Reactive Compatibilization of Recycled Low Density Polyethylene/Butadiene Rubber Blends During Dynamic Vulcanization

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Summary: For reactive compatibilization of the recycled LDPE with butadiene rubber (BR) an equal quantity of few couples of reactive polyethylene copolymer/reactive polybutadiene (1/1) were introduced into the corresponding phases before the dynamic vulcanization. The LDPE/BR thermoplastic dynamic vulcanizates (TDVs) produced using the poly(ethylene-co-acrylic acid), PE-AA/polybutadiene terminated with isocyanate groups, PB-NCO compatibilizing couple with different ratio of functional groups have demonstrated the best mechanical properties and have been characterized by X-Ray analysis and DMTA measurements. For all of systems studied the increasing components compatibility due to the formation of the essential interface layer have been observed. The PB-NCO modifier participates in two processes: it is co-vulcanised with BR in rubber phase and reacts in the interface with the PE-AA dissolved in LDPE. The amorphous phase of LDPE is dissolved by rubber phase, i.e. the morphology with dual phase continuity is formed that provides an improvement of mechanical characteristics of material obtained. The best combination of mechanical characteristics was obtained for LDPE(PE-AA)/BR(PB-NCO), PB-NCO=7.5 wt.% per PB, COOH/NCO=1/1. The tensile strength and an elongation at break for these blends were 3.9 MPa and 353 % and for the basic non-compatibilized blend 3.2 MPa and 217 %, relatively.

Keywords: butadiene rubber; dynamic vulcanization; low density polyethylene; reactive compatibilization; recycling

Introduction

It is known that thermoplastic elastomers can be produced from polymer blends consisting of non-vulcanized fresh rubber and thermoplastic polymers such as polyolefins.[1-9] Their properties can highly be improved by exploiting the technology of dynamic or in-situ curing.[2-5,7,9] During dynamic vulcanization, carried out by intense mixing above the melt

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temperature of the thermoplastic polymer, the rubber phase will be crosslinked (vulcanized) and finely dispersed (mean particle size in few microns) in the thermoplastic, which overtakes the role of the matrix.[4] The resulting thermoplastic dynamic vulcanizate (TDV) exhibits rubbery characteristics by maintaining the thermoplasticity of the matrix. As a consequence the TDV is melt (re)processable. A further benefit of this TDV compound is that it represents a high value-added product if its components are derived from waste sources ("upcycling"). Preliminary results showed that the TDV concept could be adopted for well-selected post-consumer goods. As far as a thermoplastic and rubber are usually incompatible the further improvement of TDV properties can be achieved by increase of components compatibility via an enhancement of interfacial adhesion.[10-13]

The reactive compatibilization can be realized by few ways.[10, 12] The method used in this work consisted of introduction of reactive polyethylene copolymer into thermoplastic phase and reactive polybutadiene rubber into rubber phase. Herewith, the functional groups of polymer additives used should be reactive to each other. During the intensive mixing of components at high temperature the chemical reaction occurs in the interface leading to increase of adhesion between thermoplastic and rubber phases. The fine morphology of such compatibilized TDVs provides a reinforcement of their mechanical properties.

Experimental

Materials

A fresh butadiene rubber (BR) (M_w = 21,000) was a trademark SKD-2 (Voronezhsintez-kauchuk, Russia), its Mooney viscosity, ML(1+4)130°C, was 46. As a polyolefin the post-consumer recycled low density polyethylene (LDPE) was selected. LDPE was produced from used greenhouse films of composition LDPE – 65-70%, linear low density polyethylene (LLDPE) – 12-17%, ethylene/vinyl acetate copolymer (EVA) – 12-15%, additives (kaolin, talc, silica) $\approx$ 500 ppm, UV stabilisers (amine, benzophenone) $\approx$ 2500 ppm, E-modulus – 180 MPa, tensile strength – 16 MPa, ultimate tensile elongation – 500%, melt flow index – 0.29 and 0.95 g/10 min at 190 and 230°C, respectively, under the load of 2.16 kg.

The reactive thermoplastics used were poly(ethylene-co-acrylic acid) (PE-AA), poly(ethylene-co-glycidyl methacrylate) (PE-GMA), poly(ethylene-g-maleic anhydride) (PE-g-MAN), poly(ethylene-co-vinyl acetate-co-acrylic acid) (PE-VA-AA), and reactive rubbers were polybutadiene, terminated with epoxy (PB-E), hydrazide, (PB-Hz), carboxyl, (PB-COOH), amine, (PB-NH_2) and isocyanate groups (PB-NCO). Thus, the reactive couples of functional groups can be given as follows: carboxyl – epoxy (1), carboxyl – isocyanate (2), epoxy – hydrazide (3), epoxy – amine (4), epoxy – isocyanate (5), anhydride – amine (6), anhydride – isocyanate (7) (Figure 1).

