Adhesion of Modified PE/EPDM Blends to Steel

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ABSTRACT

Crosslinking of low and high density polyethylene blends with ethylene-propylenediene terpolymer (EPDM) involving 10, 20, 30% EPDM with dicumyl peroxide (DCP) in the presence of coagent, Zn diacrylate, was investigated. It was found that such blends exhibit increased adhesion against steel and improved strength-deformation properties in comparison with similar blends crosslinked with DCP alone. The peel strength of about 16 kN/m (in the case of modified LDPE/EPDM blend) and 4 kN/m (in the case of modified HDPE/EPDM blend) was observed. The correlation between peel strength and parameters (oxygen uptake, content of oxygen containing groups, change of weight depending on temperature) which characterize thermooxidative conversations in polymer, was studied. The sol and gel fractions of crosslinked blends were characterized by IR spectroscopy, DSC and TG methods. Based on these results, it was assumed that improved peel strength of modified LDPE/EPDM blend is due to optimal ratio between oxidative crosslinking and oxidative degradation for this blend. Another reason may be the increase of interfacial adhesion caused by possible formation of graft copolymer LDPE-EPDM.

INTRODUCTION
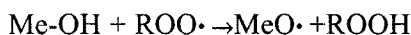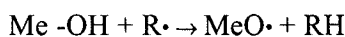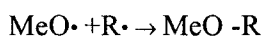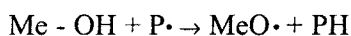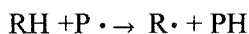
The adhesion of polyolefins to metals is of engineering importance in such varied applications as protective coatings, hot-melt adhesives or power cable insulation. Whether a polyolefin is used as substrate or adhesive, its bondability charac-

teristics is usually not good enough. Therefore, as a rule, various pretreatments have been used to improve their adhesion properties, e.g. corona discharge treatment, oxygen plasma treatment, acid etching, high temperature oxidation, grafting of acid or carbonyl groups by copolymerization, etc. Several suggestions have been ex - pressed about reasons why the adhesion of PO is improved as a result of these treatments: introduction of polar functional groups onto the polymer surface, remov- al of week boundary layers, increased possibility to mechanical keying due to change of rheological properties, etc. It is important to bear in mind that the practical adhesion is a complex phenomenon, reflecting both the interfacial properties of adhesive joint and the mechanical response of its bulk components. Sometimes, a change in the bulk properties of adhesive may affect the adhesion despite no alter- ation to the interface.

The process of adhesion between PO and metal due to direct contact of the molten polymer and metal surface often leads to the formation of a cohesively weak polymeric boundary layers, which is the most unstable link in the system. On the other hand, cohesive properties and structure of boundary layers are defined by the contact thermooxidation conversions in the polymer, catalyzed by metal surface compounds during thermal contact. So, from one side, adhesion was found to be dependent on the total content of oxygen on the polymer surface, from the other side - adhesion will be dependent also on the cohesive strength of boundary layer of the polymer. Therefore, simultaneous crosslinking and introducing of polar groups onto polymer surface could be a promising method to improve adhesion of PO against metals.

In an earlier paper [1-2], it was shown how adhesion between steel and LDPE increased in the presence of dicumyl peroxide (DCP). Improved adhesion has been attributed to an increase of cohesive strength of boundary layers of adhesive (as a result of crosslinking) and to promotion of LDPE thermooxidation which results in the appearance of polar functional groups on the surface of PE. Highly active radicals produced from the DCP can attach to PE macromolecules and develop adhesive bonds with metal:

RH +P · → R· + PH

Me - OH + P· → MeO· + PH

MeO· +R· → MeO -R

Me -OH + R· → MeO· + RH

Me-OH + ROO· →MeO· +ROOH

R - PO radical, P - DCP decomposition radical

The use of DCP as PO adhesion promoter have been limited by two negative phenomenon:

-dominant reaction in the peroxide system is crosslinking, but simultaneously chain scission occurs. It leads to the formation of low molecular weight products, which can decrease cohesive strength of boundary layers and, as a result, decrease adhesive strength with metal.

-upon introducing crosslinks in polymer adhesive its strength increase, however, with excessive crosslinking, the polymer becomes brittle and loses ductility. It was shown by Packham [3] that decreased ductility of the polymer leads to decreased peel strength of adhesive compound.

For that reason, sometimes additional chemicals, called coagents, are added to DCP to improve the crosslinking efficiency by preventing unwanted side reactions, such as chain scission and disproportionation. Typically, these coagents are reactive multifunctional monomers, most frequently ones that include acrylates and allyl compounds [4-5].

Such a crosslinking system was used by Costin *et al*. [6] to enhance mechanical properties and adhesion of saturated and unsaturated elastomers to different metals. Crosslinking agents used in this work were DCP and as coagent, Zn diacrylate, commercially known as Saret 633. The last one derived many of its physical and mechanical properties from the ionic bonds formed between the zinc cations and the carboxylate anions. Crosslinking with DCP results in the formation of a covalent C-C bond, which is rigid and stable. In contrast, the ionic bond is more elastic and mobile under stress (it can slip along the hydrocarbon chain). This mobility explain its superior tensile strength compared with DCP. During thermal treatment, the coagent developed adhesive bonds at the metal-rubber interface, while simultaneously producing strong crosslinks in the rubber.

It is also well-known [7] that Zn type ionomers, which are usually formed by copolymerization of ethylene with ~ 5% mol methacrylic acid, followed by neutralization, are very tough materials with good adhesion (for metal laminate applications) due to the presence of ionic groups on the polymer surface.

