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Studies on Morphology, Rheological, Mechanical, and Thermorelaxation Properties of Chemically and Radiation Modified Polyethylene/Ethylene Propylene-Diene Copolymer Blends

J. Zicans[a]; M. Kalnins[a]; T. Bocoka[a]; V. Kalkis[b]; A. Bledzki[c]
[a] Institute of Polymer Materials Riga Technical University, Riga, Latvia [b] Chemical Department, University of Latvia, Riga, Latvia [c] Institut fur Werkstofftechnik University of Kassel, Kassel, Germany

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STUDIES ON MORPHOLOGY, RHEOLOGICAL, MECHANICAL, AND THERMORELAXATION PROPERTIES OF CHEMICALLY AND RADIATION MODIFIED POLYETHYLENE/ETHYLENE PROPYLENE-DIENE COPOLYMER BLENDS

J. Zicans, M. Kalnins, T. Bocoka
Institute of Polymer Materials
Riga Technical University
Azenes qtr. 14
LV-1048, Riga, Latvia

V. Kalkis
Chemical Department
University of Latvia,
Valdemara str.48
LV-1013, Riga, Latvia

A. Bledzki
Institut fur Werkstofftechnik
University of Kassel
Moncheberg qtr. 3
Kassel 34109, Germany

ABSTRACT

Experimental studies of the blends consisting of chemically and radiation modified polyethylene and ethylene-propylene-diene copolymers have been carried out. Measurements of crystallinity, microhardness, strength-deformation, viscoelastic, adhesive and thermorelaxation properties, as well as electron microscope observations, have shown that the blends chemically vulcanized by a special elastomer phase crosslinking system has a typical biphasic structure within the entire composition range with characteristics specific for rubber. Subsequently, radiation vulcanized blends where crosslinking takes place in both disperse phases, formation of chemical bonds between these phases and fibrillation of molecular structures is observed. Consequently, it can be stated that radiation treatment shows the best properties of the blends in comparison with chemical vulcanization. Therefore, materials formed by such a system can be successfully used, e.g., as elastic and adhesive active thermosetting materials if the polymer is previously oriented.

INTRODUCTION

Physical modification of polyolefins by blending with various elastomers is one of the most economic ways to obtain thermoelastoplastics with characteristics both of rubber and plastic, e.g., flexibility, high impact strength at low temperatures, etc. Rheological properties of these materials permit reshaping them by highly productive plastic material processing. In many cases, the polyolefin/elastomer blends are used as rubbers in various branches of the technique [1 -3]. Applications of these materials can be considerably enlarged by chemical or high-energy treatment.

It is well known that polyethylene, ethylene-propylene or ethylene and other monomers copolymers are more often crosslinked by the use of chemical agents. In addition, the process of polymer crosslinking or vulcanization is combined with the shaping of material, e.g., casting under pressure, extrusion, etc., therefore, obtaining so-called dynamic thermoelastoplastics [4 -5]. Radiation modification of polyolefins and their compositions also have wide application in obtaining materials with increased chemical resistance, thermostability, and other unique properties, e.g., with "the memory effect" after the orientation of polymer [6-7].

There is no equally significant data about the usefulness or priority of both methods to modify polyolefin blends in the literature. Our previous investigation showed that these properties of a radiation modified polyethylene/elastomer thermoplastic system, such as increased thermostability, oil resistance, and low residual internal stresses, decreased properties of material fatigue, and others e.g., elastic, adhesive and strength-deformation properties make it possible to extend the application and preparation of elastic and adhesive active thermosetting materials (TSM) [8].

TSM, obtained by radiation or chemical crosslinking, are still very popular and widely used in various branches of technique: contractible films and belts for packaging, profiles such as couplings, sleeves and bandages for pipe connections, electric cables, etc. [9]. TSM are mainly formed of crystallizable polymers, mostly of polyolefin and their compositions (fillers, copolymers, blends with other polymers), by unaxial or biaxial orientation of certain objects at the elevated temperature and the subsequent cooling to room temperature under isometric conditions. The majority of such polymers used in engineering applications contain some level of crystallinity, which effects the mechanical properties of the polymer material. The addition of amorphous polymer to semi-crystallizable forming the blend causes noticeable changes in the crystallization behavior and therefore, in the final properties of material.

Therefore, in this work we investigate the influence of crystallization of the different crosslinked disperse phases on the structure, deformation, viscoelastic, adhesive and thermorelaxation properties of the blends.

To determine the crosslinking effectiveness of the blends, we relied on the generally accepted principles that crosslinking proceeds mainly in the amorphous phase of polymer. Our results have also shown the effectiveness of gel-fraction formation in elastomer phase and increased values of thermorelaxation stresses in oriented material. In fact, elastomer phase crystallization (as shown in several authors' works) should also be taken into consideration in the investigation of the crosslinking process. The influence of copolymer crystalline phase, determined by X-ray diffraction or DSC is not possible [10- 11] in the cases with a small crystallite size and low crystallization degree. This result will be considered in further research

EXPERIMENTAL

Polymers

Unstabilized low-density polyethylene (LDPE), trade mark 108-02-20, (obtained from Novopolotsk Chemical Enterprise, Russia) with the following characteristics was used: density, 0.919 g/cm^3; average values of molecular weight (M_η = 31200, M_w = 36500, M_n = 19500); degree of branching, 4.5 (number of tertiary substituted C atoms per 100°C atoms of a chain); melting temperature, 378°K; temperature of intensive oxidation, 488°K (both according to DTA data); melt flow index, 2.0 g/10 min. and tensile modulus of elasticity E_0 = 91.1 MPa.

Ethylene-propylene-diene (EPDM) co-terpolymer of commercial grade SKEPT-40 (Russia) with a propylene content 40 mol%, dicyclopentadiene content 0.5-2 mol%, density 0.87 g/cm^3, viscosity 40° Moony were used.

