Properties of Radiation-Modified Blends of Polyethylene with Elastomers and Liquid Crystalline Copolyester

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Summary: The results are given on the effect of γ-irradiation on properties of blends of high and low-density polyethylene (HDPE, LDPE) with elastomers – ethylene/propylene/diene rubber (EPDM) and chlorinated polyethylene (CPE), and thermotropic liquid crystalline polymer (LCP). The morphological, thermal, mechanical properties (including thermosetting properties) and adhesion properties of blended composites were investigated. A special attention was paid to the applicability of the blends as thermosetting materials (TSM). The LCP used was a copolyester of poly(ethylene terephthalate) with *p*-(hydroxybenzoic acid) in the ratio 40 : 60. It was found that addition of LCP essentially influenced the thermomechanical and adhesion properties of PE composites, irradiated up to the absorbed dose 150 kGy, as well as the dimensional stability of thermosetting products, made from polyethylene/elastomer mixtures. The results show that such ternary blends considerably improve the exploitation conditions of irradiated polyethylene and useful thermosetting materials can be obtained.

Introduction

In designing new multicomponent thermoplastic materials much attention is paid to physical or chemical modifications of the ingredients to improve deformation and strength parameters, impact resistance, processing characteristics, thermal stability, etc. 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 and high impact strength at low temperatures. Rheological properties of these materials permit processing at a high production rate. However, physical mixing of polymers with different properties leads only rarely to the desired modification, because most polymer pairs are incompatible. It is known that the required condition for the thermodynamic miscibility of

CCC 1022-1360/00/$ 17.50+.50/0

polymers is a negative value of the Gibbs free energy of mixing ($\Delta G_m = \Delta H_m - T\Delta S_m$). For polymers to be miscible on molecular level, ΔH_m must be negative or equal to zero. A presence of specific interactions between the mixed polymers is another possibility to form a compatible blend. At the same time, the thermodynamic immiscibility does not exclude the option of the technological compatibility of some important polymers. Sometimes it is possible to improve the stability of the system (nearly to thermodynamic compatibility) using radiation treatment.

In our previous work we demonstrated that crosslinking by a high-energy treatment of the disperse phase results in a formation of the continuous phase improving the compatibility1). Therefore, the application of these materials can be considerably enlarged by radiation modification.

As an example, the radiation modified thermosetting materials (TSM) can be mentioned as very popular and widely used in various application areas: shrinkable films and belts for packaging, profiles such as couplings, sleeves and bandages for pipe connections, electric cables, etc.2,3). These materials are mainly made of the semicrystalline polymers, which are mostly polyolefin-based (copolymers, blends), by orientation at the elevated temperature and subsequent cooling to room temperature under isometric conditions. The majority of such polymers used in engineering applications exhibits a certain degree of crystallinity, which affects the mechanical properties of the polymer material. The addition of an amorphous polymer to a semi-crystallizable material forming the blend causes noticeable changes in the crystallization behavior and therefore in the final properties of the material.

There is insufficient data about the effectivity or preference of some elastomers acting as modifiers of polyolefin blends. Therefore, in this work we investigate morphological, thermal, mechanical properties (including thermosetting properties) and adhesion properties of blended systems: polymer/elastomer and polymer/elastomer/modifying agent. To determine the crosslinking effectiveness of the blends, we relied on the generally accepted principles that crosslinking mainly proceeds in the amorphous phase of polymer. Our previous results demonstrated the effectiveness of gel-fraction formation in the elastomer phase and increased values of thermorelaxation stresses in the oriented material4,5). In fact, elastomer phase crystallization should also be taken into consideration in the investigation of the crosslinking process. The influence of elastomeric crystalline phase, determined by X-ray diffraction or DSC is negligible in the case of small crystallite size and low crystallization degree6). This result will be considered in the further research.