In this work, we report on the alteration in the mechanical and adhesive properties of PE/EPDM blends to steel, obtained by introducing complex crosslinking system (CCS)-dicumyl peroxide/Zn diacrylate.

In the presence of coagent crosslinking, degradation and grafting reactions can result in changes of the following molecular factors:

TABLE 1. Characteristics of Polymers Investigated

Polymer	Desig-nation	Supplier	MFI g/10 min.	Bran-ching ratio CH_3 1000C	Density g/cm^3	Crys-talli-nity %	T_m K
LDPE	640 IM	Dow (USA)	2.00	26	0.921	37	385
HDPE	Fortiflex T50-200	Dow (USA)	1.56	<3	0.953	60	405

- crosslinking of PE and EPDM with DCP, which results in the formation of carbonyl-carbonyl bond or crosslinking with the formation of ionic bond (if coagents participate),
- grafting of Zn diacrylate to backbone of PE,
- at the interface between PE and EPDM the graft copolymer can be produced, which can increase the interfacial adhesion.

EXPERIMENTAL

Materials

The polymers used include: low density polyethylene (LDPE), high density polyethylene (HDPE) and ethylene-propylene-diene terpolymer (EPDM). All of them are commercial products and commercial names and properties of polyethylenes are listed in Table 1. EPDM with propylene content 40 mol%, dicyclo-

pentadiene content 2 mol%, density 0.87 g/cm^3 and viscosity 40 degree Moony was used for preparing the blends. Crosslinking agents include dicumyl peroxide (DCP) and zinc diacrylate (Saret-SR 633) - supplied by the Sartomer Company. Both of them are also commercial products and used without further purification.

Adhesive Preparation

Adhesive compositions were prepared by thermoplastic mixing on rolling mill. Temperature of mixing: for LDPE 408°K , for HDPE - 423°K, total duration of mixing - 0.6 ks. Adhesive sheets were prepared by compression pressing in a hydraulic press, temperature was: for LDPE - 398°K and for HDPE - 423°K, duration - 0.18 ks.

Preparation of Metal Surface

A 70 mm thick steel foil 08 kp (approximately corresponding to the AJS1010 steel (USA) was used as substrate. Surface treatment of steel was traditional electrochemical etching (sulphuric acid aqueous solution 200 g/l, current density 10 A/dm^2, 0.15 ks at 343°K) with subsequent passivation in the following aqueous solution (g/l): $K_2Cr_2O_7$ - 5, Na_3PO_4 -30; temperature of the solution was 323-333°K, duration - 0.03 ks. After the passivation foil was rinsed by running warm water and dried by warm air.

Preparation of Adhering Systems

Laminated metal-polymer-metal samples were prepared by hot compression pressing at 0.4 MPa and fixed temperature and time. The adhesion was measured by T-peel test using a universal testing machine UTS-100. The peel test was carried out for strips (length - 50 mm and width - 10 mm) at a deformation rate 50 mm/min. and peel angle -180°. The reported value of peel strength (A) was an average value of 5-7 measurements.

Tensile Strength-Deformation Test of Adhesives

Samples were tested at room temperature at the cross-head rate 50 mm/min. accordingly ASTM D 638-89; a universal testing machine UTS-100 was used.

Infrared Spectroscopy

Infrared analysis was used, utilizing a IR spectrophotometer "Specord 75 IR" The aim of spectroscopic studies of adhesives was to evaluate the degree of branching (1378 cm^{-1}) and oxidation (1600-1800 cm^{-1} and 1000-1200 cm^{-1}).

The degree of branching (CH_3 groups per 1000 C atoms of the PE chain) was calculated from the equation: $CH_3/1000 \, C = 0 \, 85°K_{1378}$.

where K_{1378} - the optical density of the region related to 1 cm of the thickness of the specimen.

Gel Fraction

Gel fraction was measured gravimetrically by boiling the samples in p-xylene for 48 hours.

DSC and TG Analysis

Mettler TA 4000 scanning calorimeter was used for DSC and TG analysis. DSC thermograms (calibration by ln) of melting and crosslinking process of polymers were obtained at heating rate 283°K/min. Nitrogen was used as purge gas. Thermogravimetric (TG) curves were completed in the air (to evaluate the degree of oxidation and oxidative destruction) at the heating rate 283°K/min.

Interpretation of Data of the Dynamic TG and DSC

Kinetic parameters determined from the experimental T_g curves (change of weight as a function of temperature) are shown in Figure 1. The initial slope (the rate of weight loss dm/dT_1) characterize the weight loss due to "evaporation" of the low molecular weight part of the polymer. At the temperature T^{TG}_b (when the Δm_b of the sample weight is already lost) the rapid oxidation process starts. There is a temperature interval T^{TG}_b-T^{TG}_{max} in which the weight increase (due to chemosorption of oxygen and formation of oxygen containing groups) exceeds the weight loss due to decomposition of oxidized polymer into volatile products. The oxidation peak with area S^{TG}_{oks} and height H^{TG} corresponds to this period. The final slope (the rate of weight loss dm/dT_2 characterize the rapid weight loss due to destruction of oxidized polymer, which starts at $T^{TG}_e = T_{destr}$.

From DSC curves were determined such kinetic parameters: melting temperature (T_m), degree of crystallinity (α), heat of crosslinking ΔH_{crosl}, which starts at temperature T^{crosl}_b and ends at T^{crosl}_e.