Blend Preparation

LDPE/EPDM blends of the following compositions were prepared: 0, 5, 10, 30, 50, 70, 80, 90, 95 wt% of EPDM copolymer.

Blends have been obtained by double melt mixing in a twin-screw extruder. The average barrel and head temperature T = 433°K. The blends obtained after the mixing process, were cut into granules, then molded and pressed into sheets 0.5-4 mm thick. This procedure was identical for both chemical and radiation modified samples.

Chemical Crosslinking

For chemical crosslinking (series A), agents such as sulphur MC (2 wt%), Thiuram D (1 wt%), Nonox S (1 wt%), Neozone A (1.5 wt%) and Captax (0.5 wt%) were added in mixing, process time (mixing time 10 minutes).

Radiation Crosslinking

Treatment of samples of sheets with γ-radiation (series **B**) were carried out on Co^{60} radio target equipment RXM-20 in an atmosphere of argon, and power of absorbed dose 10 kGy/in up to absorbed doses of 200 kGy.

Determination of Gel-fraction

The gel-fraction was determined as an insoluble (crosslinked) part of the blends after a 24 hour treatment in boiling CCl_4 in a stream of nitrogen.

Viscometric Measurements

The viscosity of molten blends was measured with the help of a capillary rheometer. The shear rate is varied by the speed of the pressure cylinder 3, 15, 50 mm/min., which results in the shear rate range of 5-1000 s^{-1}. Volumetric flow rate Q, as a function of pressure drop ΔP in the capillary length L = 8.0 mm and radius R = 1.8 mm (primary flow curve), was measured at 413, 433 and 453 ± 0.5°K.

These data were used to calculate the shear stress τ_w, shear rate $\gamma^{\cdot}{}_w$ and apparent viscosity η_a according to the following equations:

$$\tau_w = R\ \Delta P / 2\ L \tag{1}$$

$$\gamma^{\cdot}{}_w = 4vr^2/R^3 \text{ where v - speed of the pressure cylinder and} \tag{2}$$
r - radius of cylinder

$$\ln \eta_a = \ln \tau_w - \ln \gamma^{\cdot}{}_w \tag{3}$$

Determination of Melting Parameters and Crystallinity

DSC measurements were carried out on Perkin-Elmer DSC-4 and Mettler TA 3000 devices, calibrated with indium standard. Thermograms were recorded using a heating rate 10°K/min and a temperature range from 15 up to 473°K under nitrogen atmosphere. All thermograms were recorded at identical experimental settings and almost equal sample weights, hence, they have a good base for comparison in their locations and shape a temperature scales. The size of the experimental points on the figures correspond to the respective error bars (corresponds also to the other measurements).

X-ray diffraction measurements were done on a X-ray diffractometer in the 2Θ range from 10-30°, using CuK_α radiation at scan speed 1°/min.

Density Measurement

The densities of samples were measured by a method of hydrostatic weighting in isoproponol (ASTM D 1505-85).

Mechanical Testing

Tensile and elongation properties were determined using standard (ASTM D 638, type 4) specimens and universal testing machine UTS 100 at a constant strain rate 50 mm/min, at room temperature. The tensile parameters of interest were the tensile strength at break (σB) and elongation at break (εB).

A microhardness tester with a Vickers square pyramidal diamond indenter was used. The microhardness value (in MPa) was evaluated from the expression $H = kp/d^2$ where d is the mean diagonal length at the indention; p - applied force and k - geometrical factor equal to 1.854. A loading cycle of 0.1 min to minimize creep at the material under the indentor and a load of 0.5 N were used.

Impact strength (in J) within the temperature range of 133-153°K was determined on a Dynstat apparatus similar to DIN 51222.

Adhesive Measurements

Laminated metal-polymer-metal (closed systems) samples were made. A 70 μm thick steel foil (corresponding to USA AJS 1010 steel) was used as a substrate. The steel surface was subjected to electro-chemical degreasing in an alkaline solution (composition of solution in g/l: Na_3PO_4 -60, Na_2CO_3 -30, NaOH -15) at temperatures 343-363°K and current density 10 A/dm^2 as a cathode for 2.5 minutes, then as an anode for 0.5 minutes). The polymer films (thickness 500 μm) were bonded with the substrate by direct hot-pressing at a temperature 443 and 463°K under pressure 1 1 MPa for a time 1-5 minutes (specified parameters similar to the thermosetting process of TSM).

The peel strength, A (in kN/m), of samples was determined in a tensile testing machine ZT-20 at a crosshead speed of 0.8 mm/s at room temperature. Standard deviation of the measurements was from 10 to 15%.

Measurement of the Thermorelaxation and Residual Setting Stresses

Thermorelaxation stresses (σ_{TR}) of the oriented chemically and radiation crosslinked samples were measured by the static method under isometric heating conditions. Residual setting stresses (σ_{SE}) were also measured by this method: after the isometric-heating process was done, a subsequent cooling process was done under equal isometric conditions. Unified ultrasonic methods based on the peculiarities of propagation of flectural (surface) ultrasonic waves in polymers for the control ofthese parameters (as well as an absorbed doses) have been used [12].

The samples (length 20 mm, width 5 mm, thickness 0.25), oriented at 403°K and subsequently cooled under isometric conditions to room temperature were fixed in special clamps. The thermosetting force was measured tensometrically: one of the clamps was fastened to a graduated springy steel plate, with four tensoresistors attached to it. The sensitivity ofthe device ± 0.01 N.

Electron Microscope Observations

Morphological studies of the specimens were conducted using Philips EM-500 scanning electron microscope (SEM). Observations were carried out on an external surface of the specimens, which were fractured in liquid nitrogen and coated with gold in argon atmosphere.

