

DYNAMIC MECHANICAL PROPERTIES OF POLYMER BLENDS OF POLYPROPYLENE AND POLY(ETHYLENE-CO-VINYL ACETATE) IRRADIATED WITH FAST ELECTRONS

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Abstract. Extruded blends of polypropylene (PP) and poly(ethylene-co-vinyl acetate) (EVA) irradiated with fast electrons were studied. The dynamic mechanical properties were investigated with respect to the blend composition and irradiation dose. Two glass transition temperatures corresponding to the glass transitions of the pure components were observed. Their existence is an evidence of the immiscibility of the components. Nevertheless, the peaks broadening, the single jump in the storage modulus values and the changes of T_g with the blend ratio suggest the creation of an interface region, leading to the improvement of the compatibility of the components. The irradiation with fast electrons at doses higher than 100 kGy results in single T_g transition because of the broadening of the interface layer.

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1. Introduction

Blending of polypropylene (PP) with elastomers has focused considerable interest as a route to the improvement of the impact properties of PP. To this purpose, various elastomers have been investigated [1-7]. It has been established that poly (ethylene-co-vinyl acetate) (EVA) is among the best impact modifiers for

PP [1]. The mechanical properties and morphology of bulk blends of isotactic PP (i-PP) and EVA with different VA content were studied by Thomas et al [3-5] and Gupta et al [1]. It was established by Gupta et al [1] that EVA improves the impact strength of PP by a factor of 2.6. The two-phase morphology was clearly visible at all compositions of the blends, confirming the immiscibility of EVA and PP. The final properties of the immiscible blends were determined by the morphology and properties of the pure polymers, the geometrical arrangements of the components and the nature and thickness of the interface. EVA phase dispersed in the matrix of PP was observed for samples with up to 30 wt % EVA. In the blends with 40 wt % EVA, co-continuous PP/EVA structure was established [1, 3]. Crosslinking by irradiation with electrons, γ -rays or dynamic crosslinking with dicumyl peroxide have been used in order to modify the properties of the blends and to improve the adhesion at the interface regions [4, 5, 8-15]. Several studies have been reported on the effect of radiation on i-PP/EVA blends [4, 5, 9, 10, 14, 15]. Both crosslinking and degradation occurred during irradiation, causing remarkable changes in the mechanical properties [5]. The modulus and elongation at break of the samples rich in PP, irradiated with a dose $D = 100$ kGy were considerably reduced. Thomas and Gupta [5] suggested that these changes might be associated with the predominant chain scission of the PP component. The same conclusion was drawn on the basis of gel- fraction and DSC analysis [10], WAXS [14] and positron annihilation lifetime spectroscopy [15] applied to extruded polymer films of PP/EVA blends. Minkova and Nikolova [10] have found that the melting temperatures do not depend on the composition of the blends and decrease slowly with increasing the irradiation dose. The temperature range of heat shrinkage spans from the beginning of the EVA melting interval 80-90 °C to the beginning of i-PP melting 130 °C [10]. On the basis of WAXS studies of PP/EVA extruded films, Mihailova et al supposed partial interpenetration of the two components in the amorphous regions. It was shown that the width of the interface regions grew with increasing irradiation dose [14].

The most widely used criterion for the degree of compatibility of two polymers relies on the measurement of glass transition temperature T_g . The detection of a single T_g , with value between the T_g 's of the individual components was an indication of a miscible system [16-18]. On the contrary, an immiscible system would reveal two T_g 's, corresponding to those of the individual components. A shift in the T_g 's of the components of an immiscible blend with respect to those of the pure polymers might indicate some degree of miscibility [16-19]. Dynamic mechanical thermal analysis (DMTA) is a method sensitive to the relaxation behavior of polymer materials [16] and provides quantitative measurements of the changes in mechanical modulus during phase and relaxation transitions [16].

This paper deals with DMTA studies of EVA/PP polymer blends, aiming at the determination of the influence of polymer composition and irradiation dose on dynamic mechanical relaxations. These studies also allow us to verify our previous suggestion about a partial compatibility of these polymers [14, 15].