RESULTS AND DISCUSSION

All blends listed in Table 2 were prepared by mixing on a two-roll mill at a temperature of 408°K (LDPE) and 423°K (HDPE) prior to thermal contact with steel. We expect that some part of DCP would be decomposed during mixing, therefore, it was necessary to clear up how much DCP and Saret remain unchanged in the blend after mixing. Such information was obtained from DSC curves and summarized in Table 3. The value of crosslinking heat ΔH_{crosl} characterizes the
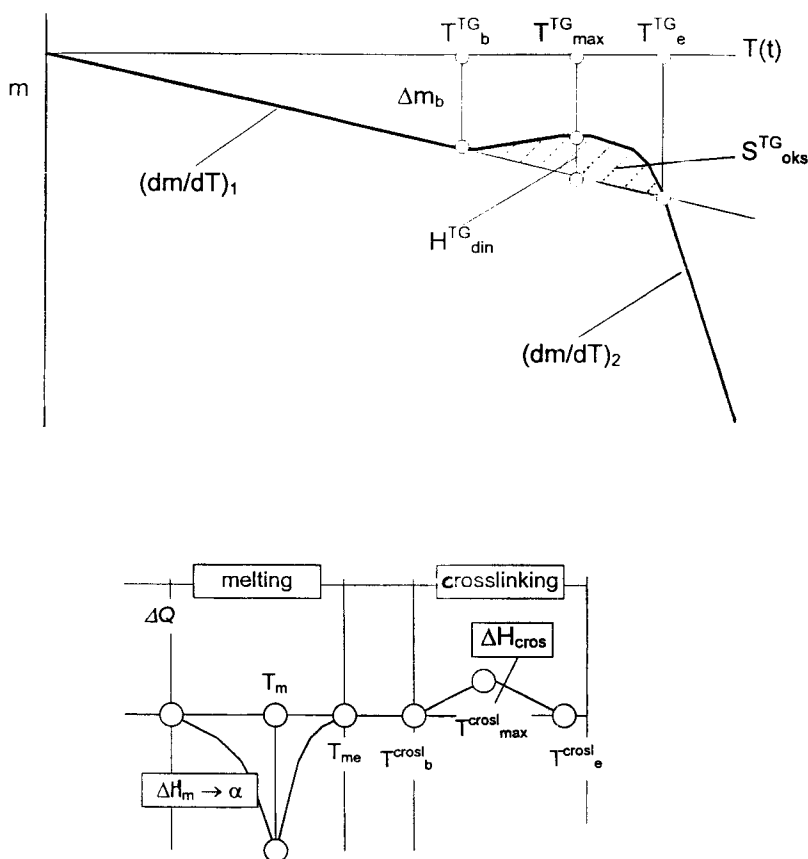
Figure 1.   Schematic interpretation of TG and DSC curves.

content of DCP, which remains in the blend after mixing and can participate in further radical reactions. It is seen that the blend LDS 0.5 exhibits a lower value of ΔH_{crosl} in comparison with LD 0.5. This means that even during a quite moderate mixing procedure, there is a kind of slight crosslinking of LDPE. It is also possible that in the presence of a coagent, part of DCP can be consumed in grafting reactions.

As expected, increasing the amorphous phase of blend LED 0.5 (by intro-ducing 20% EPDM), also leads to a decrease of ΔH_{crosl}.

The increase of DCP content causes the increase of gel and decrease of crystallinity (from 37% to 32%) and T_m (from 385°K to 384-382°K), if LDPE was crosslinked with DCP alone. Simultaneously with crosslinking, some chain scission also occurs. As we can see from Table 4, blends LD 0.5 and LD 1.0 are charac-

TABLE 2. Materials Used in Crosslinked Polyethylene Blends

Sample designation	Composition w%/w%	Crosslinking system w %
L	LDPE	-
LD0.5	LDPE	0.5DCP
LD1	LDPE	1 DCP
LS0.5	LDPE	0.5Saret
LDS0.5	LDPE	0.5DCP/0.5Saret
LDS1	LDPE	1DCP/1Saret
EDS0.5	EPDM	0.5DCP/0.5Saret
LE	LDPE(80)/EPDM(20)	-
LED0.5	LDPE(80)/EPDM(20)	0.5 DCP
LEDS1.0	LDPE(80)/ EPDM(20)	1.0 DCP/1.0 Saret
LEDS0.5	LDPE(80)/EPDM(20)	0.5DCP/0.5%Saret
HD0.5	HDPE	0.5 DCP
HEDS1.0	HDPE(80)/EPDM(20)	1.0DCP/1.0 Saret
HEDS0.5	HDPE(80)/EPDM(20)	0.5DCP/0.5%Saret

terized by a decrease of value of T_{destr} and an increase in content of low molecular weight destruction products, which evaporate at a lower temperature (Figure 2a).

Gel fraction increases significantly (till 46%), if EPDM was introduced in blend. Also, an increase of crystallinity and T_m was observed (Table 3). It may be explained by a greater extent of degradation of more amorphous blend LDPE/EPDM. Such implication was supported by a greater extent of degradation products which evaporate at low temperature. As seen in Figure 2a, blend LED 0.5

TABLE 3. Effect of the Crosslinking System on the Content of gel (G), Crosslinking Temperature (T_{crosl}) and Entalphy (ΔH_{crosl}), Melting Temperature (T_m) and Degree of Crystallinity (α) of PE and PE/EPDM Blend