RESULTS AND DISCUSSION

In the present work, the influence of γ-radiation and chemically crosslinking agent's action on properties and crystalline region of LDPEIEPDM blends formation is reported. The observed variances in initial and crosslinked samples melting behavior derived from differential scanning calorimetry and X-ray diffraction measurements of crystallinity are discussed in the light of high-energy, as well as chemical influence on the structure of the blends. Furthermore, in addition to reporting the results about mechanical, viscometric, adhesive, relaxation and structures properties of the blends in studied range of blends' composition, the conditions of forming TSM with specific exploitation properties are presented.

The melting temperatures from DSC thermograms, recorded during the heating cycle for LDPE/EPDM blends, are depicted in Figure 1. DSC thermograms show endothermic melting peak of LDPE in all the blend samples. The LDPE shows a narrow and sharp peak, while the blends, especially with chemically crosslinked EPDM, depict relatively broad and weak peaks. These endothermic peaks are situated around 373-382°K. The peak temperature decreases with

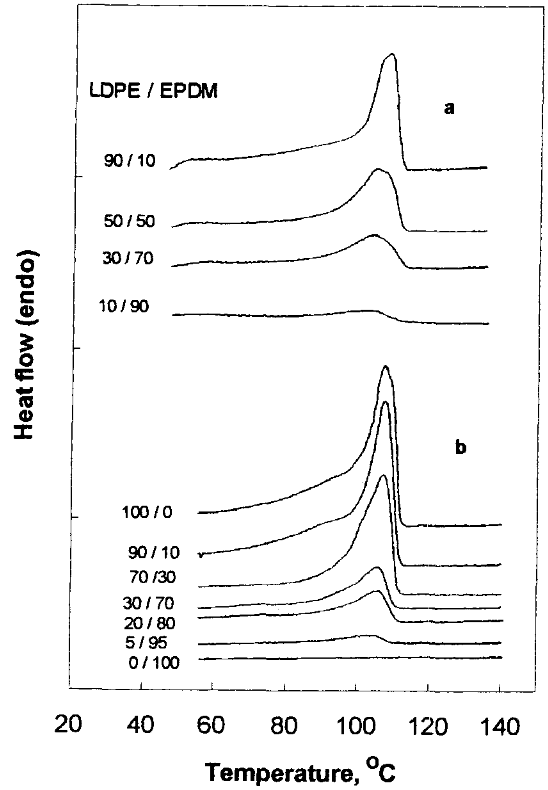

Figure 1. DSC melting thermograms in LDPE/EPDM blends: chemically crosslinked (**a**); irradiated up to 150 kGy (**b**).

increasing EPDC content in the blend composition. The peak height simultaneously decreases. From the analysis of thermograms the following parameters were established: T_p- an endothermic peak temperature, determined as the point at intersection of the tangents of the two sides at the endotherm; T_{on} and T_{en} - the onset and endset temperature estimated as the intercept points (at the baseline) of the tangents of the high and low temperature side of the endotherm; the quantity $\Delta T_c = T_{en} - T_{on}$ (this quantity reflected the temperature range of crystallite melting and relates to the distribution of crystallite size and "perfection"); ΔH_f - entalphy of crystallite melting, proportional to the area under the endotherm per unit mass of the sample; w_c - mass crystallinity of the sample: $w_c = \Delta H_f / H_f^*$ where ΔH_f^* represents the enthalpy of melting 100% crystalline polyethylene, estimated applying " total enthalpy " method.

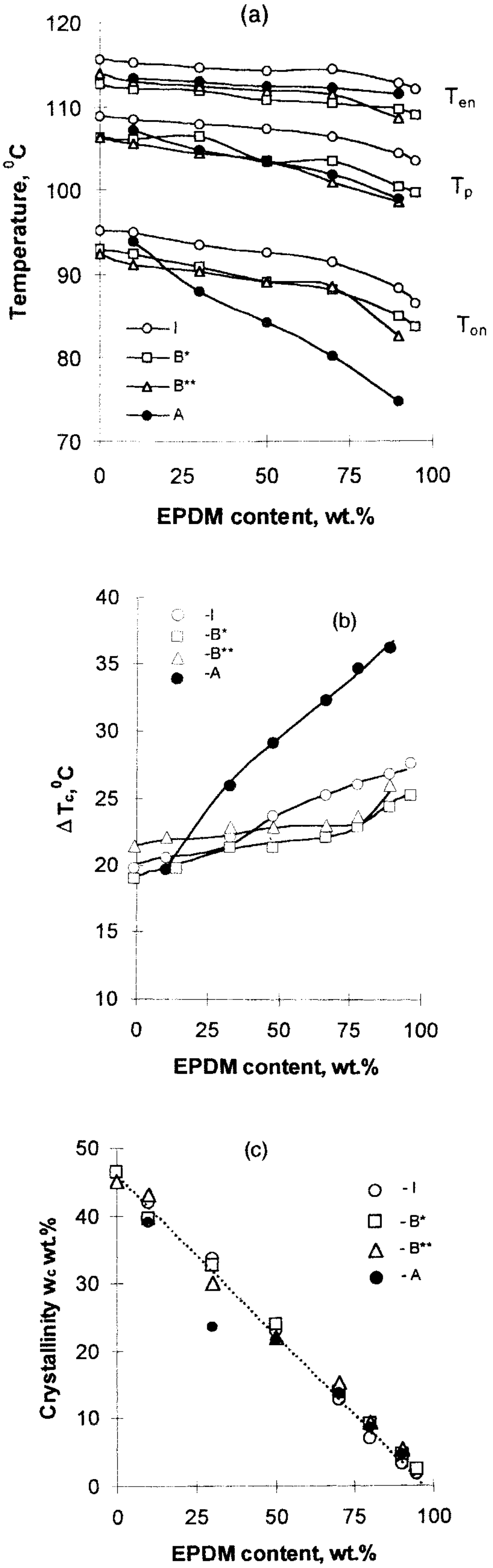
(a)
Temperature, ^0C
120
110
100
90
80
70
0
25
50
75
100
EPDM content, wt.%
T_{en}
T_p
T_{on}
I
B*
B**
A
(b)
$\Delta T_c, ^0C$
40
35
30
25
20
15
10
0
25
50
75
100
EPDM content, wt.%
-I
-B*
-B**
-A
(c)
Crystallinity w_c wt.%
50
40
30
20
10
0
0
25
50
75
100
EPDM content, wt.%
- I
- B*
- B**
- A

