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Reactive Compatibilization of Polyethylene/Ground Tire Rubber Inhomogeneous Blends via Interactions of Pre-Functionalized Polymers in Interface

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Summary: Reactive compatibilization of recycled low- or high-density polyethylenes (LDPE and HDPE, respectively) and ground tire rubber (GTR) via chemical interactions of pre-functionalized components in their blend interface has been carried out. Polyethylene component was functionalized with maleic anhydride (MAH) as well as the rubber component was modified via functionalization with MAH or acrylamide (AAm) using chemically or irradiation (γ-rays) induced grafting techniques. The grafting degree and molecular mass distribution of the functionalized polymers have been measured via FTIR and Size Exclusion Chromatography (SEC) analyses, respectively. Thermoplastic elastomer (TPE) materials based on synthesized reactive polyethylenes and GTR as well as ethylene-propylene-diene rubber, EPDM were prepared by dynamic vulcanization of the rubber phase inside thermoplastic (polyethylene) matrix and their phase structure, and main properties have been studied using DSC and mechanical testing. As a final result, the high performance TPE with improved mechanical properties have been developed.

Keywords: compatibilization; composites; functionalization of polymers; reactive processing

Introduction

It is well known that reactive compatibilization is one of the most suitable methods for compatibility enhancement in immiscible polymer blends.[1–11] Reactive compatibilization of polypropylene (PP)/nitrile-butadiene rubber (NBR) blend by using PP grafted with maleic anhydride or PP modified with phenolic compound due to interaction of functional groups of reactive PP with active groups of NBR chains was realized in work.[1] Reaction between carboxylated NBR and epoxidized PP has allowed improving the tensile properties of PP/NBR blend.[2] Bassani and coauthors[3] proposed using of *p*-phenylenediamine (PDA) as coupling agent for improvement of interfacial adhesion in PP/hydrogenated styrene-butadiene-styrene triblock copolymer (SEBS) blends modified by carboxylated PP/maleated SEBS reactive blend. 4,4′-diaminediphenilmethane was used[4] as reactive additive for compatibility enhancement in PP/styrene-butadiene-styrene triblock copolymer (SBS) blend with maleated PP/maleated SBS reactive couple. Furthermore, the main principles of compatibilization techniques were also applied for producing of high performance polyolefin/rubber composites (including thermoplastic elastomers, TPE).[5–13]

In this work for reactive compatibilization of polyethylene/GTR blends and

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development of high performance polyethylene/rubber TPE a preliminary functionalization of recycled polyethylenes, LDPE or HDPE, and GTR with reactive monomers, MAH or AAm, by chemically or γ-irradiation induced grafting technique has been fulfilled. In some cases, the amine-functionalized coupling agents (p-phenylenediamine, PDA, or polyamide fibers, PAF) were used. The initial components, their functionalized analogues and the TPE prepared have been characterized using methods of Size Exclusion Chromatography (SEC), FTIR, DSC and mechanical testing.

Experimental Part

Materials

Recycled low-density polyethylene, LDPE, from post-consumer greenhouse films (Sicilia, Italy) and recycled high-density polyethylene, HDPE, from post-consumer bottle transportation crates (Kyiv, Ukraine) were used as thermoplastics. As the rubber components the ground tire rubber, GTR, fraction with a particle size of 0.4 to 0.7 mm (Viborg, Danmark) and ethylene-propylene-diene rubber, EPDM (Buna® EP G 6470, Bayer, Germany) were used. The reactive monomers, MAH and AAm, free radical initiator for chemical grafting (dicumyl peroxide, DCP) as well as coupling agents p-phenylenediamine, PDA, supplied by Aldrich Chemicals and polyamide fibers, PAF, from polyamide wastes (Lysychansk, Ukraine) were used as received.