Compo-sition	G* %	T^{DSC}_{crosl}, K			ΔH_{crosl} J/g	T_m K	α %
		T^b	T^{max}	T^e			
L	-	-	-	-	-	385	37
LD0.5	31	413	450	475	4.9	384	33
LD1	35	430	455	477	5.1	382	32
LS0.5	0	-	-	-	-	389	38
LDS0.5	28	423	456	487	3.6	386	38
LDS1	-	428	450	478	5.3	381	34
EDS0.5	-	416	459	484	6.0	-	-
LED0.5	46	413	460	481	2.1	387	40
LEDS0.5	47	418	460	483	4.3	386	37
LEDS0.5*	-	-	-	-	-	383	34
LEDS1.0	53	412	442	476	6.8	387	32
HEDS1.0	75	441	456	482	1.2	411	74
HEDS0.5*	73	--	-	-	-	405	58

* Thermal treatment at 453 K, 0.18 ks

TABLE 4.   Effect of the Crosslinking System on the Oxidation Temperature (T_{oks}), Area (S_{oks}) of Oxidation Peak and Weight Loss (Δm_b) of PE and Blends with EPDM

Compo-sition	Δm_b %	T^{TG}_{oks}, K			S_{oks} area units/g
		T_b	T_{max}	T_e	
L	0.19	465	506	523	17.9
LD0.5	0.27	-	-	493	-
LD1	0.22	431	494	513	40.0
LS0.5	0.36	-	-	496	-
LDS0.5	0.42	463	489	512	19.1
LDS1	0.22	472	496	507	6.4
EDS0.5	0.70	525	539	550	5.6
LED0.5	0.55	476	494	510	10.3
LEDS0.5	0.54	465	497	519	25.5
LEDS0.5*	0.43	458	497	543	97.5
HEDS0.5*	0.40	468	503	529	59.1
LEDS1.0	0.28	458	496	533	61.7
HEDS1.0	1.03	463	499	513	27.3

* thermal treatment at 453 K, 0.18 ks.
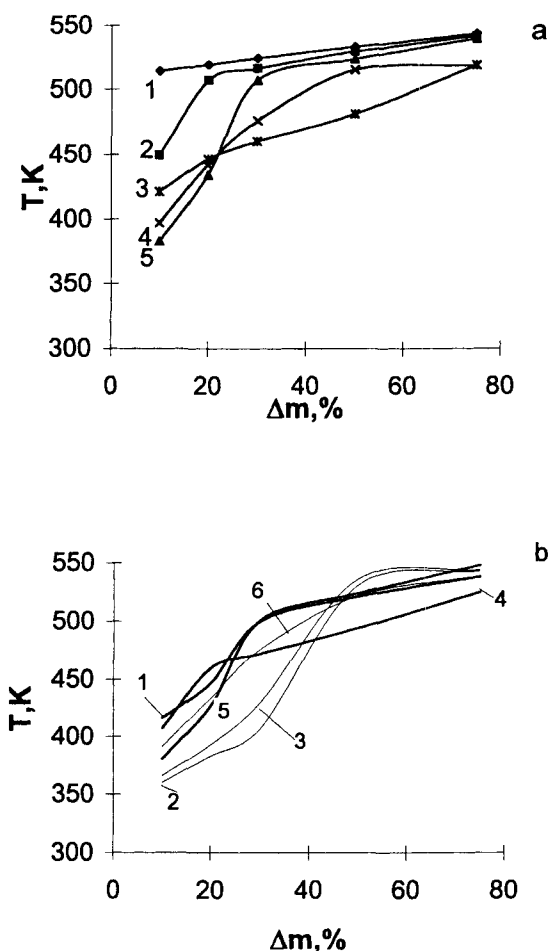
Figure 2. Effect of temperature (T) on weight loss (Δm) of compositions: (a) 1 - L, 2 - LD 0.5, 3 - LS 0.5, 4 - LDS 0.5, 5 - EDS 0.5 and (b) 1, 2 - LEDS 0.5, 3 - HEDS 0.5, 4 - LEDS 1.0, 5 - HEDS 1.0, 6 - LED 0.5; 2, 3 - after thermal treatment at 453°K,0.18 ks.

lost 10% weight at 391°K compared to LD 0.5, which lost the same amount at 449 °K.

The greatest value of gel (47%) was obtained when CCS was used for crosslinking of the LDPE/EPDM blend. At the same time, values of degree of crystallinity and T_m were similar for LDS 0.5 and LEDS 0.5.