Figure 2 shows the detailed results from DSC measurements. The melting peak temperature T_p and T_{en} reduces slightly with increasing EPDM content up to 70 wt% in the blend composition. The temperature, which characterizes the low temperature wing of melting, e.g., T_{on} is influenced by blending with elastomer phase at a higher level. The blends with EPDM content, higher than 30 wt%, show an obvious decrease of onset temperature T_{on}. Consequently, the characteristic melting interval ΔT_c increases for compositions containing more than 50 wt% of EPDM. Similar parameters have been determined for melting of the γ-irradiated samples. Characteristic temperatures of all melting peaks decreases with increasing absorbed dose of γ-radiation. T_p varies proportionally with absorbed dose, T_{on} and T_{en} reduces at the higher level at first 100 kGy. Further irradiation of the sample up to 200 kGy causes only a slight decrease of these two characteristics. The melting enthalpy for irradiated blend compositions does not show a noticeable variance with an absorbed dose increase up to 200 kGy. Crystallinity obtained by DSC naturally decreases according to the increase of elastomer content in the blends (Figure 2c). Chemical crosslinking effects the greater changes, and will be discussed in connection with the other changes.

Crystallinity value (X_c) obtained from X-ray diffraction is somewhat higher than those from DSC. The X_c for series **A** and series **B** blends decreases with the lowering of LDPE content in the same manner as the w_c values.

In the beginning, the effort force through capillar as time function P=f(t) of the investigated rheological properties of the blends was determined. Figure 3 shows the example for composition (LDPE/EPDM ratio 50/50) of series **A** and **B** samples. It is shown that P increases steadily until it reaches equilibrium state. The remarkable difference is observed between radiation and chemically crosslinked samples. The parameters become equal for chemically crosslinked samples (gel-fraction content 46 wt%) with radiation modified if the absorbed dose reaches 100 kGy (gel-fraction content 45 wt%). It should be noted that the observed stationary flow rate for all investigated series **A** and **B** samples obviously shows that the further chemical structuring, as well as the presence of radiation post effects, were not observed. Therefore, the microgels instead of the macrogels form the structure of the material. Viscometric measurements of the blends at 453°K show that the viscosity increases by increasing the EPDM content. As a result, the copoly-

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Figure 2. Variation of the melting parameters with LDPE/EPDM blend composition content (**a**); correlation between the quantity ΔT and EPDM content (**b**); variation of LDPE/EPDM blend crystallinity with EPDM content (**c**). I - initial blend; A - chemically crosslinked; B* - irradiated up to 100 kGy; B** - 200 kGy; T_p - peak temperature; T_{on} and T_{en} - onset and endset temperature.

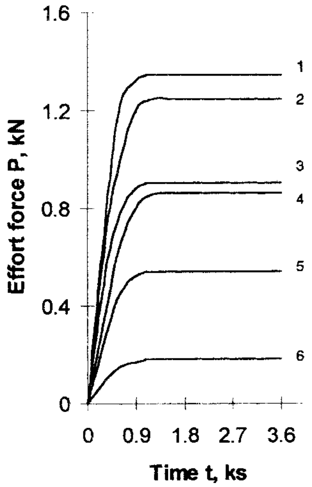


Figure 3. Variation of effort force through capillar P with time t for the blend composition (LDPE/EPDM ratio 50/50) at temperature 413°K: 1 - chemically crosslinked (ratio 5/95); 2 - irradiated, 200 kGy; 3 - chemically crosslinked; 4 - irradiated, 100 kGy; 5 - irradiated, 50 kGy; 6 - 0 kGy (initial).

mer macromolecules are more crosslinked than polyethylene molecules. In the case of series **A**, when only the elastomer phase is selectively crosslinked during chemically vulcanization, this disperse phase causes the greatest changes in the blend viscosity, respectively; these are greatest at the EPDM content 70-90 wt%. On the contrary, an increase of LDPE phase leads to the remarkable decrease in viscosity and at LDPE/EPDM (90/10) this value is comparable with the value of initial pure polyethylene (see Figure 4).

Negative derivations of the viscosity, from the rule of logarithmic additivity observed for LDPE/elastomer blends, may result from a reduction in the aggregation degree of macromolecules in the blend. This is due to the low affinity of molecules with different structures that make mutual slip easier. An increase in free volume content in the interphase regions of chemically crosslinked blends leads to an acceleration of relaxation processes. Thus, it can be concluded that a two-phase structure probably exists in the melting state in the whole composition range of the tested blends in which the component with the smaller content constitutes the dispersed phase in the form of isolated spherical conglomerates. Radiation treatment of these isolated conglomerates joins each other and forms the continuous phase. The described behavior is supported by SEM micrographs of surfaces of the blends (see Figure 8).

