HDPE-EPDM THERMOPLASTIC VULCANIZATES. MECHANICAL AND IR SPECTROMETRIC PROPERTIES

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The present work is concerned with the preparation and characterization of some thermoplastic vulcanizates based on high-density polyethylene (HDPE) and ethylene-propylene-diene terpolymer (EPDM). The polymer blends were obtained using binary vulcanizing accelerators systems. One of the components was tetramethylthiuram disulfide (TH) and the second one, 2-mercaptobenzothiazole (M) or 2,2'–dithiobenzothiazole (DM). An important part of our study is focused on the mechanical properties of the prepared thermoplastic vulcanizates. These properties were then correlated with the IR spectra obtained by applying the ATR-FTIR technique. The polymer blend containing as cure system Sulfur+TH+M in the weight ratio 0.41/1.8/0.8 and 1/1.2/0.7 were found to have better properties, especially tensile strength, modulus 300% and tear strength.

INTRODUCTION

The appearance of thermoplastic elastomers (TPEs) in the 1950s[1] provided a new dimension to the field of polymer science and technology. The field of TPEs based on rubber thermoplastic composites has grown along two different product-lines or classes: one consists of simple blends and is commonly designated as thermoplastic elastomeric olefins (TEO) according to ASTM D5593.[2] In the other class the rubber phase is dynamically vulcanized, giving rise to a thermoplastic (TPV) or dynamic vulcanizate (DV) according to ASTM D5046.[3] Morphologically, TPVs are characterized by the presence of finely dispersed crosslinked rubber particles distributed in a continuous thermoplastic matrix.[4,5] If the rubber particles are sufficiently vulcanized, the physical and chemical properties of the blend are generally improved.

The dynamic vulcanization process was first reported by Gessler[6] in 1962 and further developed by Fisher[7], Coran et al.[8, 9] and Abdou-Sabet and Fath.[10] The thermoplastic vulcanizates presents improved physical and chemical properties, such as: higher values of Shore "A" hardness, modulus 300%, stress at break, tear strength and lower value of strain at break, greater stability of phase morphology in the melt, more reliable thermoplastic processing, greater resistance at high temperature and to attack by fluids e.g., hot oils, alkaline and acid solutions.

Polyethylene-ethylene-propylene-diene terpolymer (PE-EPDM) composites have both practical and theoretical significance. To be able to utilize all the advantages offered by such composites, the basic processes taking place during their formation must be known.

In this paper, a tentative explanation which tries to help to understand better the relations between structure and properties of PE-EPDM composites is given. For this purpose, a correlation between IR spectra and physico-mechanical properties of the prepared thermoplastic elastomers was proposed.

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RESULTS AND DISCUSSION

It is widely recognized that the formulation has a strong influence on the properties of polymer composites. For this reason, the effect of the type of cure system and of the ratio of cure agents on the physico-mechanical properties of the prepared polymer blends was investigated. The EPDM-HDPE composites were obtained by different chemical methods of vulcanization and in different formula. All polymer samples have the same ratios (parts by weight) EPDM:HDPE:ZnO:stearic acid:2,2,4–trimethyl-1,2-dihydroquinoline:Irganox 1010 = 50:50:5:0.4:1:1. The cure agents are given in Table 1. We mention that usually when the ratio of sulfur to accelerator is less than one the receipt is known as Efficient Vulcanization System (EV).

Table 1

Cure agents in formulation of some microstructured polymer blends (parts by weight)

Cure agents	Cure system / Symbol of polymer blends									
	Conventional cure system						Semi-EV system		EV system	
	S1	S2	S7	S8	S12	S13	S17	S18	S22	S23
Sulfur	2	2	2	2	2	2	1	1	0.41	0.41
TH	1	1	0.5	0.5	0.5	0.5	1.2	1.2	1.8	1.8
M		0.5		1		0.3		0.7		0.8
DM	0.5		1		0.3		0.7		0.8	