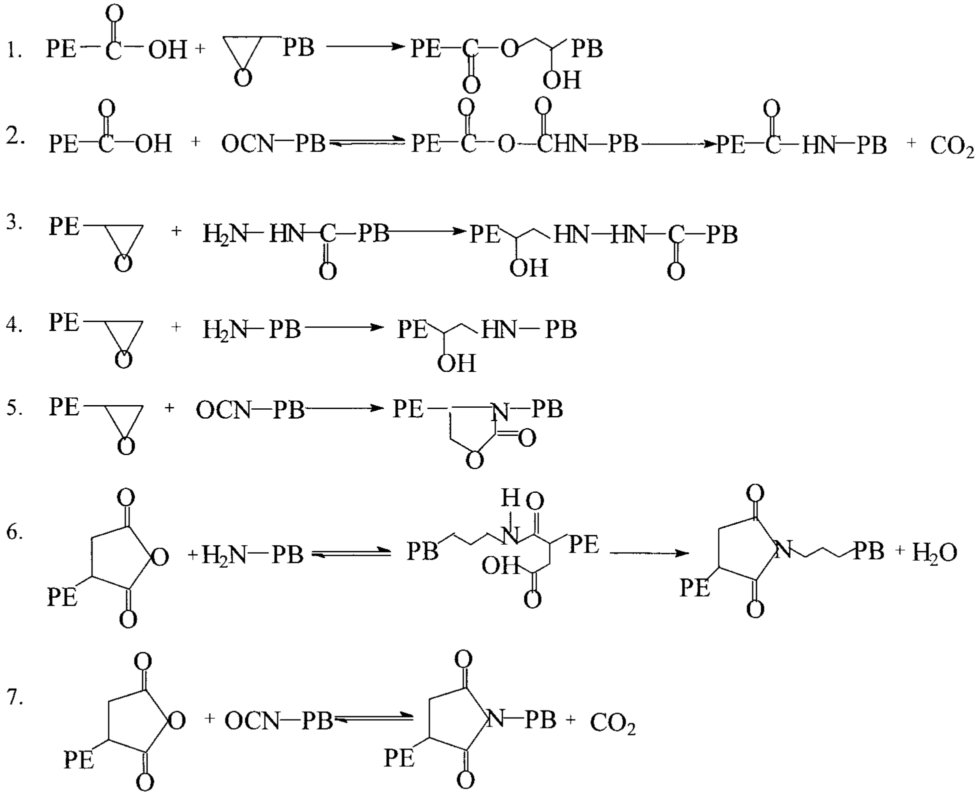

Fig. 1. Reactions used for compatibilization of polyethylene / rubber phases during TDVs preparing.

All reactive thermoplastics and rubbers have been used as received. The curatives used were (wt% per BR): Sulfur (3.0), bis-(2-benzothiazolyl)disulphide (1.0), zinc oxide (5.0), stearic acid (1.0).

Reactive Compatibilization and TDVs Preparation

The components of the blends LDPE/BR = 60/40 wt % were mixed in a twin-rotor mixer of the Brabender type at 180 °C, 100 rpm for 10 min. In all cases, the LDPE was melted first for 2 min before the addition of BR. For dynamic vulcanization, curatives as well as reactive couple chosen were introduced after 2 min of mixing BR with molten LDPE and mixed for further 6 min. Timing terms (10 min) were determined from the curve "torsion torque-time" as the time of the maximum value of torsion torque.

The resulting blends were pressed in the form of 1 mm-thick plates by molding at 150 °C under the pressure of 10 MPa followed by cooling under pressure at a rate of about 15 °C/min.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measurements in tensile test mode were obtained on a viscoelastometer (Rheovibron type) with temperature scans from –100 to 170 °C at a frequency of 100 Hz and the heating rate of 2.0 °C/min. Dimensions of samples were 5.0 x 0.5 x 0.1 cm^3. The temperature corresponding to the maximum of the E" peak position was considered as the dynamic glass transition temperature (T_g).