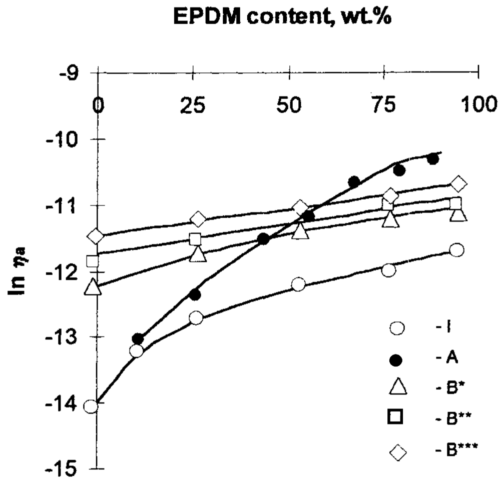


Figure 4. Effect of copolymer content on viscosity of LDPE/EPDM blends at temperature 453°K: I - initial blend; A - chemically crosslinked; B* - irradiated up to 50 kGy; B* * - 100 kGy; B* * * - 150 kGy.

One of the characteristic features of the tested systems is the great difference between flow activation energies of chemically and radiation crosslinked blends, especially at 413°K. Activation energy E of the blends, determined from the Arrhenius equation for series **B,** increases steadily with an increasing content of EPDM in the mixture with LDPE which can testify to the heterogeneity of the system (Table 1). Radiation crosslinking at the used absorbed doses still does not create the complete molecular network of the entire system, however, the microgels appear and E values proportionally increase. In the beginning, activation energy values of the series **A** blends at low EPDM content (10 wt%) are similar to the value of initial polyethylene, and it increases steadily with the heightening of the copolymer content. When the EPDM content becomes great (90 wt%), the sharp E decrease is observed which proves the changes in the transportation mechanism through channel are complete. It is possible that the process contains simultaneously the flow act, as well as slipping of some phase or turbulent action. In this case, only a small (10 wt%) non crosslinked part of LDPE is able to flow. Therefore, the observed decrease of E value does not correspond to the energy which is necessary to create the complete flow process of all systems and it could not be seen as a base for hydrodynamic calculations. This phenomenon is not expressed at the greater temperatures.

TABLE 1. Activation Energy of Flow E of LDPE/EPDM Blends at 413°K

EPDM content, wt.%	E, kJ/mol 0 kGy	50 kGy	100 kGy	150 kGy	Chemically crosslinked
0	45.0	45.8	49.8	55.	-
10	46.7	48.0	52.1	57.2	45.1
30	47.7	48.2	54.7	58.4	61.0
50	48.5	48.2	55.3	59.6	63.2
70	49.1	48.8	56.3	60.1	101
90	50.1	52.5	57.2	66.0	66
95	51.1	55.1	57.5	68.5	-

TABLE 2. Some Properties of LDPE/EPDM Blends (Irradiated 150 kGy/Chemically Crosslinked)

EPDM cont.,wt.%	Tensile strengh at break, MPa	Elongation at break, %	Impact strengh at 133 K, J	Microhardnes MPa	Density g/cm^3
0	17.6 / -	543 / -	1.30 / -	16.8 / -	0.917 / -
10	16.0 / 10.9	547 / 560	1.10 / 0.86	12.7 / 13.0	0.915 / 0.918
30	13.9 / 7.5	555 / 460	0.8 0/ 0.58	6.5 / 72	0.903 / 0.911
50	12.6 / 5.0	610 / 380	0.78 / 0.39	3.0 / 5.2	0.893 / 0.906
70	10.5 / 4.0	685 / 217	0.70 / 0.28	1.5 / 3.8	0.883 / 0.900
90	7.8 / -	874 / -	0.70 / 0.17	-	0.872 / 0.892
95	7.6 / -	933 / -	0.70 / 0.15	-	0.870 / 0.890

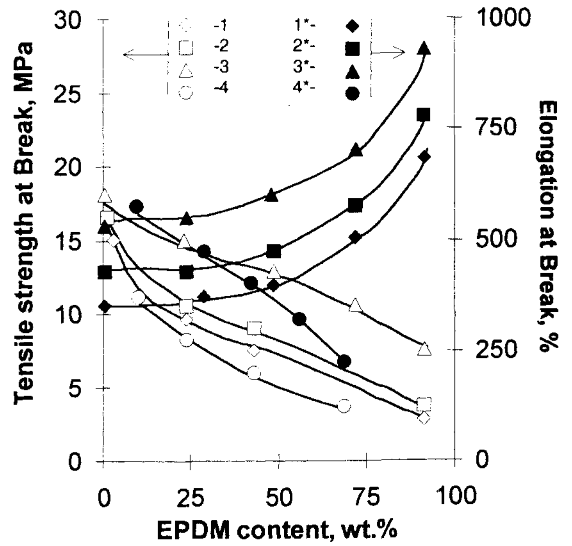
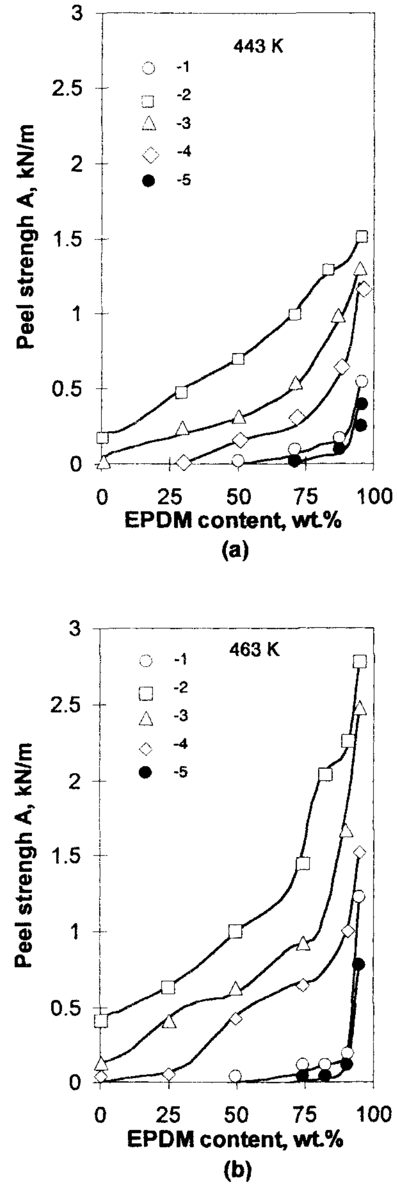


Figure 5. Variation of mechanical properties of series **A** and **B** samples with copolymer content. Tensile strength at break: 1 - initial blend; 2 - irradiated up to 50 kGy; 3 - 150 kGy; 4 - chemically crosslinked. Elongation at break: 1* - initial blend; 2* - 50 kGy; 3* - 150 kGy; 4* - chemically crosslinked.