2. Experimental

The EVA used was a random copolymer of ethylene and vinyl acetate, LUPOLEN V5510SX (BASF). It contained 33 wt % vinyl acetate. The PP used was i-PP-PE block copolymer with 10 wt % PE, trademark BUPLEN 7623, Bulgaria. The compositions of the blends under study, the corresponding flow indices and densities are given in Table 1. All samples were irradiated in a linear electron accelerator (E-250, Russia) in air, with doses of 53, 83, 100 and 113 kGy. The energy of the electrons was 250 keV.

Table 1. Polymer composition, flow index and density of samples studied

Sample	Buplen 7623 (wt)	Lupolen V5510SX (wt %)	Flow index (g/10 min)	Density at 23 °C (kg/m ³)
EVA 100	0	100	18.4	954
EVA 90	10	89.85	0.82	916
EVA 70	30	69.85	0.81	912
EVA 50	50	49.85	2.00	913
EVA 40	60	39.85	1.93	910
PPE 100	100	0	2.00	903

DMTA measurements were performed on a DMTA Mk II (Rheometric Scientific) in the temperature range from -150°C to $+100^{\circ}\text{C}$, at frequencies of 3, 10 and 30 Hz. These measurements were done with all unirradiated samples as well as with the samples irradiated with 100 kGy. The DMTA curves for sample EVA 50, irradiated with doses of 53, 83, 100, 113 kGy were recorded in order to study the influence of the irradiation dose on the mechanical properties and relaxation transitions. In this case, the measurements were performed by means of an Auto-Reovibron Dynamic Viscoelastometer (Imass Inc.) at a frequency of 11 Hz in the temperature range from -100 to $+160^{\circ}\text{C}$. In both cases, the heating rate was $1^{\circ}\text{C}/\text{min}$.

3. Results and Discussion

The storage modulus E' , the loss tangent $\tan \delta$ and the loss modulus E'' of the unirradiated sample EVA 50 are presented in Fig. 1a, b, c, respectively. Two relaxations are clearly seen. The first one, at -125°C , corresponds to the γ -relaxation of EVA and its position depends on the frequency. According

to Reading et al [20], this relaxation could be associated with molecular motion, involving only a few ethylene units. In the discussion to the same paper, Schatzki assumed a "crankshaft" model for this motion—rotation around two consecutive colinear bonds. This motion involves at least four CH₂ groups in sequence. If one assumes Arrhenius dependence of the frequency f versus temperature, the activation energy of this relaxation should not exceed considerably 6 kcal/mol (25 kJ/mol) [20]. The activation energy ΔH^* could be calculated according to the equation [16]

$$\ln f = \frac{\Delta H^*}{RT} + \ln f_0 \quad (1)$$

where f_0 is a constant.

