico-mechanical Properties of the Blends Against EMBA Content

Sample	Unitary Stress at the Limit of Elasticity (MPa)	Strain at the Limit of Elasticity (%)	Resistance at the Limit of Elasticity (MPa)	Elastic Resilience (MPa)	Resistance at the Break (MPa)	Strain at the Break (%)	Initial Modulus (MPa)
PU	0.190	17.423	3.311	18.998	44.537	212.891	61.472
B-1	0.084	14.227	1.194	8.392	9.646	115.232	50.790
B-2	0.071	15.828	1.120	7.078	8.842	114.831	27.549
B-3	0.067	24.799	1.671	6.738	8.609	113.712	25.555
B-4	0.060	43.120	2.604	6.039	6.774	80.366	16.250
B-5	0.039	36.597	1.463	3.987	4.408	76.129	12.067
B-6	0.038	18.506	0.764	4.129	5.138	70.339	13.839
B-7	0.027	21.223	0.576	2.714	3.053	53.437	10.879

The plots in Figure 7 show some typical sigmoidal forms. Generally, the thermal degradation of the synthesized blends in dynamic conditions and in the presence of the oxygen shows three, up to five, decomposition stages. Some data derived from TG curves are shown in Table 3, in which T_i is the initial decomposition temperature, T_m is the temperature corresponding to the maximum rate of decomposition, T_f is the final temperature and W is the weight loss. The same Table 3 includes the activation energy (E_a), the order of reaction (n) and the pre-exponential factor (Z), which are determined using Coats-Redfern [30] and Levi-Reich [31] methods.

The curves in Figure 6 and the data in Table 3 show that the decomposition of the blends occurs mainly in the range between 180 and 500°C, with different rates and W around 70 wt%. Decomposition of EMBA homopolymer starts at a lower temperature (100°C) than that of PU (218°C). For the blends, T_i is placed between T_i of PU and T_i of the EMBA polymer. The order of reaction of the blends

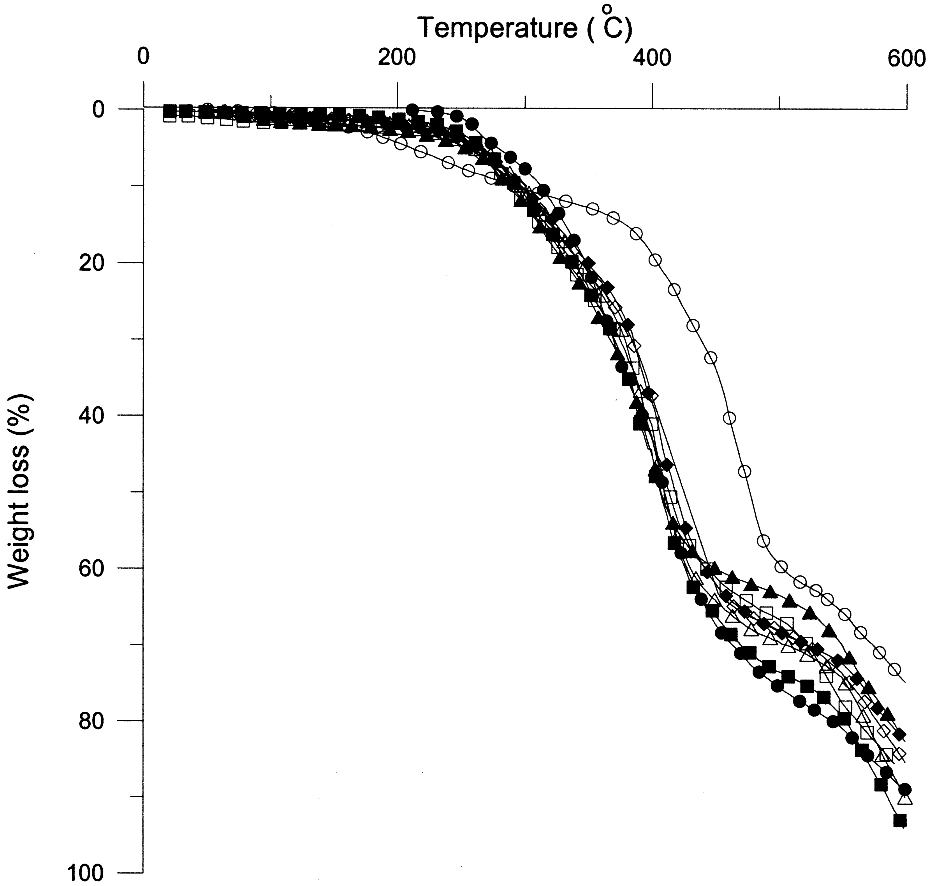

Figure 7. The TG-curves of the synthesized PU-EMBA blends: (●) PU; (O) EMBA; (■) B-1; (□) B-2; (▲) B-3; (△) B-4; (◆) B-5; (◇) B-6.