Grafting Procedure

Chemical grafting (identified below as ^{Ch}) of MAH or AAm to recycled polyethylenes and GTR polymer chains was carried out in an internal mixer (Brabender Plasticorder, PL 2000 type) at 160 °C and 80 rpm for 7 min under a nitrogen stream. A polymer/monomer/initiator ratio was 100.0/10.0/0.5 (by weight). Polymer component was melted first and mixed with MAH for 2 min, then DCP was added and mixed for a further ~5 min. γ-Induced grafting (identified below as $^{\gamma}$) of reactive monomers onto HDPE and GTR surface was also carried out as follows. First, HDPE (GTR) and MAH (AAm) were mixed in the PL 2000 mixer at 160 °C and 80 rpm for 4 min. Component ratio (without DCP) was used as described above. Further, the blends were irradiated by γ-rays at full absorbed dose of 10 kGy and at radiation rate of 2.27 kGy/h. In accordance with methods presented the functionalized components (LDPE-MAH^{Ch}, HDPE-MAH^{Ch}, HDPE-MAH$^{\gamma}$, GTR-MAH^{Ch}, GTR-AAm^{Ch} and GTR-AAm$^{\gamma}$) were synthesized and then used for preparing of the TPE.

TPE Preparation

For preparation of HDPE-based TPE samples the components were melt blended in the internal mixer PL 2000 at 160 °C and a rotor speed of 80 rpm for 10 min.[12] LDPE-based TPEs were prepared by a similar method using a coupling agent (PDA or PAF). All the TPE compositions obtained are presented in Table 1.

Characterization Techniques

Analysis of molecular mass distribution (MMD) of functionalized polymers was performed using a chromatograph DuPont LC System 8800.

Grafting degree of MAH in LDPE-MAH and HDPE-MAH samples was calculated from FTIR data on integral absorbance of characteristic bands in the spectral region of 1860–1700 cm^{-1} and a polyethylene reference band of $(\text{–CH}_2\text{–})_{n>5}$ at ~1460 cm^{-1} using a Bruker Tensor™ 37 FTIR analyzer. Differential scanning calori-

Table 1.
Composition recipes used for TPE produced.

Composition	Component ratio (parts by weight)
LDPE/EPDM	40/35
LDPE/EPDM/GTR	40/35/25
LDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}/PDA	40/35/25/1
LDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}/PAF	40/35/25/1
HDPE/EPDM	40/35
HDPE/EPDM/GTR	40/35/25
HDPE-MAH^{Ch}/EPDM/GTR-AAm^{Ch}	40/35/25
HDPE-MAH$^{\gamma}$/EPDM/GTR-AAm$^{\gamma}$	40/35/25

metry, DSC, analysis of TPEs was carried out using Perkin Elmer thermal analyzer Pyris 6 DSC in the temperature range from −100 to 200 °C with a programmed heating rate of 20 °C/min. Glass transition temperature (T_g), specific heat capacity (ΔC_p), melting temperature (T_m), enthalpy of melting (ΔH_m) were determined. A crystallinity degree (X_{cr}) values were calculated using experimental ΔH_m values and ΔH_m value of standard polyethylene sample with 100% crystallinity (293 J/g). Tensile testing was performed using universal testing machine Instron-1122 on dumbbell specimens at ambient temperature and at a crosshead speed of 100 mm/min. The parameters such as tensile strength at break, σ_b, and elongation at break, ε_b, were determined.

Results and Discussion

Grafting of Reactive Monomers to the Polymers

Analysis of functionalized polyethylenes has allowed determining a degree of grafting. It is well known[14–16] that the reaction of grafting of monomers (including MAH and AAm) to polymer (polyethylene or rubber) chains can be realized by different ways: formation of polyethylene (rubber) grafted with monomeric MAH or AAm, with poly(MAH) or poly(AAm), as well as a formation of carboxylated polyethylenes (available only for MAH-functionalized polymers due to their hydrolysis with opening of anhydride rings). From the detailed analysis of FTIR spectra of functionalized LDPE and HDPE samples the grafting degree values were calculated and the results are presented in Table 2.

As we can observe the grafting degree values of all functionalized polymers obtained are lower compared to the standard sample. Moreover, one can see that γ-induced grafting is slightly more effective than chemically induced one. The grafting degree values of functionalized GTR samples were not determined.

The MMD curves of initial and functionalized polymers are presented in Figure 1, as well as their molecular weights and polydispersity indexes were determined and are presented in Table 2.

One can see from Figure 1 that MMD curves of functionalized polymers are shifted to the lower log M_w region compared to the initial components. It should be noted, that for the functionalized HDPE samples the shift is clearly greater. So, the grafting procedure is accompanied by decreasing M_w and M_n values of the corresponding polymers due to chain scission process that is confirmed by the comparison of the M_w and M_n values of initial and corresponding functionalized polymers from Table 2.