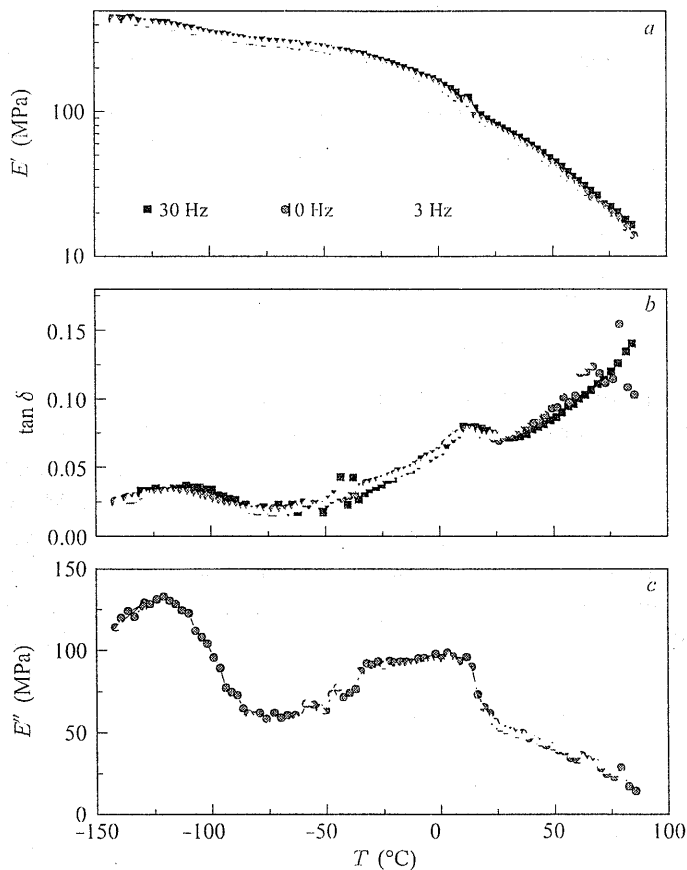


Fig. 1. Storage modulus E' (a), $\tan \delta$ (b), and loss modulus E'' (c) vs temperature for the sample EVA 50, unirradiated

The values of ΔH^* can be calculated from the maximum of the loss modulus E'' as well as from the $\tan \delta$ curves. They are calculated from the E'' curves (Fig. 1c) because the maximum of the peak and the dependence on the frequency are better pronounced. The ΔH^* and T_γ values are presented in Table 2. All samples have the same ΔH^* value within the error limits, except for the sample EVA 50, showing lower value. Nevertheless, all values are significantly higher than 24 kJ/mol, predicted by the Schatzki model. This might be due to the involvement of longer molecular segments in this motion. T_γ does not depend on the polymer composition.

Table 2. γ -relaxation temperature T_γ and activation energies ΔH^* for different compositions

Samples	T_γ (E'') (°C)	ΔH^* (E'') (kJ/mol)
EVA 90	-125	51±12
EVA 70	-124	63±7
EVA 50	-124	47±2
EVA 40	-123	59±6

Table 3. Glass transition temperatures for samples unirradiated and irradiated with dose of 100 kGy

Samples	Unirradiated		Irradiated	
	T_g EVA (°C)	T_g PP (°C)	T_g EVA (°C)	T_g PP (°C)
EVA 90	-29	—	—	—
EVA 70	-24	+3	-25	—
EVA 50	-19	+7	-30	+1
EVA 40	-30	+6	-45	0

The ΔH^* value of EVA 50, irradiated with 100 kGy, increases to 71 kJ/mol. In our previous work [15] it has been established that at this irradiation dose the processes of chain crosslinking predominate over the chain scission. The macromolecular network hindered the "crankshaft" motion that is mainly responsible for this transition [21–23].

The second maximum corresponds to the glass transition and consists of two components. The temperature dependences of E'' vs. temperature are shown for unirradiated samples in Fig. 2. The glass transition temperature of EVA with 33 wt % VA is -25 °C [20] and that of i-PP is 0 °C [24]. It can be seen in the figures that the position as well as the shape of this transition depend on the composition of the samples. The glass transition peaks of both phases are broad and overlapping. It is impossible to distinguish the peak corresponding to

the PP phase in sample EVA 90. The existence of crystal phase in the samples contributes to the broadening of the glass transition, as the chain flexibility is greatly reduced [20]. According to our previous studies, both components are semicrystalline, with a degree of crystallinity of about 30 % [14].