Descriptions for the blends mechanical properties are given in Table 2. As predicted, tensile strength at break (σ_B), microhardness, and density parameters decrease proportionally to the increase of EPDM content. Differences in elasticity and impact strength are observed for series **A** and **B** samples. Elongation at break (ε_B) of radiation crosslinked LDPE/EPDM system increases with the increasing of elastomer content. On the contrary, for chemically crosslinked systems, this parameter decreases which indicates nonhomogenity and distinguishing features of the formed structure (see Figure 5, curve 4*). In this case, considerably crosslinked (gel-fraction content 82 wt%) and comparatively "solid" elastomer phase increases the system hardiness. An observed relationship of the blends impact strength shows that with an increaseof EPDM content up to 30 wt%, impact strength values of series **B** samples, at the - 133°K, monotonously decrease, but furtherr increasing of elastomer phase does not change impact strength. On the contrary, impact strength monotonously decreases for series **A** samples with the increasing of elastomer phase content up to 95 wt%.



(a)

(b)

Figure 6. Variation of peel strength, A, with EPDM content in the blends compositions under different contact conditions: **a**) temperature 443°K, time 240 s, pressure 1 MPa; **b**) temperature 463 K, time 240 s, pressure 1 MPa. 1 - unirradiated; 2 -irradiated up to 50 kGy; 3 -100 kGy; 4 -150 kGy; 5 - chemically crosslinked. **c**) effect of temperature and contact time for LDPE/EPDM blend (ratio 10/90): 1 - irradiated up to 50 kGy, T = 190°C; 2 - 50 kGy, T = 170°C; 3 - unirradiated, T = 190°C; 4 - chemically crosslinked, T = 190°C; 5 - unirradiated, T = 170°C; 6 - chemically crosslinked, T = 170°C.

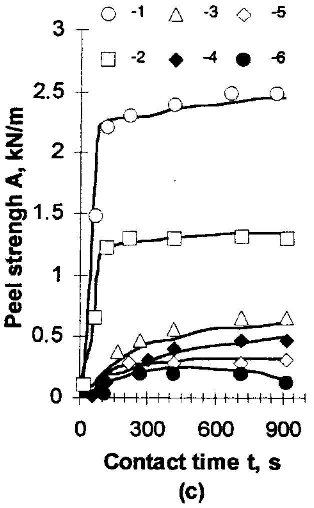


Figure 6. Continued

The blends adhesive parameters are important in this case, if it is necessary to form the TSM. In this work, adhesion contact creating conditions (temperature, pressure, and time) are choosen similar to those which are formed during setting time. As seen, adhesive combination strength of all investigated systems increases, when the contact time and temperature, as well as elastomer content in the compositions increase. Consequently, the adhesion interaction strength increases considerably in the case of radiation modification (see Figure 6a and b). The samples, which are irradiated up to small absorbed doses 50-100 kGy, have the largest values of peel strength. Some factors promote adhesion increase: firstly, the full-bodied spatial grating structure did not form in the blends (gel-fraction content does not exceed 25-40 wt%) at these doses; secondly, absorbed oxygen presence on the polymer surface and into amorphous interphase part, which activates radiation oxidative processes, and as the result, it increases the surface polarity; and thirdly, thermooxidative processes during contact time, which are accelerated by the presence of tertiary carbon atom, formed as a result of radiation crosslinking. It is necessary to also take into consideration the low viscosity of the blends at the chosen temperature. This allows us to make a more perfect contact with surface of substrates. Therefore, these factors together increase the adhesion interaction. Viscosity increases with increasing the absorbed dose, and the possibility of filling surface pores is difficult, and in this connection, adhesion decreases.. Kinetics of adhesion interaction of polyolefins with metals under conditions of contact thermooxidation, as well as dissolution and diffusion of iron compounds into the bulk of polymer, has been studied in the works [13-14]. Adhesive properties of series **A** samples do not expressed and are equal with initial LDPE. In this case, biphasic structures nonhomogenity, the great elastomer phases crosslinking degree and, as well as an increased viscosity of the chemically crosslinked system **A** considerably decreases the adhesion interaction. The maximal values of the adhesive parameters for the irradiated series **B** samples at the contact time 60 s are determined. But, for non-irradiated and chemically modified series **A** samples, the necessary time is even greater and it is not lower than 3 minutes (see Figure 6 c).

The thermorelaxation stresses (σ_{TR}), which determine the thermosetting force of TSM, result from the release of internal stresses of crosslinking oriented macromolecules. This is due to thermal disorientation in heating under isometric conditions. These stresses are particulary expressive and are great in the case when the orientation of a polymer has been previously carried out at a temperature which is lower than the melting point of the crystalline part of the polymer. If the heating is continued above the melting point of the crystalline part, the residual stresses (the stresses that really cause thermosetting force) are determined by the crosslinking degree of the amorphous part of the polymer. In this work, we used relatively high orientation temperature up to 423°K and in such conditions, TSM sets uniformly without internal stresses made by crystalline phase and forms a good adhesive interaction.

However, residual setting stresses (σ_{SE}), which remain in cooling time under isometric conditions also are an important characteristic of TSM. That parameter which determines the quantity of crystalline phase fixed residual force after setting and formed, e.g., the necessary conditions for hermetically connection of TSM.