An essential difference was observed between crosslinked blends on the base of LDPE and HDPE. The lower value of H_{crosl} (1.2 J/g) of HEDS 1.0 com-
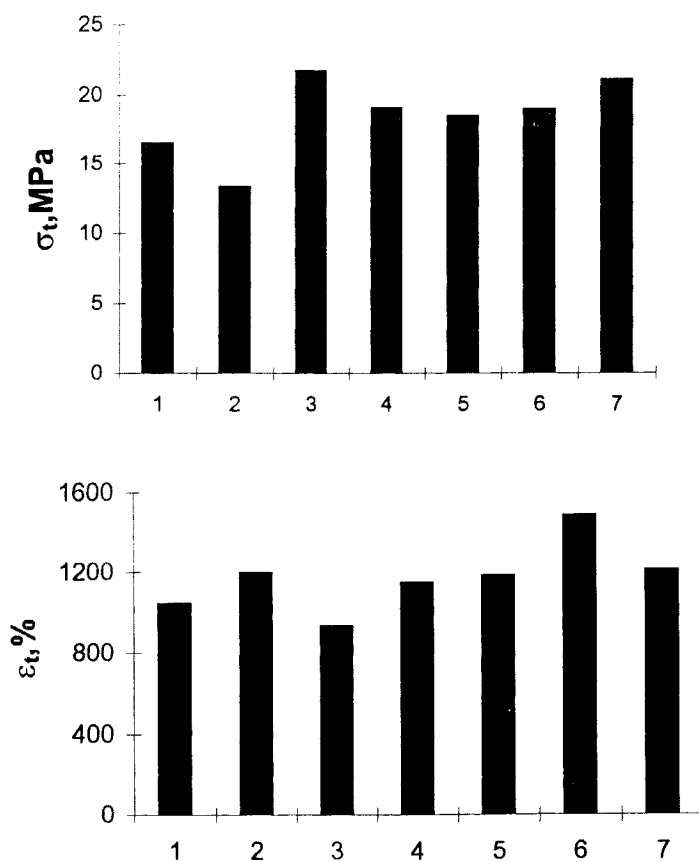
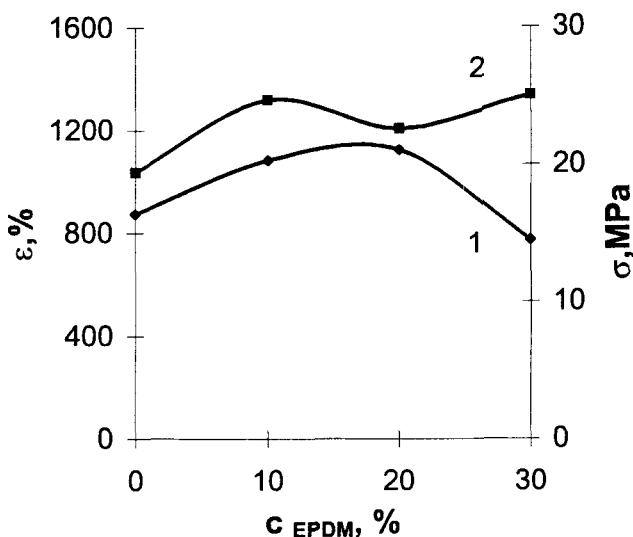**Figure 3.**   Tensile strength (σ_t) and tensile elongation at break (ε_t) of modified LDPE and LDPE/EPDM blends depending on crosslinking system: 1 - L, 2 - LE, 3 - LD 0.5, 4 - LS 0.5, 5 - LDS 0.5, 6 - LED 0.5, 7 - LEDS 0.5.

pared to 6.8 J/g in the case of LEDS, 1.0 may be due to higher temperature of mixing (HEDS1.0 was prepared at 423°K). A greater amount of DCP can decompose at this temperature. The HDPE blend is also more sensitive to oxidative degradation: it has a lower value of T_{destr} and a greater content of oxidative degradation products (Δm_b =1.03% as far as only 0.28% was detected in the case of LEDS 1.0). The significant fact is that, at the same time high value of gel (75%) was obtained for HEDS 1.0 (Table 4).

It is important to point out that the crosslinking peak on DSC curves disappears if modified blends pass thermal treatment at 453°K. It means that cross-

Figure 4. Variation of tensile strength (σ_t) - 1 and tensile elongation at break (ε_t) - 2 of LDPE/EPDM blend crosslinked with DCP/Saret = 0.5/0.5 wt% with content of EPDM (C_{EPDM}).

linking was completed during such treatment. It is supported by lower values of α and T_m (Table 3).

The ratio of competing reactions of crosslinking-degradation will affect strength-deformation behavior of PE blends. Figures 3-4 show a change of tensile strength (σ_t) and elongation at break (ε_t) of LDPE modified by different cross-linking agents. We would expect to see decrease of σ_t and an increase of ε_t for the blend LE if compared with LDPE. It is interesting to point out that crosslinking of LE with DCP alone results in a simultaneous increase of both parameters (we have to keep in mind that the gel content for LED 0.5 was 46%). If CCS was used as a crosslinking agent, despite the identical values of gel for LED 0.5 and LEDS 0.5, the last one exhibited a higher value of σ_t and a lower value of ε_t in comparison with LED 0.5 (Figure 3).

Figure 4 shows the effect of EPDM content in the blend on its strength -deformation parameters. As expected, curve σ_t = f(C_{EPDM}) show a maximum at 20 wt% EPDM, but the value of σ_t remains unchanged in the interval of C_{EPDM} = 20-30%. Such behavior supports the idea that PE/EPDM blends cured with CCS exhibit improved cohesive strength, which is important if they will be used as adhesives.

Adhesion is mainly believed to be dependent on the total content of oxygen on the polymer surface. Therefore, the ability of modified PE and their blends with EPDM to chemosorb oxygen and form polar groups was investigated by TG and IR spectroscopic methods. The value of S_{oks} (see Experimental section), also values of T_{oks} were used to estimate the degree of oxidation. To observe the effect of different modificators on the oxidative stability of polymers, the change of weight (Δm) depending on temperature also was measured. It should be noted at first that two compositions LD 0.5 and LS 0.5 do not have a oxidation peak on the TG curve. In the case of a small amount of DCP, this is thought to be due to consumption of all DCP in crosslinking/degradation reactions. When the content of DCP increases to 1%, we can see expressed oxidation peak ($S_{oks} = 40$ compared to 17.9 in the case of unmodified LDPE) and correspondingly decreased values of T^{oks}_b and T^{oks}_e (Table 4). In the case of LS, Saret alone does not act as a cross-linking agent; it affects oxidation as a peculiar stabilizer (absence of an oxidation peak supports such a conclusion). Some increase of Δm_b was observed (from 0.19% (L) to 0.36% (LS). In composition, Saret contains such low molecular weight components as fatty ester and alkylated phenol, which evaporate at low temperature. If CCS was used, LDPE possesses a higher value of S_{oks} (19.1) and a lower value of T_{oks} (Table 4), than LDPE crosslinked with DCP. Increasing the CCS content to 1% leads to a decreasing of S_{oks} and an increasing of ΔH_{crosl} (Tables 3-4). It means that the ratio of crosslinking/degradation reactions can be changed by changing the content of crosslinking agents.