Materials and methods

Polyolefins obtained from Novopolotsk Chemical Enterprise (Byelorussia) was used as basic materials: low-density polyethylene (LDPE), trademark 160803-070, melting temperature, 108°C; high-density polyethylene (HDPE), trademark 20908-040, melting temperature, 130°C. Polymer - composite blends with following elastomers were used: a) ethylene-propylene-diene (EPDM) copolymer (trademark SKEPT-40, Russia) with propylene contents 40 mol%, dicyclopentadiene content 0.5 - 2 mol%; b) chlorinated polyethylene with chlorine content 36 % (Dow Chemical). The copolyester of poly(ethylene terephthalate) (PET) with p-(hydroxybenzoic acid) (HBA) in the ratio 40 : 60, LC-3000 produced by the Unitika Ltd., Kyoto, was used as the LCP.

Samples in the form of plaques were irradiated by an experimental ^{60}Co γ-radiation source in an argon atmosphere up to various levels of the absorbed dose. The maximum absorbed dose was 200 kGy using the irradiation rate 10 kGy/h.

Preparations of samples for adhesion measurements were made as laminated polymer-metal open systems. The peel strength of samples was determined in a tensile testing machine ZT-20, at a crosshead speed of 0.8 mm/s at room temperature.

The viscosity of molten blends was measured using a capillary rheometer. The shear rate was varied by the speed of the pressure cylinder 16 mm/min. Volumetric flow rate as a function of pressure drop in the capillary of length 8.0 mm and radius 1.8 mm was measured at 190°C. Melt flow index was measured in compliance with standard ISO/TK-61.

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 (σ_b), elongation at break (ε_b) and permanent deformation after fracture (ε_p). A microhardness tester with a Vickers square pyramidal diamond indenter was used.

Thermorelaxation stresses (σ_{TR}) and residual setting stresses (σ_{SE}) of the oriented (100%) and crosslinked samples were measured by the static method (tensometrically) under isometric conditions (heating and cooling). The sensitivity of the device was ± 0.01 N.

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

Morphological Structure of Polyolefin Blends with Elastomers

The morphology of cryogenically fractured cross-sections of the specimen is displayed in Fig. 1. According to SEM data, irradiation results in a partial decay of sharp phase boundaries. Subsequently, by crosslinking of both disperse phases, formation of chemical bonds between these phases and fibrillation of molecular structures and finer microheterogeneity are observed. This is particularly apparent for the blend containing EPDM elastomer (Fig. 1i and 1j).

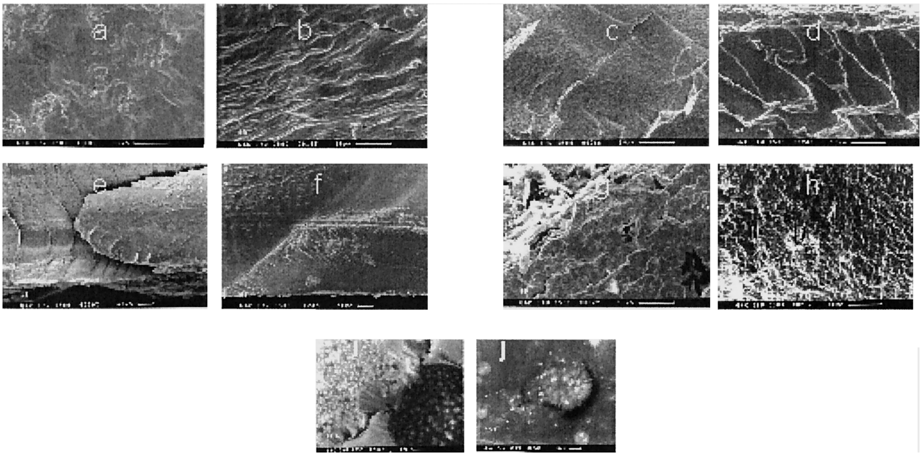

Fig. 1. SEM micrographs of: **a** – unirradiated 100% CPE (bar equal to 10 μm); **b** – 100% CPE irradiated by 150 kGy (bar equal to 10 μm); **c** – unirradiated 100% LDPE(bar equal to 10 μm); **d** – 100% LDPE irradiated by 150 kGy (bar equal to 10 μm); **e** – unirradiated 100% LDPE (bar equal to 30 μm); **f** – 100% LDPE irradiated by 150 kGy (bar equal to 30 μm); **g** – unirradiated LDPE/CPE blend (ratio 50/50) (bar equal to 10 μm); **h** – LDPE/CPE blend (ratio 50/50) irradiated by 150 kGy (bar equal to 10 μm); **i** – unirradiated LDPE/EPDM blend (ratio 50/50) (bar equal to 3 μm); **j** – LDPE/EPDM blend (ratio 50/50) irradiated by 150 kGy (bar equal to 3 μm).