Figure 7 shows formation kinetic of σ_{TR} and σ_{SE} for oriented LDPE/EPDM blends samples under isometric heating and the following isometric cooling conditions. It has been shown that for series **A** samples values of these parameters are not great, although the σ_{TR} value increases with increasing of cross-linked elastomer content in the mixture. At low EPDM content, the composition hardly shows thermorelaxation stresses due to the fact that LDPE is not crosslinked (the small stress up to 413°K keeps 10 wt% crosslinked elastomer part). However, comparatively large σ_{SE} forms the great LDPE crystalline phase amount (see Figure 7a, curve 1). As expected, the greater values of σ_{SE}, nevertheless chemically crosslinked part of elastomers, obviously makes it difficult for the formation of crystallization centers. Therefore, the polymer crystallization degree at the last stage of orientation crystallization is not as great. An increase of EPDM content naturally

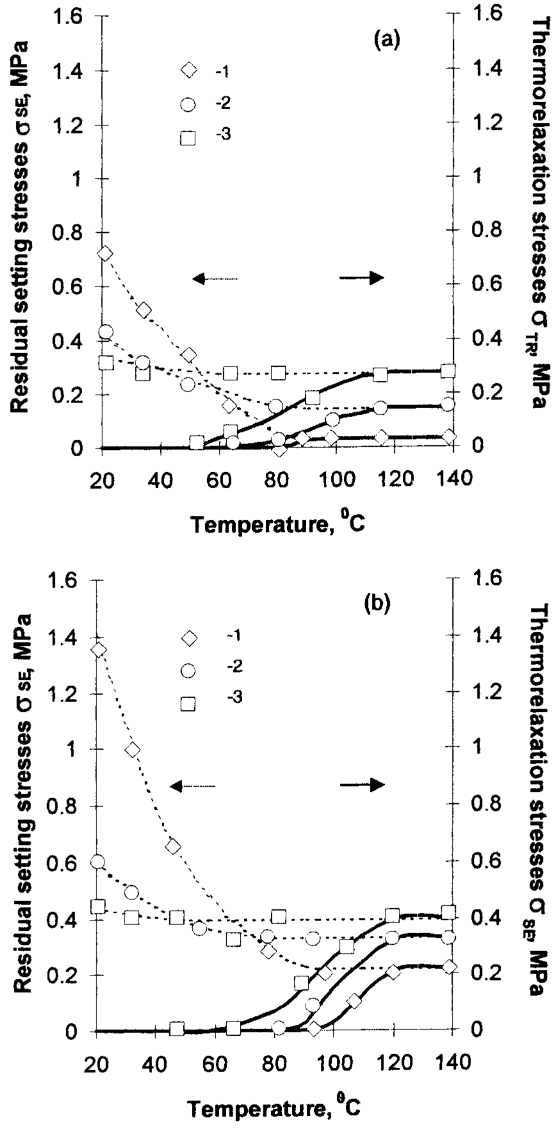


Figure 7. Temperature dependence of thermorelaxation stresses σ_{TR} and residual setting stresses σ_{SE} under isometric conditions for samples of series **A** (**a**) and **B** (**b**). The initial samples were stretched to the degree 100% at 403°K. Samples were irradiated up to 150 kGy. Content of EPDM in blends: 1 - 10; 2 - 50; 3 - 70 wt%.

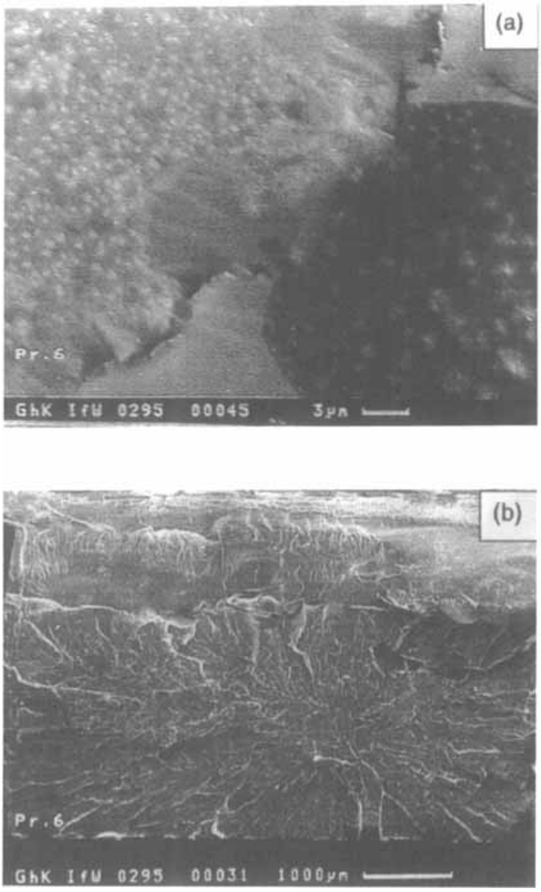


Figure 8. Scanning electron micrographs of LDPE/EPDM blend (ratio 50/50): **a**, **b** - chemically crosslinked; **c**, **d** - irradiated up to 150 kGy.

decreases the crystalline phase formed σ_{SE}, which at the EPDM content 70 wt% is almost equal with σ_{TR}.