Reactively Compatibilized TPE

The pre-functionalized initial components via grafting of MAH to polyethylene chains and MAH or AAm to GTR chains were used for preparing of the TPE compositions. When both the components are MAH-functionalized, the coupling agents, PDA or PAF with reactive amine (amide) groups are added. The schemes of chemical interactions in interface at TPE producing are presented in Figure 2.

Table 2.
Grafting degree and MMD parameters of initial and functionalized polyethylenes.

Polymers	Grafting degree	Molecular weight		Polydispersity
	(wt.%)	M_w	M_n	M_w/M_n
LDPE	–	29300	4200	6.98
LDPE-MAH^{Ch}	0.74	16100	3100	5.19
LDPE-MAH$^{\gamma}$	1.15	12900	1700	7.59
HDPE	–	67100	8000	8.38
HDPE-MAH^{Ch}	0.72	18400	2800	6.57
HDPE-MAH$^{\gamma}$	1.25	18400	3300	5.76

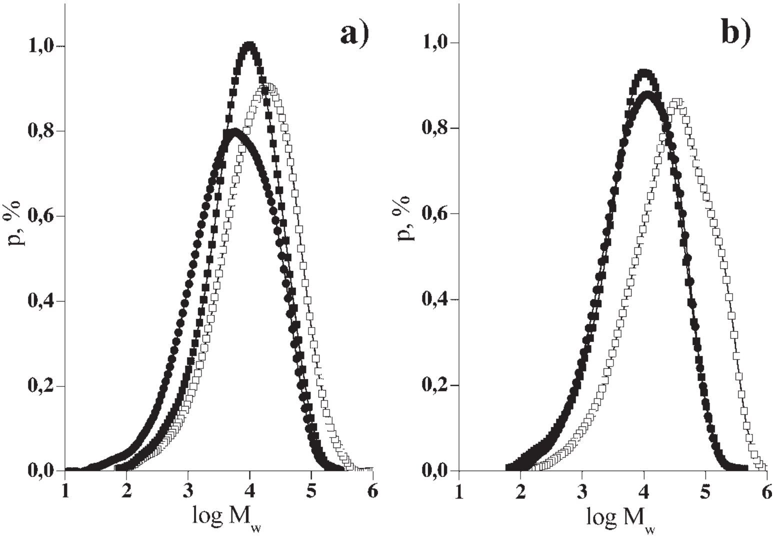

Figure 1.

MMD curves of initial and MAH-grafted (a) LDPE and (b) HDPE samples; □ = LDPE (HDPE); ■ = LDPE-MAH^{Ch} (HDPE-MAH^{Ch}); ● = LDPE-MAH$^{\gamma}$ (HDPE-MAH$^{\gamma}$).

The calorimetric studies of the reactively compatibilized TPE obtained as well as their uncompatibilized analogues were carried out and the results are presented in Table 3. The typical DSC curves of the LDPE- and HDPE-containing TPE prepared were presented in Figure 3. Analysis of the changes in amorphous phases of the components in the blends obtained compared to the individual components were performed. The glass transition temperature (T_g) of the individual polymers have been found to be for HDPE −62.2 °C ($\Delta C_p = 0.010$ J/(g · K)), for LDPE–18.2 °C ($\Delta C_p = 0.058$ J/(g · K)), for EPDM–37.3 °C ($\Delta C_p = 0.108$ J/(g · K)).

Analysis of DSC data of HDPE-based TPE shows that mixing of EPDM with HDPE leads to shift of T_g of the both components to higher temperatures: from −62.6 to −54.4 °C for HDPE component and from −37.3 to −32.2 °C for EPDM component. The changes in relaxation behavior of amorphous phase of the HDPE and EPDM components can be explained by interpenetrating of polymer chains of the components and formation of mixed amorphous phases rich in HDPE or EPDM.

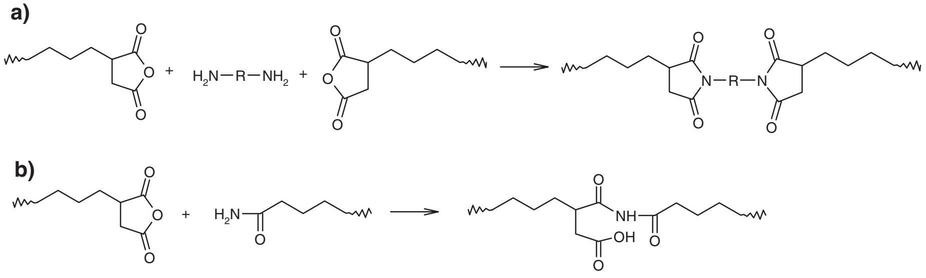

Figure 2.