Table 3. Kinetic and TG Data Evaluated for the Thermal Decomposition of PU-EMBA Blends

Sample	EMBA (wt %)	T_i (°C)	T_m (°C)	T_f (°C)	W (%)	n	E_a (kJ/mol)	Z (min^{-1})
PR-207	0	218	353	427	59.2	1.2	81.8	466.61
B-1	9	216	405	500	73.2	0.9	49.2	972.6
B-2	16.7	209	401	479	64.4	0.4	36.4	679.2
B-3	23	200	404	473	61.5	0.4	34.9	311.3
B-4	28.6	215	403	472	66.7	0.3	38.9	177.5
B-5	33.3	217	405	499	67.8	0.4	36.9	416.1
B-6	37.5	200	409	481	66.5	0.2	33.5	485.1
B-7	41.2	182	383	454	68.1	0.1	14.0	13.33
EM	100	100	467	532	63.1	0.0	14.3	0.329

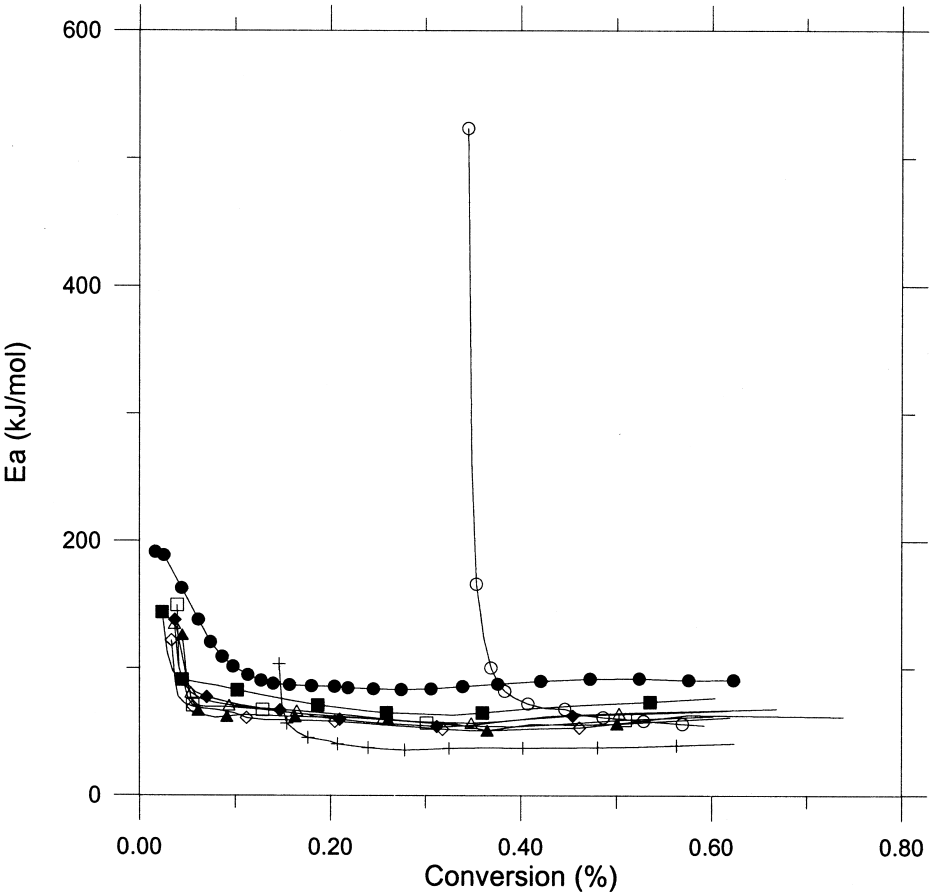

Figure 8. Dependence of Ea on conversion for PU-EMBA blends: (●) PU; (O) EMBA; (■) B-1; (□) B-2; (▲) B-3; (△) B-4; (◆) B-5; (◇) B-6; (+)B-7.

is placed between that of PU (1.2) and EMBA (0) and decreases with an increase of EMBA content in PU. Simultaneously, the Ea decreases from PU (81.8 kJ/mol to EMBA (14,3 kJ/mol) along with an increase of EMBA content in PU.

The dependence of Ea against conversion of the studied blends is illustrated in Figure 8.

The Ea of both PU and the blends shows a decrease caused by the loss of the light decomposition compounds (CO_2, H_2O) up to 0.1 conversion, and then remains roughly constant on the whole conversion interval, with same the convoluted steps. The Ea for EMBA homopolymer could be measured only for conversions higher than 0.34%. It shows a very sharp decrease in the interval of conversions between 0.34 and 0.40%, after which it remains constant.

CONCLUSION

Blending of polymers offers attractive opportunities for developing new materials with useful combinations of properties. PU in mixture with EMBA showed a good miscibility, which was established by the presence of a single T_g using DSC technique. The physico-mechanical properties of the blends are lower as those evaluated for PU in comparision with PU-EMBA interpenetrating polymer networks which show excellent mechanical properties. The thermal behavior of the PU-EMBA blends showed no large differences to that of PU taken alone.

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