The low ability to chemosorb oxygen exhibits EPDM (value of S_{oks} is only 5.6 and oxidation starts at 525°K). At the same time, this polymer exhibits low stability against thermooxidative degradation, it has greatest content of low molecular weight components - $\Delta m_b = 0.70\%$.

The greatest value of S_{oks} (25.5) shows LEDS 0.5 in comparison with similar compositions LDS 0.5 and EDS 0.5. It allows us to predict good adhesiveness of this blend.

As expected, HEDS 1.0 exhibits a smaller value of S_{oks} and a greater value of Δm_b (1.03%) in comparison with LEDS 1.0. It also lost 10% of its weight at a significantly lower temperature (380°K) compared to LEDS 1.0 (407°K) (Figure 2b).

After thermal treatment at 453°K, both LEDS 0.5 and HEDS 0.5 show increased values of S_{oks} (97.5 and 59.1, respectively) and very similar Δm_b (0.43% and 0.40%). At the same time, we can see in Figure 2b, that both polymers lost 30% of their weight at relatively low temperatures, 407°K and 430°K. If low molecular

weight products will not be compatible with polymers, or will accumulate in the boundary layer of adhesive compound, it can decrease adhesion.

We believe that a significant increase of adhesion due to contact oxidation should be expected if contact will be executed in the temperature interval T^{oks}_b - T^{oks}_{max}. A great value of S_{oks} should also be an indication of the potential increase of adhesiveness. If we analyze the data of Table 4 in light of such suggestions, we see that T^{oks}_b for all compositions investigated exceed 463°K. On the other hand, it must be remembered that T^{crosl}_{max} for the same polymers lay in the interval 443 - 460°K. There is some contradiction when we have to choose optimal contact temperature. To clarify this situation, it is important to bear in mind that TG and DSC data represented in Tables 3-4, were measured for polymers after their mixing. The coatings on the steel will be obtained during direct contact of molten polymers with metal. In this case, catalytic influence of metal took place. It will decrease T_{oks}, as shown by us [8], when the catalytic effect of steel on LDPE thermooxidation depending on the polymer layer thickness was investigated. Therefore, we can assume that optimal contact temperature of blends investigated with steel lay in the interval 453-463°K

The influence of crosslinking agents on the peel strength (A) of LDPE and HDPE blends was shown in the Figure 5-6. As expected, the greatest value of A was obtained for PE/EPDM blends modified with CCS; and a significantly higher value of A exhibits LEDS 1.0 in comparison with HEDS 1.0. Such behavior correlates with previously obtained data (change of Δm, S_{oks} and ΔH_{crosl}). It can be observed in Figure 6 that the content of EPDM, also contact temperature and time, results in influence on the value of peel strength. The increase of contact temperature from 433 to 473°K leads to a decrease of A in the case of LEDS 0.5, and does not affect A in the case of HEDS 0.5. It appears that thermooxidative degradation of the LDPE decreases A. This suggestion is supported by a change of Δm as a function of temperature (Figure 2b).

To better understand the differences between blends modified with DCP alone and CCS, examination of sol and gel fractions of three blends (LED 0.5, LEDS 0.5 and HEDS 0.5) was carried out (Tables 5-6).