Shore "A" Durometer Hardness is the measure of elastic modulus of the polymer blend. This parameter is often indirectly obtained by measuring the elastic indentation of prescribed size and shape pressed into the surface under specified loading conditions. Higher values of this parameter correspond to harder compounds and vice versa. As can be seen in Figure 1, the values of this parameter were not significantly different for all the investigated composites; the loading with cure agents and the presence of HDPE gives a greater hardness to the cured compounds.
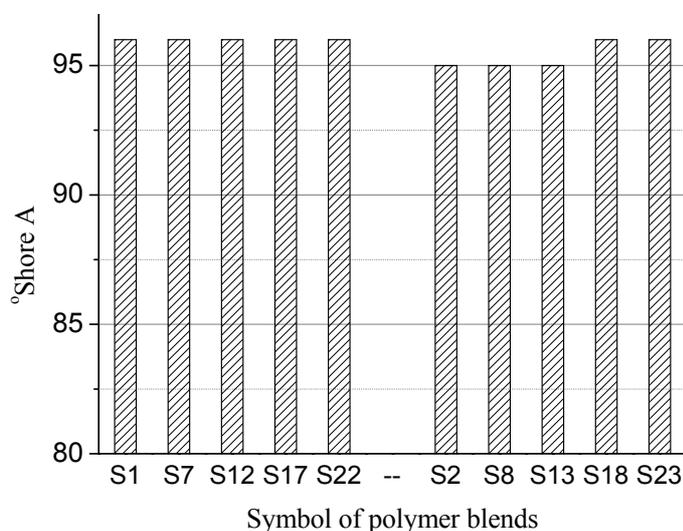

Fig. 1 – Shore "A" Durometer Hardness.

Stress at 300% (Modulus) and tensile strength (stress-at-break) for all polymer composites were investigated. The importance of 300% modulus lies in the fact that it can be taken as an index of the sum of chemical and physical crosslinks, such as chain entanglements.[11] As it is shown in Figure 2, the value of modulus at 300% is higher for the compounds S17, S18 and S23.

The stress-at-break values for all polymer composites are shown in Figure 3. The highest tensile strength corresponds to the compounds S17, S18 and S23. The other compounds, i.e., S1, S2, S13 showed nearly equal or low tensile strength values. This suggests that the strain crystallization behavior of the first mentioned composite samples was encouraged by the use of the semi-EV and EV procedures of compounding. The cure conditions obtained by semi EV and EV systems always results in higher tensile values.
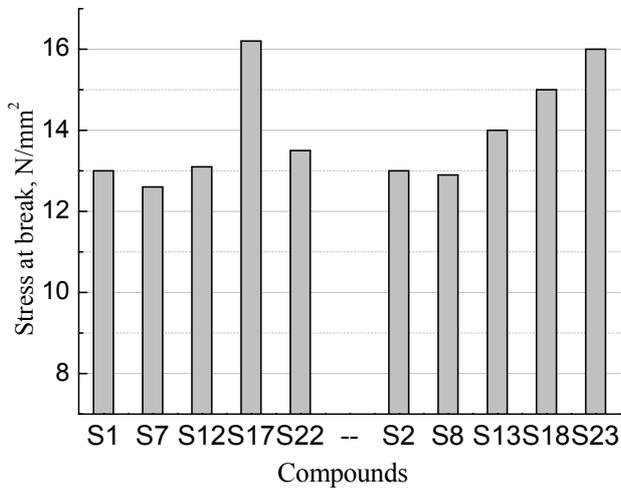
Fig. 2 – Stress at 300% strain (modulus), N/mm^2.
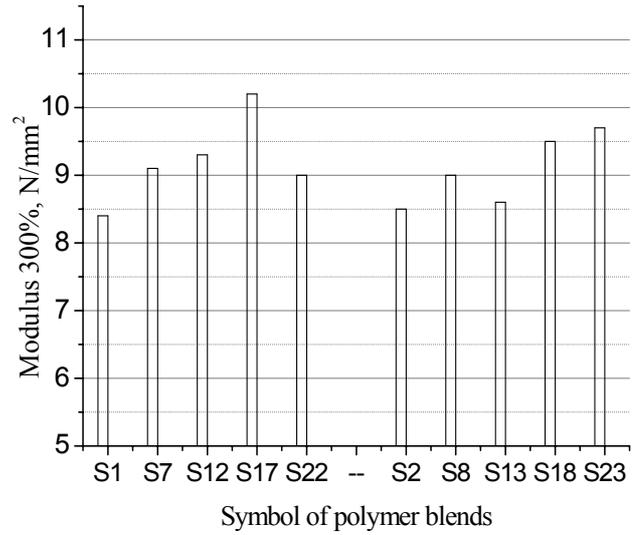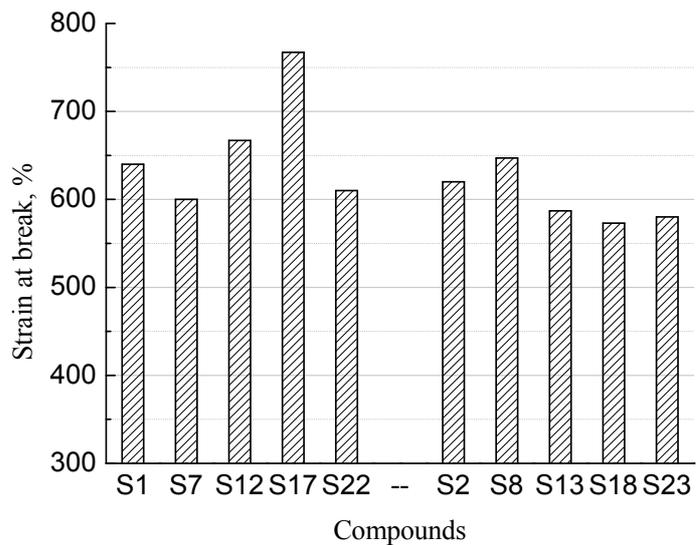
Fig. 3 – Stress at break, N/mm^2.