The difference of mentioned stress values of the series **B** samples is observed. An increase of elastomer phase content considerably increases σ_{TR} value (see Figure 7b, curve 3). It has been observed that in this case, residual setting stresses formed by orientation crystallization are greater than for the samples of series **A**. In the system where radiation crosslinking proceeds in both dispersed phases as in the case of orientation crystallization, the intermolecular conformation transitions can proceed. These are connected with a flexibility decrease of both

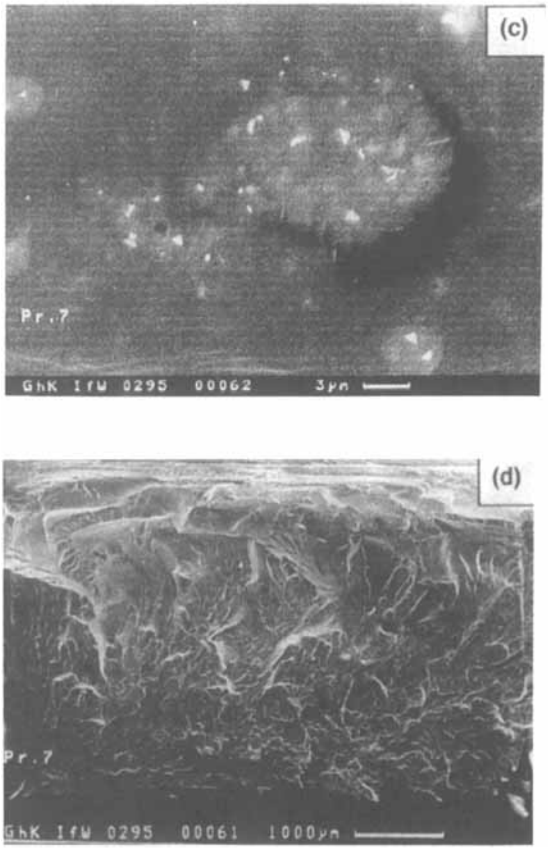


Figure 8. Continued

crosslinked and stretched phase macromolecules, which determine the group turning, deformation of the valence angle, and formation of mutual bonds and contacts on phases border-surface (e.g., possible grafting and passable molecule formation). In such conditions, the system starts to act as the static molecule system with increased hardness. As known, the hard molecules crystallize more easily, therefore, σ_{SE} values of series **B** samples are greater than for series **A** samples.

The morphology of cryogenically fractured crossections of the specimen is displayed in Figure 8. In Figure 8 (a, b) the SEM micrograph of chemically crosslinked LDPE/EPDM blend (ratio 50/50) is differentiated from Figure 8 (c, d) which represents irradiated systems up to 150 kGy. According to SEM data, irradiation causes levelling of both disperse phases. At the beginning, there are specific EPDM phase microgels in the blend such as series **A** samples (the sphere at magnification of 3 μm is shown in Figure 8a). Subsequently, by crosslinking of both disperse phases, formation of chemical bonds between these phases and fibrillation of molecular structures (especially as has been shown at magnification of 1000 μm) are observed (see Figure 8c, d). It is also proven by isometric heating and cooling curves character.

CONCLUSION

We have studied the characteristics of chemically and radiation crosslinked LDPE/EPDM blends for the purpose of determining the difference between these modification methods and also to choose specific compositions for engineering applications with heightened elasticity and adhesive interactions, e.g., with steel.

Morphological, rheological, mechanical, and thermorelaxation results were interpreted that all investigated blends with heightened EPDM content can be used as TSM, especially modified by ionizing radiation. Radiation crosslinking, considerably affects various properties of LDPE/EPDM blends, especially adhesion interaction with steel and thermosetting characteristics of oriented material. It has been stated that crosslinking of both disperse phases by radiation modification forms the continuous phase, and that affects the forming of increased thermorelaxation stresses and residual setting forces for oriented materials.

The above-mentioned relationships allow us to choose the corresponding conditions for the formation of TSM, e.g., if necessary, to obtain material with increased elasticity and good adhesive properties. In this case, the radiation modified blend (absorbed doses 150-200 kGy) with EPDM phase content 50-70 wt% is more suitable. If the EPDM content in the composition is increased up to 90-95 wt%, the material has the greater thermosetting forces, increased viscosity and better adhesive properties, but the residual setting stresses are not as expressive. Therefore, this material is recommended for use as an interlayer material of TSM, and so this material irradiated up to absorbed doses 50-100 kGy does not melt at heightened temperatures. It can be used simultaneously in orientation with basic materials, e.g., polyethylene or other polyolefin compositions.

REFERENCES

[1] D. R. Paul and S. Newmen, *Polymer Blends*, Academic Press, New York 1978, Vol. 1, p. 549; Vol. 2, p. 453.

[2] W. N. Kulesnev, *Polymer Blends*, Chimia Publishers, Moscow 1980, p. 304 (in Russian).

[3] N. Tokita and J. J. Scott, *Rubber Chem. and Technol., 42*, (3), 944 (1969).

[4] A. J. Coran and R. P. Pater, *Rubber Chem. and Technol.*, *53*, (1), 141, (4), 781 (1980).

[5] D. W. Wineak and C. P. Kaden, *Plast. Eng., 45*, (3), 87 (1989).

[6] M. Dole, *J. Macromol. Sci., 15*, (7), 1403 (1981).

[7] A. Barlow and L. A. Hill, *Radiation Phys. and Chem., 14*, (3), 783 (1979).

[8] T. Bocok, J. Zicans, M. Kalnins, and V. Kalkis, *Polymer Chemistry and Technology: Kaunas (Lithuania) International Conference*, Programme-Kaunas, 1997, p. 70.

[9] E. E. Finkel', V. L. Karpov, and S. M. Berlant, *Technology of Radiation Modification of Polymers*, Energoatom Publishers 1983, p. 47 (in Russian).

[10] S. Bahadur and K. Ludema, *J. Appl. Polymer Sci., 15*, (5), 1099 (1971).

[11] M. Morimoto and Y. Okamoto, J. *Appl. Polymer Sci., 16,* (11), 2795 (1972).

[12] V. Kalkis, M. Kalnins, and J. Zicans, *Mechanics of Composite Materials, 33*,(3), 14 (1997).

[13] M. Kalnins and J. Malers, *J. Adhesion, 50,* 83 (1995).

[14] M. Kalnins, and J. Malers, *J. Adhesion, 61,* 175 (1997).