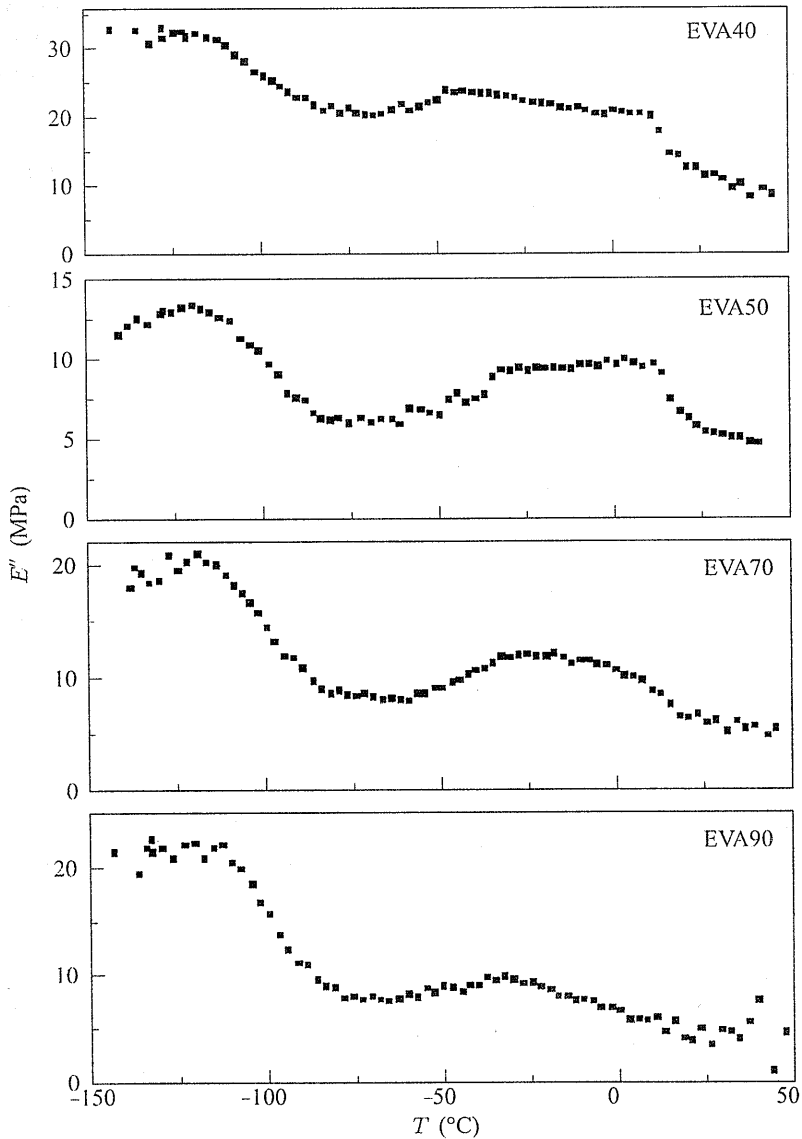


Fig. 2. Temperature dependences of E'' for different concentrations of the EVA component. Frequency 10 Hz

The curves are deconvoluted by Gaussian functions. The obtained glass transition temperatures for all unirradiated samples as well as for that irradiated with 100 kGy are shown in Table 3. The calculations are based on the loss modulus curves. It is seen that T_g significantly depends on the composition. The sample EVA 50 has the highest value of T_g for both components. At this composition ratio, the co-continuous structure has been observed by SEM studies [3]. Broader interface regions could be assumed for this sample. The presence of short ethylene blocks in the PP chains may help for formation of an interface between the components. The same suggestion has been made in our previous work on the basis of the analysis of the amorphous halo of the blends [14].

Irradiation with 100 kGy leads to a shift in the peaks positions to lower values (Table 3). The shift is smaller for samples rich in EVA. The observed changes of T_g after irradiation show that irradiation influences the components in a different way. The crosslinked regions as well as the low molecular fractions and branches produced as a result of irradiation take part in the glass transition process. As it is well known, PP is a polymer in which the processes of chain scission predominate over the processes of crosslinking, while crosslinking predominates in the case of EVA [8, 9, 15, 25]. This explains the different changes in the glass transition after irradiation of different samples.

The temperature dependences of E' and E'' in the range from -80°C to $+160^\circ\text{C}$ for the irradiated samples of EVA50 are presented in Fig. 3a, b, respectively. The storage modulus values at low temperatures do not depend on the irradiation dose. A single stepwise reduction of E' in the glass transition interval is well expressed (Fig. 3a). The storage modulus keeps relatively high values above the melting point of EVA and diminishes sharply in the melting interval of PP. These observations support our previous suggestions, made on the basis of WAXS investigations, about the presence of partial interpenetrating of amorphous chains of both components at the interface.

An intensive and broad peak of E'' in the temperature interval from $+40^\circ\text{C}$ to $+120^\circ\text{C}$ is clearly seen in Fig. 3b. Its position and intensity depend on the irradiation dose. The intensity of this peak significantly increases up to the irradiation dose of 83 kGy and at higher doses it reduces to the value of the unirradiated sample. The α_c relaxation of PP and PE are situated in that temperature range [16] and they are overlapped by the melting interval of the EVA component [10]. The temperature dependence of the intensity of this transition is most probably related to the improvement of the crystal perfection with irradiation dose, observed in our previous work [14]. It could be suggested that the shift of the peak position to lower temperatures with the rise of the irradiation dose could be due to the processes of chain scission in chain folds on the surfaces of crystal lamellae.