Wide-angle X-ray Scattering (WAXS)

Wide angle X-ray scattering curves were recorded by X-ray diffractometers DRON-4-07. Nickel-filtered Cu-K_α radiation (monochromatized by Ni filter, radiation wavelength, $\alpha = 0.154$ nm) was produced by an IRIS-M7 generator at an operating voltage of 30 kV and a current of 30 mA. The scattering intensities were measured by a scintillation detector scanning in 0.2° steps over the range of angles of 5-40°. The degree of crystallinity <X> was calculated from the WAXS data by Matthews method.[14]

Mechanical Testing

Mechanical measurements were performed with an Instron 1122 testing machine at the ambient temperature at the elongation rate (the speed of upper cross-arm) 50 mm/min. The average data for 6-7 specimens were taken for consideration. The parameters such as tensile strength (σ_b) and elongation at break (ε_b) were determined.

Results and Discussion

Effect of Reactive Compatibilization on Properties of Reclaimed LDPE/BR TDVs

As mentioned above the TDVs are the blends of heterogeneous structure because of thermodynamic incompatibility of components, therefore an approach to development of TDVs by dynamic vulcanization is a multi-level problem. The selection of curatives in case of using post-consumer blend components is complicate problem, because it is necessary to avoid, as far as possible, the degradation of a pretreated ingredient in the utilization processes. In this work, the most effective agents, in terms of reaction time and final properties of vulcanizates, were used. The properties of TDVs and the blends with an uncured rubber phase were analyzed and given in Figure 2.

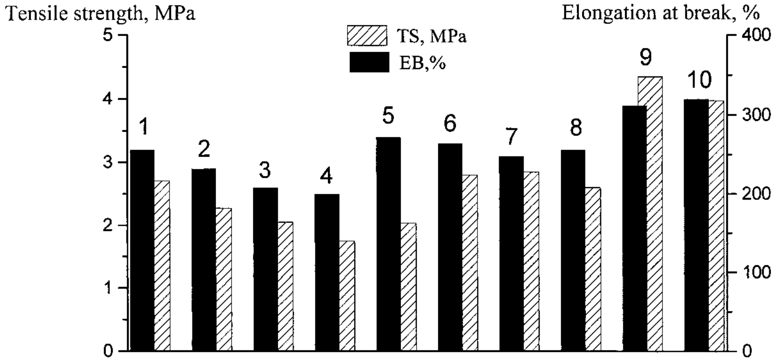

Fig. 2. Effect of reactive compatibilization on tensile strength and elongation at break of different LDPE/BR=60/40 wt.% TDVs (1) compatibilized by: PB-E/PE-AA (2); PB-Hz/PE-GMA (3); PB-COOH/PE-GMA (4); PB-NH_2/PE-GMA (5); PB-NH_2/PE-GMA (6); PB-NH_2/PE-g-MAN (7); PB-NCO/PE-g-MAN (8); PB-NCO/PE-AA (9); PB-NCO/PE-VA-AA (10). All PB-modifiers were used in amount of 7.5 wt.% per BR. The ratio of functional groups of PB and PE was 1/1.

One can see that the best mechanical characteristics were obtained for LDPE/BR TDVs compatibilized by couple PE-AA/PB-NCO (PB-NCO=7.5 wt.% per PB) with equivalent functionalities. The tensile strength and an elongation at break for these blends were 3.9 MPa and 353 % and for the basic non-compatibilized blend 3.2 MPa and 217 %, relatively, indicating a better compatibility between the rubber and polyolefin phases in system. This fact is explained by the effective reaction between PE-AA and PB-NCO in the interface leading to increase of interfacial adhesion and therefore compatibilization effect of PE-AA/PB-NCO. It was found that the value of tensile strength reaches a plateau with value of 4.2 MPa at 10 wt. % PB-NCO content and further increase of PB-NCO content up to 15 wt. % provides a reduction of elongation at break to the value approximately equal to the one of non-compatibilized LDPE/BR TDV. One can suppose that an excess of PB-NCO in the blend acts as a curing agent increasing a degree of vulcanization of the rubber phase through the reaction of NCO-groups excess with unsaturated bonds of the BR. It was found that the excess of PE-AA (PE-AA=1.5 e.e.w.) does not influence significantly on values of tensile strength and elongation at break. It can be explained by low reactivity of COOH-group towards BR chains.