Thermal Properties of Polyolefin Blends with Elastomers

Investigation of the rheological properties of the structured blend revealed substantial differences in melt viscosities (Fig. 2). The systems modified by radiation, however, do not differ significantly in the melt viscosity and follow the rheological behavior of the isotropic heterogeneous blends.

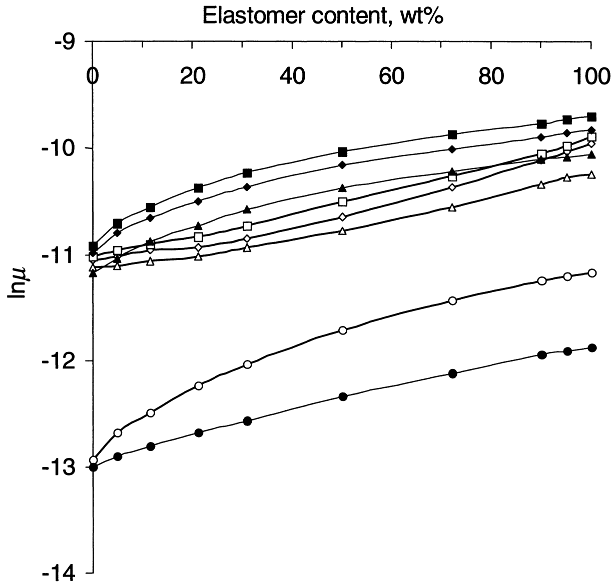

Fig. 2. Effect of elastomer content on viscosity of blends at 190°C and speed of rheometer pressure cylinder 16 mm/min:
○ LDPE/CPE (D_{abs} = 0 kGy); ● LDPE/EPDM (D_{abs} = 0 kGy); Δ LDPE/CPE (D_{abs} = 50 kGy); ◊ LDPE/CPE (D_{abs} = 100 kGy); □ LDPE/CPE (D_{abs} = 150 kGy); ▲ LDPE/EPDM (50 kGy); ◆ LDPE/EPDM (D_{abs} = 100 kGy); ■ LDPE/EPDM (D_{abs} = 150 kGy).

Mechanical Properties of Polyolefin Blends with Elastomers

Fig. 3. illustrates dependence of tensile strength and elongation at break and permanent elongation on the content of CPE elastomer in blend, respectively.