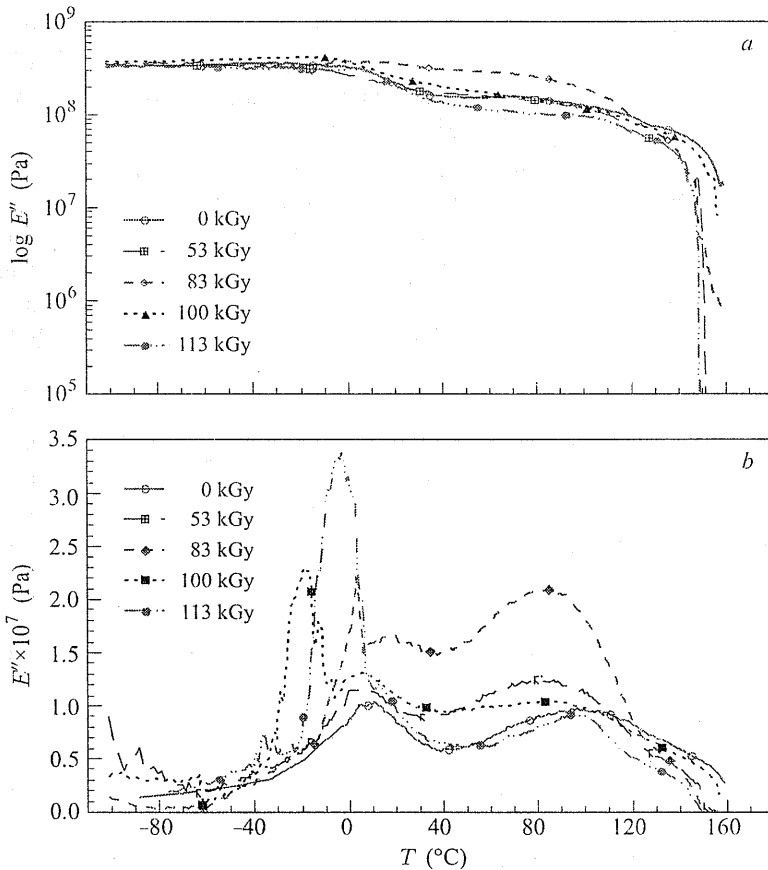


Fig. 3. Temperature dependences of E' (a) and E'' (b) for the sample EVA50 irradiated with different doses

The glass transition also depends strongly on the irradiation dose (Fig. 3b). The character of the T_g process changes abruptly at the dose of 83 kGy. A sharp peak at 0°C appears and the broad peak shifts to +20°C. No peak is observed in the glass transition range of EVA (ca -25°C). The intensity of the narrow peak increases at the irradiation dose of 100 kGy and both peaks shift to lower temperatures. At the irradiation dose of 113 kGy, the broad peak completely disappears and a single intensive T_g peak situated at -5°C is observed. It could be assumed that the relaxation, corresponding to the sharp low temperature T_g peak is related to relaxation of entities with higher flexibility, i. e., low molecular fractions, produced by chain scission and molecular branches, obtained by grafting of low molecular segments to the main chains. The higher temperature T_g peak can be assigned to the relaxation of the crosslinked part of the material.

The low molecular products of irradiation contribute to the increase in the concentration of chain ends at the interface, resulting in the reduction of the interface tensions, broadening of the interface and improvement of the components compatibility [26]. This can explain the appearance of a single intensive T_g peak for the sample, irradiated at 113 kGy.

4. Conclusions

The dynamic mechanical properties of extruded polymer blends of EVA and PP were studied with respect to the blend ratio, irradiation dose and temperature. Two glass transition temperatures were observed. Their existence was an evidence of the immiscibility of the components. Nevertheless, the peaks broadening, the single jump of the storage modulus values and the changes of T_g with the blend ratio suggested the creation of the interface region, leading to the improvement of the compatibility of the components.

The irradiation with fast electrons at doses higher than 100 kGy resulting in a single T_g transition was due to the broadening of the interface layer.

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