Dynamic Mechanical Thermal Analysis

Two main transition regions (Figure 3a and b) evidence about two–phase morphology of the LDPE/BR TDVs studied: the first one from 50 to 110°C corresponds to α-relaxation of LDPE (T_g = 79°C); the second one is observed in the temperature interval –50°C to 25°C and it is a result of superposition of both the T_g of BR (T_g = –20°C) and the β-relaxation of LDPE (region from -75 to 50°C). A partial compatibility has been fixed between amorphous phases of LDPE and BR as a result of their chemical and structure affinities. So, it is supposed that one phase of TDV is crystalline one of LDPE and the other one is that formed by BR and LDPE amorphous parts.

A shift of transitions toward one another is observed in $E'' = f(T)$ dependencies that evidences of increase of component compatibility in the LDPE (PE-AA) / BR (PB-NCO) TDVs due to the formation of the essential interface layers. The PB-NCO modifier participates in two processes: it is co-vulcanized with BR in rubber phase and reacts in the interface with the PE-AA dissolved in LDPE. The amorphous phase of LDPE is dissolved by rubber phase. This leads to the transformation of the morphology of the basic blend (continuous LDPE phase and dispersed rubber phase) to the morphology with dual phase continuity that provides an improvement of mechanical characteristics of TDVs obtained. The glass transition temperatures for different TDVs produced are summarized in Table 1.

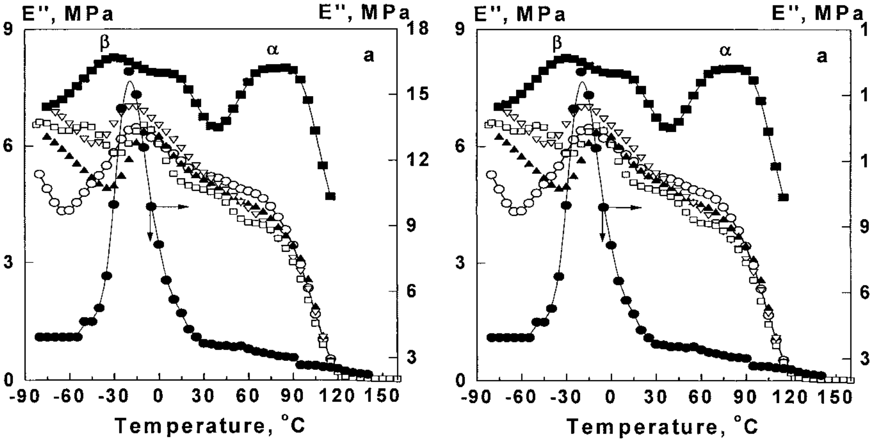

Fig. 3. Temperature dependence of the loss modulus, E'', (a) and storage modulus, E', (b) from DMTA measurements in tensile mode for: ■ - LDPE; ○ - LDPE/BR; ▲ - LDPE (PE-AA)/BR (PB-NCO = 1.5%); ▽ - LDPE (PE-AA)/BR (PB-NCO = 7.5%); □ - LDPE (PE-AA)/BR (PB-NCO = 10 %); ● - BR.

Table 1.Glass transition temperatures for different TDVs studied.

Composition, wt.%	T_g[a], °C
LDPE	79
BR	-20
LDPE/BR[b] = 60 / 40	-15, 35, 60
LDPE (PE-AA) / BR (PB-NCO = 1.5 %)	-6, 40, 57
LDPE (PE-AA) / BR (PB-NCO = 7.5 %)	-18, 56, 73
LDPE (PE-AA) / BR (PB-NCO = 10.0 %)	-47, -9, 37, 70

[a] T_g values taken from the E'' peaks.

[b] LDPE/BR = 60 / 40 is constant for all samples studied.

We consider that the LDPE (PE-AA) / BR (PB-NCO) TDVs studied can be considered as Interpenetrating Polymer Networks (IPNs).[15]

Wide-angle X-ray Scattering

All WAXS diffractograms of the modified LDPE (PE-AA) / BR (PB-NCO) TDVs (Figure 4) show two sharp peaks located at scattering angles of 21.5 and 23.8° (characteristic for orthorombic crystal cell of LDPE) and the diffuse maximum located at 19.5° which corresponds to LDPE amorphous phase scattering maximum. Note that three sharp peaks in the region from 31 to 36° (observed in diffractogram of the cured BR) are not characteristic for amorphous BR and can be attributed to low molecular weight additives used in the process of curing.