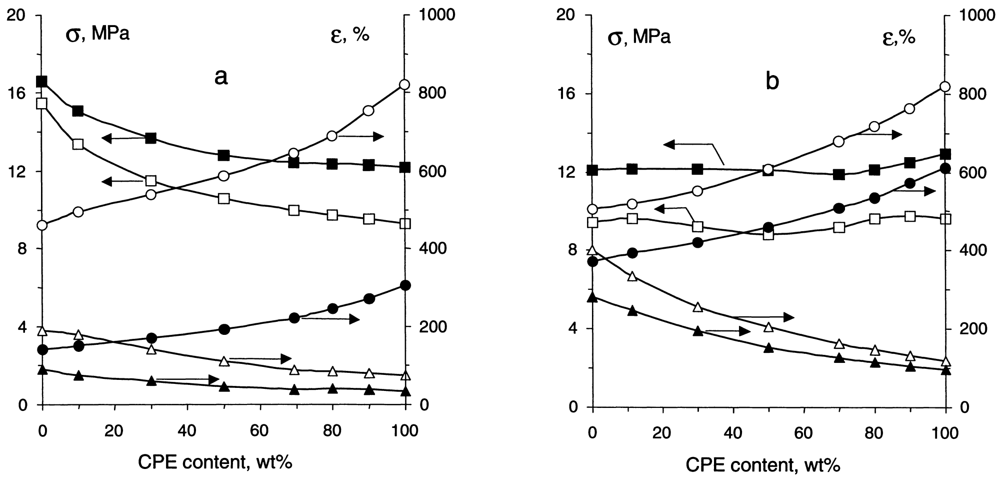

Fig. 3. Tensile strength at break (□, ■), percentage of elongation (○, ●) and permanent deformation (Δ, ▲) as a function of weight percentage of CPE: **a** – HDPE blend; **b** – LDPE blend; unirradiated – open symbols, irradiated by 150 kGy – filled symbols.

Table 1. Selected mechanical properties of polyolefin/CPE blend uncrosslinked or crosslinked by 150 kGy

Blend ratio, wt%	Peel strength, N/mm		Microhardness, MPa	
	0 kGy	150 kGy	0 kGy	150 kGy
HDPE/CPE				
100/0	54.0	52.5	77.8	150.7
80/20	49.6	45.5	61.1	99.1
50/50	35.9	25.6	42.4	59.4
20/80	22.7	17.7	22,3/	29.5
0/100	8.7	7.5	-	-
LDPE/CPE				
100/0	33.2	24.8	22.3	24.6
80/20	24.6	20.0	16.3	18.8
50/50	14.4	10.4	11.0	13.4
20/80	12.4	9.7	6.2	10.3
0/100	8.7	7.5	-	-

Selected important mechanical properties of polyolefin blend with CPE are shown in the Table 1. Similar results were obtained for samples of polyolefin/EPDM blends. An example of the kinetics of development of the thermorelaxation stresses σ_{TR} and residual setting stresses σ_{SE} under isometric conditions (heating and cooling) for some blends is shown in Fig. 4. Obtained results reveal that all radiation-modified systems used in this study, especially blends with CPE, possess thermosetting properties .

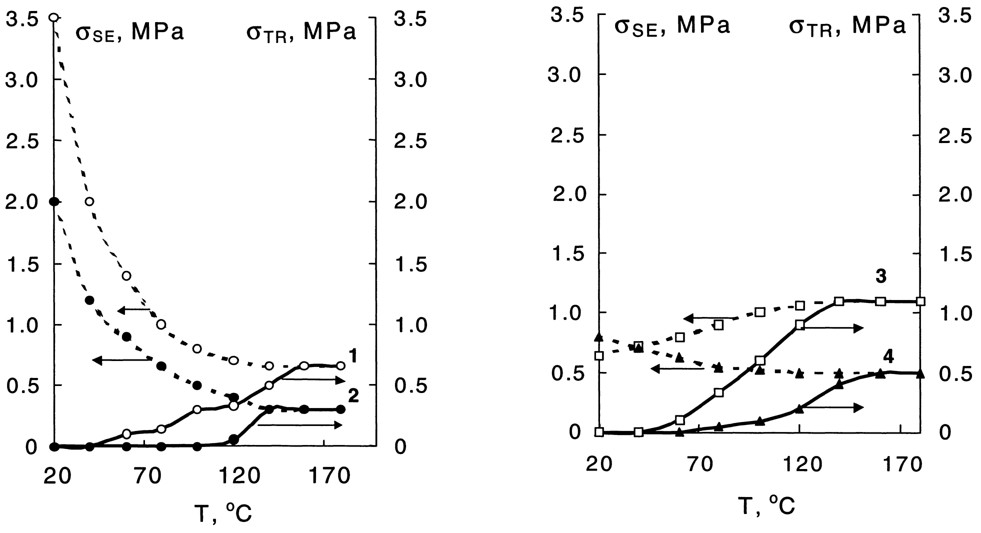

Fig. 4. Kinetics of development of thermorelaxation stresses σ_{TR} and residual setting stresses σ_{SE} under isometric conditions (heating and cooling) for blends irradiated by 150 kGy and oriented (ε = 100%): *1* – 90 % HDPE/10% LCP; *2* – 100% HDPE; *3* – 10% HDPE/80% CPE/10% LCP; *4* – 10% HDPE/80% EPDM/10% LCP.