Basic schemes of: (a) reactive compatibilization of the components of TPE based on LDPE-MAH and (b) TPE based on HDPE-MAH.

Table 3.
DSC data for individual components and TPE prepared.

Composition	DSC characteristics for phases rich in:									
	PE					EPDM				
	T_{g1}	ΔC_{p1}	T_m	ΔH_m	X_{cr} [b]	T_{g2}	ΔC_{p2}	T_m	ΔH_m	X_{cr} [b]
	°C	J/(g · K)	°C	J/g	%	°C	J/(g · K)	°C	J/g	%
EPDM	–	–	–	–	–	−37.3	0.108	47.6	22.9	8
HDPE	−62.6	0.010	131.8	198.2	67	–	–	–	–	–
HDPE/EPDM	−54.4	0.008	125.9	202.2	69	−32.2	0.061	47.4	11.4	4
HDPE/EPDM/GTR	−58.0	0.009	127.5	228.5	78	−36.9	0.042	–	–	–
HDPE-MAH^{Ch}/EPDM/GTR-AAm^{Ch}	−55.6	0.007	127.5	205.1	70	−34.4	0.045	46.9	11.0	4
HDPE-MAH$^{\gamma}$/EPDM/GTR-AAm$^{\gamma}$	−54.0	0.007	127.0	249.1	85	−34.5	0.048	45.9	9.1	3
LDPE	−18.2	0.058	108.6	95.6	33	–	–	–	–	–
LDPE/EPDM	–[a]	–[a]	105.0	67.4	23	−32.4	0.051	53.3	18.0	6
LDPE/EPDM/GTR	–[a]	–[a]	104.5	73.3	25	−34.8	0.046	47.9	17.3	6
LDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}/PDA	–[a]	–[a]	104.4	87.9	30	−33.1	0.050	49.1	11.9	4
LDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}/PAF	–[a]	–[a]	104.4	117.2	40	−32.8	0.073	48.1	11.1	4

[a] T_{g1} is overlapped with T_{g2}.
[b] The ΔH_m and X_{cr} values were calculated for 100% polymer in the blends.

Addition of GTR to HDPE/EPDM matrix leads to shift of T_g's of the both amorphous phases riches in HDPE or EPDM to lower temperatures: by 3.6 °C for HDPE component and by 4.7 °C for EPDM component. One can also see some reducing ΔC_p value for EPDM component. The mentioned changes are an evidence of partial mixing of HDPE or EPDM components with dispersed crosslinked GTR particles and disordering of thermoplastic (polyethylene/rubber) matrix.

For reactively compatibilized HDPE-MAH^{Ch}/EPDM/GTR-AAm^{Ch} and HDPE-MAH^{Ch}/EPDM/GTR-AAm^{Ch} TPEs shift of T_g values by 2.4 and 4.0 °C, respectively, of HDPE-rich amorphous phase to higher temperatures is observed compared to uncompatibilized HDPE/EPDM/GTR TPE. The T_g values of EPDM-rich amorphous phase of the compatibilized TPE are also shifted to higher temperature region by ∼2.5 °C. It can be concluded that the results obtained evidence of a reducing of