Comparison of the blends LED 0.5 and LEDS 0.5 shows that their gels are characterized by the identical degree of crystallinity and T_m, but differ greatly in the ability to chemosorb oxygen (Table 5). LED 0.5 gel shows a great value of S_{oks} = 71.9, at the same time, there is no oxidation peak on the TG curve of LEDS 0.5 gel. Also, T_{destr} values for the two gels are different (525°K in the case of LED 0.5 gel and, 512°K in the case of LEDS 0.5 gel). However, we conclude that LED 0.5
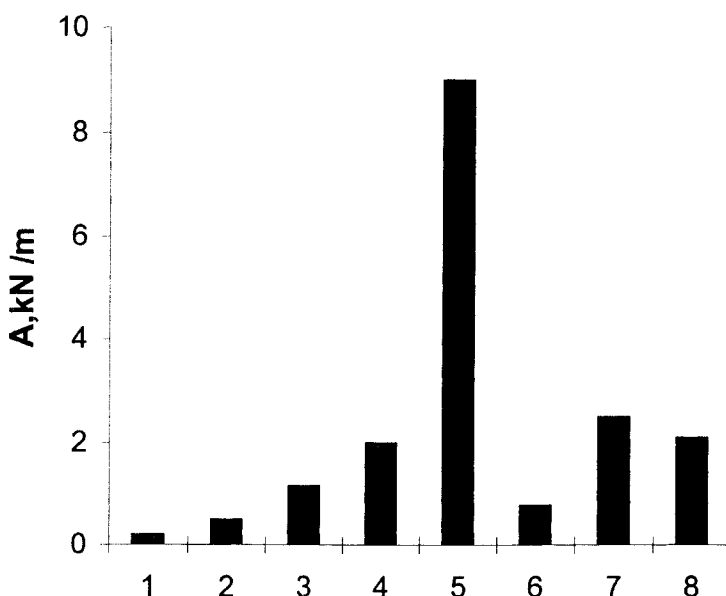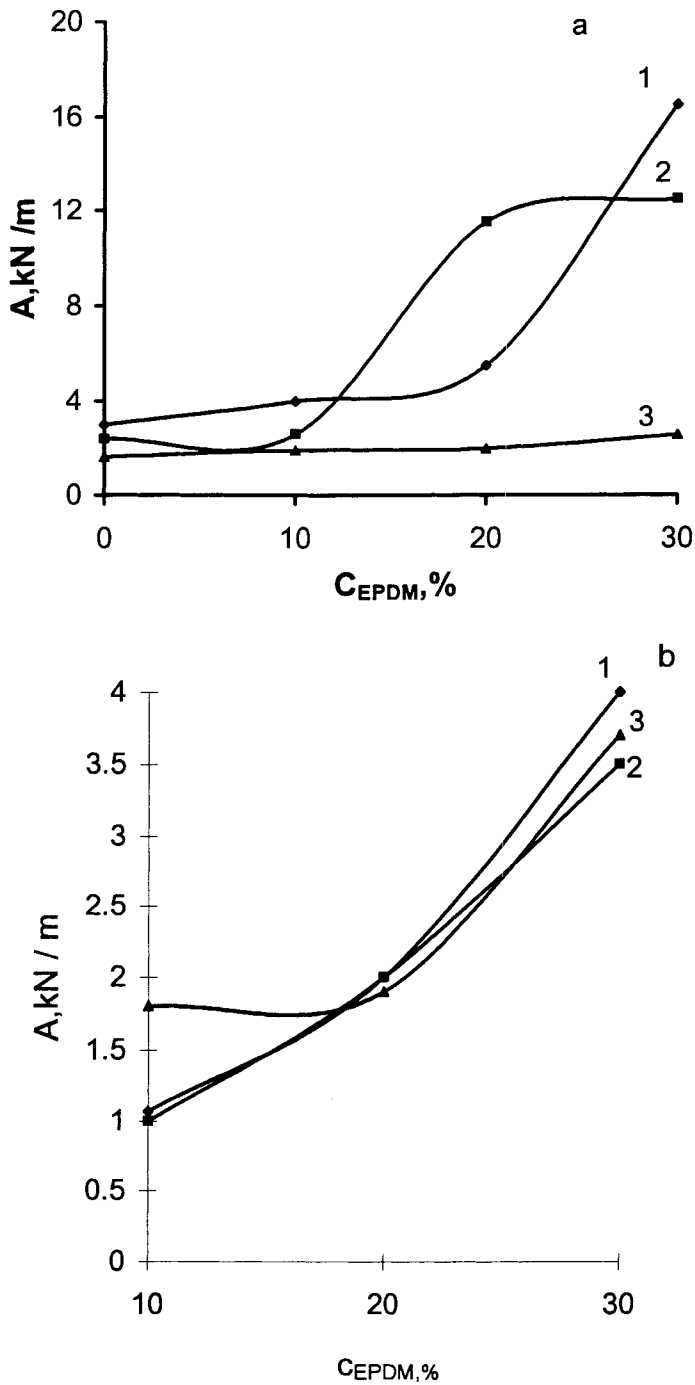
Figure 5. Peel strength (A) of modified PE and PE/EPDM blends to steel depending on crosslinking system: 1 - L, 2 - LE, 3 - LD 1.0, 4 - LDS 1.0, 5 - LEDS 1.0, 6 - HD1.0, 7 - HEDS 1.0, 8 - EDS 1.0. Contact temperature and time: 453°K, 0.18 ks.

gel exhibits lower stability against thermooxidative destruction because it lost 10% of its weight at a relatively low temperature-387°K, (LEDS 0.5 gel lost the same amount only at 488°K) (Figure 7). Unexpectedly high values of ΔH_{crosl} showed gels of both blends (Table 5), this means that crosslinking agents can participate in further radical reactions.

The higher values of crystallinity and two melting peaks are exhibited in the thermograms of LED 0.5 and LEDS 0.5 sol fractions. Such behavior is in agreement with similar melting characteristics observed for branched LDPE and the sols of crosslinked LDPE [9]. Our sols also shows an increased degree of branching (Table 6). Higher values of α for sols can be explained by a higher degree of degradation in comparison with gels. In the same way as gel fraction, sol of LED 0.5 exhibits oxidation peak on TG curve, but sol of LEDS 0.5 is characterized by absence of this peak. Again, LED 0.5 sol, as well as gel fraction, shows lower stability against thermooxidation in comparison with LEDS 0.5 (see change of Δm_b in Table 5 and change of $\Delta m=f$ (T) in Figure 7).

Figure 6.   Variation of peel strength (A) of LDPE/EPDM (a) and HDPE/EPDM (b) blends crosslinked with DCP/Saret= 0.5/0.5 wt% with EPDM content (C_{EPDM}). Contact temperature and time: 1 - 423°K, 0.6 ks, 2 - 453°K, 0.06 ks, 3 - 473°K, 0.06 ks.

TABLE 5. DSC and TG Analysis of Modified PE/EPDM Blend Sol and Gel Fraction

Compo-sition	T_m K	α %	ΔH_{crosl} J/g	T^{TG}_{oks} K	S_{oks} area units/g	Δm_b %	T_{destr} K
LED0.5							
sol	359;387	37	3.8	502	14.9	0.36	512
gel	386	34	11.6	492	71.9	0.13	525
LEDS0.5							
initial	386	37	3.5	497	25.5	0.54	519
453 K,	383	34	0	497	97.5	0.43	543
0.18 ks							
sol	367;388	40	0	-	-	0.44	512
gel	386	34	17.7	-	-	0.15	512
HEDS0.5							
sol	407	68	0	-	-	0.39	505
gel	409	56	2.5	493	81.9	0.15	258