The value of degree of crystallinity represents the overall crystallinity of blend material and can be compared with the theoretical ones calculated in an assumption of retaining by LDPE component its original value of crystallinity ($x = 30.7\%$). The results of the calculations are 30.7 multipled by 0.6 (60 wt.% of LDPE) is equal to 18.4 %, Δx values in Table 2 show the difference between the experimental crystallinity value and the corresponding theoretical ones. Comparison of the figures allows concluding that the only consequence of BR introducing is the changing of the relative intensities of crystalline LDPE peaks. Blending LDPE with BR leads to increase of crystallinity degree by 5.1%. The modifier (PE-AA/PB-NCO) introduction leads to lowering the Δx difference to 0.5% (1.5% of modifier), -0.8% (7.5% of modifier). Further increasing the modifier content to 10% leads to restoring the crystallinity values to the level characteristic of unmodified LDPE/BR TDV.

Table 2. Degree of crystallinity for TDVs produced.

Compositions	x [a], %	Δ x [b] ,%
BR	0	-
LDPE	27.5	-
LDPE / BR (unmodified)	19.3	5.1
LDPE (PE-AA)/BR (PB-NCO = 1.5%)	18.5	0.5
LDPE (PE-AA)/BR (PB-NCO = 7.5%)	18.3	-0.8
LDPE (PE-AA)/BR (PB-NCO = 10 %)	19.3	4.7

[a] Experimental degree of crystallinity.
[b] Difference between experimental and theoretical degree of crystallinity.

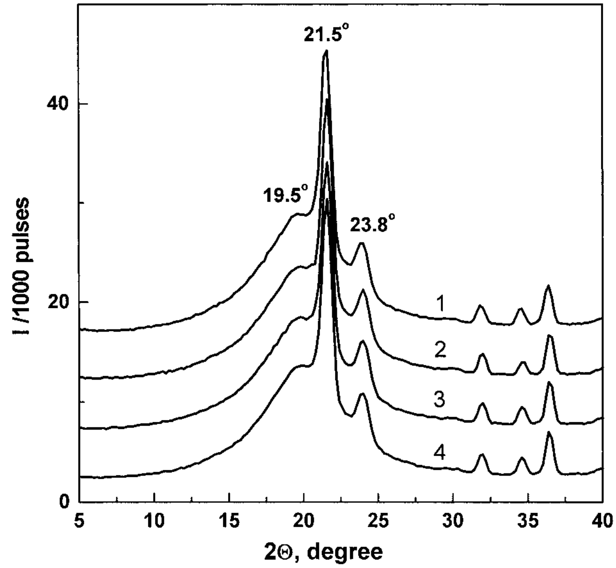

Fig. 4. WAXS curves for LDPE / BR (1); LDPE (PE-AA)/BR (PB-NCO= 1.5%) (2); LDPE (PE-AA)/BR (PB-NCO= 7.5%) (3); LDPE (PE-AA)/BR (PB-NCO= 10 %) (4). Beginning from the second curve from the bottom, each next curve was shifted upwards by 5 digits.

The reason for the crystallinity values increasing for unmodified LDPE / BR TDVs can be the influence of the rubber component on the LDPE component crystallization conditions, i.e. on phase separation between amorphous and crystalline phases. In such a case a lower value of difference between the experimental and the corresponding theoretical crystallinity values can be attributed to the increase of the blend components compatibility. Thus, the TDVs modified by PE-AA/PB-NCO are characterized by higher compatibility of LDPE and BR. Optimal content of the PE-AA/PB-NCO modifier corresponds to 7.5% PB-NCO per BR.

Conclusions

A partial compatibility has been fixed between amorphous phases of LDPE and BR as a result of their chemical and structure affinities. It is supposed that one phase of TDV is crystalline one of LDPE and the other one is that formed by BR and LDPE amorphous parts.

A shift of T_g of the components toward one another evidences of an increase of component compatibility in the LDPE (PE-AA) / BR (PB-NCO) TDVs due to the formation of the essential interface layers. The PB-NCO modifier participates in two processes: it is co-vulcanized with BR in rubber phase and reacts in the interface with the PE-AA dissolved in LDPE.

The amorphous phase of LDPE is dissolved by rubber phase. This leads to the transformation of the morphology of the basic blend (continuous LDPE phase and dispersed rubber phase) to the morphology with a dual phase continuity that provides an improvement of mechanical characteristics of material obtained. LDPE (PE-AA) / BR (PB-NCO) TDVs studied can be considered as IPNs.

The best combination of mechanical characteristics was obtained for LDPE/BR TDVs compatibilized by couple PE-AA/PB-NCO (PB-NCO=7.5 wt.% per PB, COOH/NCO=1/1). The tensile strength and an elongation at break for these blends were 3.9 MPa and 353 % and for the basic non-compatibilized blend 3.2 MPa and 217 %, relatively.

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