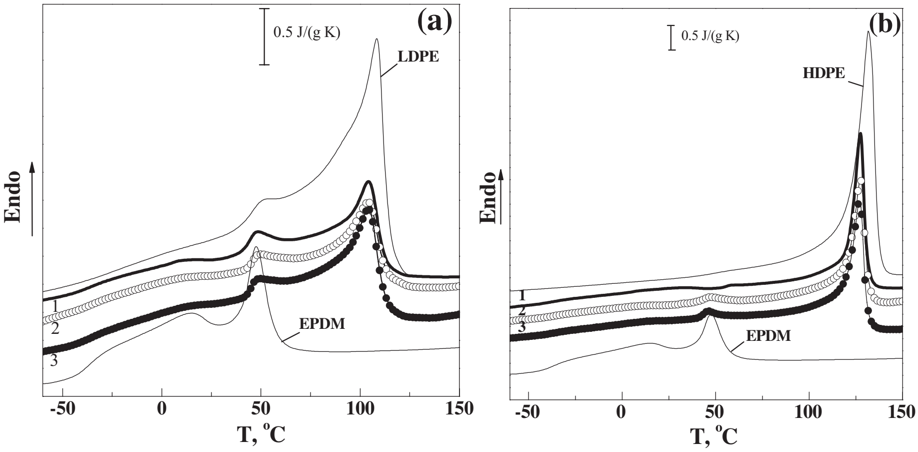

Figure 3.
DSC curves for individual components (LDPE, HDPE, EPDM), (a) LDPE- and (b) HDPE-containing TPE **(a)**: 1 = LDPE/EPDM/GTR (HDPE/EPDM/GTR); 2 = LDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}/PDA (HDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}); 3 = LDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}/PAF (HDPE-MAH$^{\gamma}$/EPDM/GTR-MAH$^{\gamma}$).

molecular (segmental) mobility of the components polymer chains due to formation a number of chemical cross-links between both functionalized thermoplastic polyethylene and GTR during the reactive compatibilization.

Analysis of the DSC data for LDPE-based TPE (see Table 3) has shown that dynamic vulcanization of EPDM rubber in LDPE-matrix leads to increasing T_g value of EPDM component by 4.9 °C (from −37.3 to −32.4 °C). Introducing of GTR into LDPE/EPDM blend shifts T_g value to lower temperature by 2.4 °C that is caused by disordering of thermoplastic polyethylene/rubber matrix due to incorporation of crosslinked GTR particles into the matrix.

Reactive compatibilization of LDPE-based TPE leads to some increasing T_g by 1.7–2.0 °C compared to similar unmodified TPE (Table 3) that is a result of hampering segmental mobility of polymer chains of the components of TPE studied due to chemical bonding between functionalized LDPE-MAH^{Ch} (or LDPE-MAH^{Ch}) and GTR-MAH^{Ch} (or GTR-MAH^{Ch}) components in the TPE.

The reactive compatibilization of the components provided changes in some parameters (melting behavior, heat capacity changes, etc.) of crystalline phases of the TPEs prepared (Table 3).

The mechanical properties of the compatibilized TPE were also studied. The chemical grafting of MAH and AAm to HDPE and GTR, respectively, leads to improvement of tensile strength, σ_b, and elongation at break, ε_b, values from 4.4 MPa and 114%, respectively, for uncompatibilized HDPE/EPDM/GTR TPE to 8.2 MPa and 165%, respectively, for HDPE-MAH^{Ch}/EPDM/GTR-AAm^{Ch} TPE. The highest effect on mechanical properties enhancement was found for the TPE based on the components functionalized via γ-induced grafting (σ_b and ε_b values growed up to 9.5 MPa and 322%, correspondingly).

For the reactively compatibilized LDPE-based TPE the σ_b values increased from 4.1 MPa for uncompatibilized LDPE/EPDM/GTR composition to 6.0 MPa for LDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}/PDA TPE and to 9.2 MPa for LDPE-MAH^{Ch}/EPDM/GTR-MAH^{Ch}/PAF TPE, whereas ε_b values increased from 440% for uncompatibilized blend to 470–510% for the compatibilized compositions. However, the most substantial influence of reactive compatibilization on the tensile properties was observed for the above-mentioned HDPE-containing TPE.

Conclusions

Reactive compatibilization of the blends of recycled polyethylenes (LDPE, HDPE) and ground tire rubber, GTR, via their pre-functionalization by grafting of reactive monomers followed by mixing was carried out. Functionalization of recycled polyethylenes and GTR was performed by free radical grafting of reactive monomers, such as maleic anhydride, MAH, and acrylamide, AAm, using addition of peroxide initiator or γ-irradiation technique. Interactions between anhydride and amide functional groups of reactive polymers or between anhydride-functionalized polymers and coupling agents with amine/amide groups led to compatibility enhancement between thermoplastic matrix and dispersed GTR particles and, as a result, the tensile properties of the reactively compatibilized GTR-containing TPE are improved. The best effect of compatibility and mechanical properties enhancement was achieved for HDPE-containing TPE based on the components functionalized via γ-induced grafting of reactive monomers.

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