Comparison of the blends LEDS 0.5 and HEDS 0.5 shows that gel fraction of HEDS 0.5 chemosorb a great amount of oxygen (S_{oks} =81.9), but the value of crosslinking is small (ΔH_{crosl}=2.5J/g). The sol fraction of HEDS 0.5 exhibits an absence of oxidation peak on TG curve, but it is more degraded in comparison with LEDS 0.5 sol. (Table 5 and Figure 7). The lower content of crosslinking agents which remain in the HEDS 0.5 after blend preparation and higher tendency to

TABLE 6. IR Spectra of Modified PE/EPDM Blend Sol and Gel Fractions

Composition	$\underline{CH_3}$ 1000 C	D_{1170} cm^{-1}	D_{1710} cm^{-1}	D_{1617} cm^{-1}	D_{1575} cm^{-1}	D_{690} cm^{-1}	D_{620} cm^{-1}
LED0.5							
sol	48	12.8	13.1	0	0	0	0
gel	-	16.3	9.8	0	0	0	0
LEDS0.5							
sol	46	14.2	13.4	0	0	0	0
gel	-	22.4	20.7	0	13.0	0	0
HEDS0.5							
sol	40	62.9	19.4	20.7	0	16.4	16.2
gel	-	10.9	8.17	12.3	9.68	0	0

thermooxidative degradation may be the reason for lower values of A in the case of HEDS 0.5.

IR spectra were also obtained for sol and gel fractions of all three blends (Table 6). For all samples, there are strong absorption bands at 1710 cm^{-1}, which are due to the stretching vibrations of ν_{CO} from keto, carboxylic or ester groups and 1170 cm^{-1}, which are due to C-O-C ester groups [10]. The concentration of C=O group is important from the adhesion view point. As can be seen in Table 6, in the case of LED 0.5 and HEDS 0.5, their sols are characterized by higher intensity of the band at 1710 cm^{-1}, as compared to spectra of gel fractions. LEDS 0.5 sol and gel (Table 6) exhibit the exact opposite behavior

A suprisingly high band intensity at 1170 cm^{-1} shows sol of HEDS 0.5. As far as soluble sol containing more degraded parts of polymer, we conclude that a high intensity of corresponding bands, in the case of LED 0.5 and HEDS 0.5, is
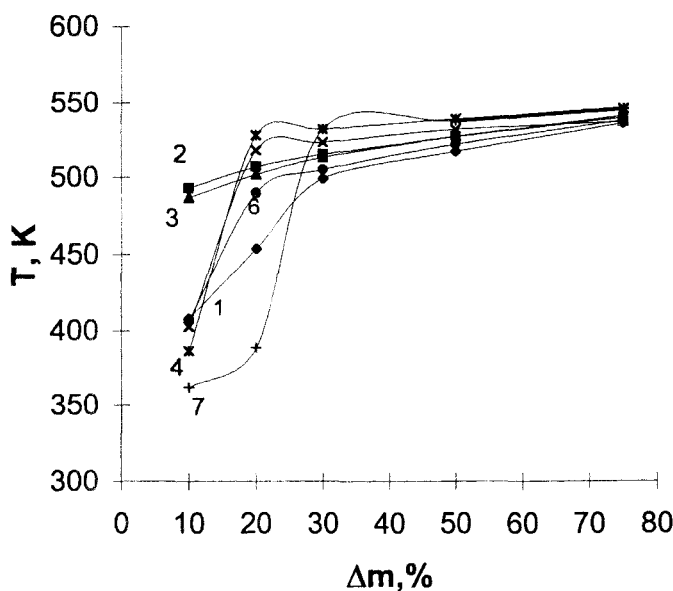
Figure 7.   Effect of temperature (T) on weight loss (Δm) of 1, 2, 3 - LEDS 0.5, 4, 5 - LED 0.5, 6, 7 - HEDS 0.5; Sol fractions - 2, 4, 6, gel fractions - 3, 5, 7; Thermal treatment at 453°K,0.18 ks.

related to a high degree of degradation of these polymers. On the other hand, the great content of oxygen containing groups in the crosslinked part of LEDS 0.5 could increase its adhesiveness (Figure 5). The band at 1575 cm⁻¹ may be assigned to a carboxylate group of Saret. The absence of this band in the spectra of LED 0.5, and presence of this band in the spectra of gel fractions, both LEDS 0.5 and HEDS 0.5 means that a coagent is incorporated in crosslinks of these blends.

Lastly, it should be noted that only spectra of HEDS 0.5 sol has bands at 1617 cm⁻¹, 620, and 690 cm⁻¹. Accordingly, [11] these bands can be attributed to the presence of EPDM. We suggest that in the case of LEDS 0.5, a certain degree of interfacial adhesion was obtained between EPDM particles and LDPE, which results in graft copolymer producing. The formation of such a copolymer may partially cause the increase of cohesive strength (and, correspondingly , peel strength) of that blend. In the case of more linear HDPE, such interaction does not occur, or occurs to a lesser extent. Therefore, uncrosslinked EPDM was found in soluble sol fraction. However, it is impossible to completely verify this phenom-enon on the basis of our present investigations.

CONCLUSION

It was shown that the mechanical properties and adhesion to steel of LDPE/EPDM and HDPE/EPDM blends, crosslinked with dicumyl peroxide in the presence of coagent, Zn diacrylate, were significantly improved.

A correlation was found between parameters (oxygen uptake, content of oxygen containing groups and changes of weight) characterizing thermooxidative conversions in the polymer and peel strength of modified PE/EPDM blends.

The improved cohesive and peel strengths of modified LDPE/EPDM blends, in comparison with HDPE/EPDM blend, was explained by the possible production of graft copolymer during crosslinking in the case of a more branched low density polyethylene.

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