Dimensional stability of polymer melts, containing EPDM rubber phase, is revealed in Fig. 5. Similar relationships have been observed also for blends with CPE. The dimensional stability is an important TSM characteristic representing the shape stability of products (under storage, etc.) at the temperature from 20 to 50°C.

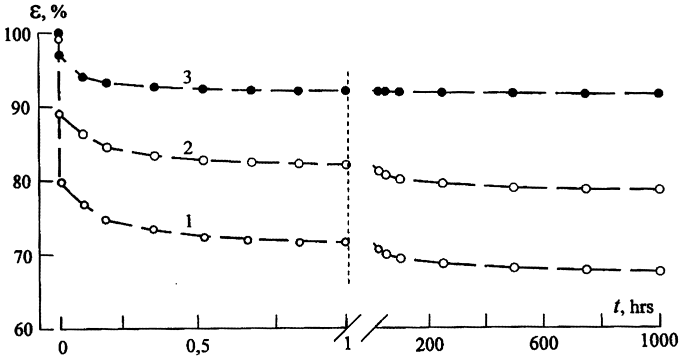

Fig. 5. Recovery curves at 20°C for relaxed samples previously irradiated up to the dose 150 kGy, stretched at 150°C up to a 100% elongation and isometrically cooled back to 20°C: 20% HDPE/80% EPDM (1), 30% HDPE/70% EPDM (2), and 25% HDPE/65% EPDM/10% LCP (3).

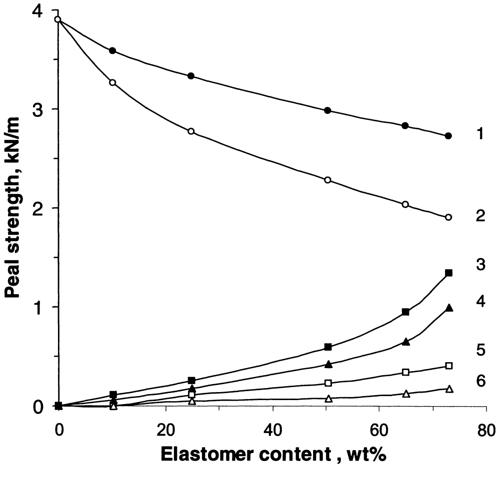

Fig. 6. Adhesion to steel of blends irradiated up to 150 kG determined by the peel strength measurements: *1* – HDPE/EPDM/10 LCP; *2* – HDPE/CPE/10 LCP; *3* – LDPE/EPDM; *4* – HDPE/EPDM; *5* – LDPE/CPE; *6* – HDPE/CPE. Contact conditions: temperature 200°C; pressure 1 MPa; time 3 min.

Adhesion Properties of Polyolefin Blends with Elastomers

The adhesive properties of the blends are important in case of the thermosetting materials. In this work, the conditions for formation of the adhesive contact (temperature, pressure, and time) are selected to be similar to those formed during the setting time. Fig. 6 demonstrates the adhesion properties of the blends.

The LCP additives substantially improve adhesion between the blend and metallic surface. It is suggested that active groups of oxybenzoic acid control the adhesion by forming the adhesive boundary layer on the surface of polymer and metal.Additionally, LCP additives promote filling of the adhesive in the cavities of the substrate. The process is driven by migration of liquid crystalline particles towards boundary layer of the polymer blends.

Conclusion

It has been shown that the radiation modified ternary blends of polyethylene with elastomer and liquid-crystalline copolyester after orientation demonstrate the form-memory effect with repeated heating. Addition of the small amount of LCP up to 10 wt.% leads to an increase of the dimensional stability after orientation of radiation-crosslinked blends with the high content of elastomer phase, as well as to a considerable increase of the adhesion properties. The ternary blends of HDPE/HPE/LCP previously irradiated up to absorbed dose 150 kGy and 100% oriented by tension exhibit the best thermorelaxation stresses and sufficient residual stresses, which allow to produce the rubberlike thermosetting materials applicable at elevated temperatures.

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