Fig. 4 – Strain at break, %.

Strain at break (elongation, %). Strain at maximum elongation, *i.e.*, the extensibility of the studied composites is illustrated in Figure 4. It is known that the elongation of the polymer blend decreases with the increases of crosslinking[12] (which is confirmed from its elongation, % value).

The results illustrated in Figure 4 seem to confirm this assumption. The effect of crosslink

density on the extensibility is evident in the case of the compounds S18 and S23, which have the lower value of elongation. On the other hand, the following ratios vulcanizing accelerators/sulfur can be seen in Table 1: 0.75 for the conventional cure systems S1, S2, S7, S8; 1.85 for the semi-EV cure systems S17, S18; 6.34 for EV cure systems S22, S23. So, even the conventional systems have higher sulfur loading, but more efficient seem to be the semi-EV and EV cure systems, which contain lower amounts of sulfur. This behavior could be explained as follows: too many crosslink junctions (assured by the polysulfide bonds) will hinder the structural regularity needed for crystallization (it is the case of samples S1, S2, S8, S12, S17), which have higher values of strain at break. The highly crosslinked compounds can not crystalline easily because of the immobility of the network structure. In the case of semi-EV system S18 and EV system S23 the crosslinking obtained is beneficial, providing the mobility to align the chains on

deformation; as a result, the strain at break is lower. On the other hand, the semi-EV and EV systems (containing the accelerators TH+M, in samples S18 and S23) seem to be more efficient than those containing TH+DM (in samples S17, S22). This could be a consequence of the moderate action of M (see the value of elongation for S18 and S23 comparative with S17 and S22).

Tear behavior. The tear strength values for the polymer composites are presented in Figure 5. As we can see, the tearing strength values are influenced by the sort of sample. As a confirmation of this assumption, the literature data reported that tear strength values depend on the type of sample itself, filler type and test conditions.[11-15] The compounds S13, S18, S22, S23 have higher tear strength values than the others. This behavior could be explained by the strain crystallization of the mentioned compounds.
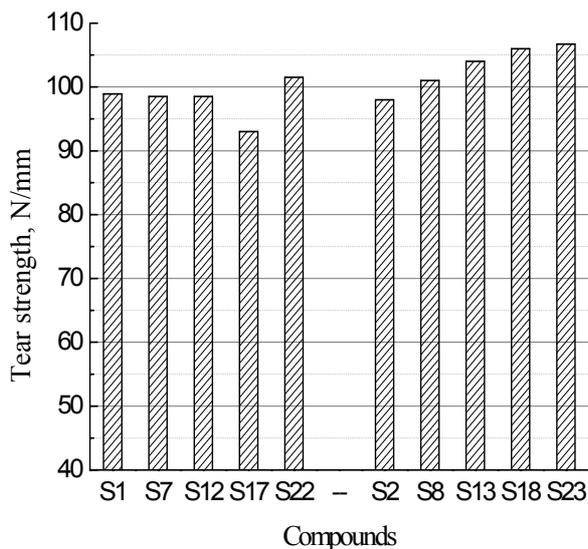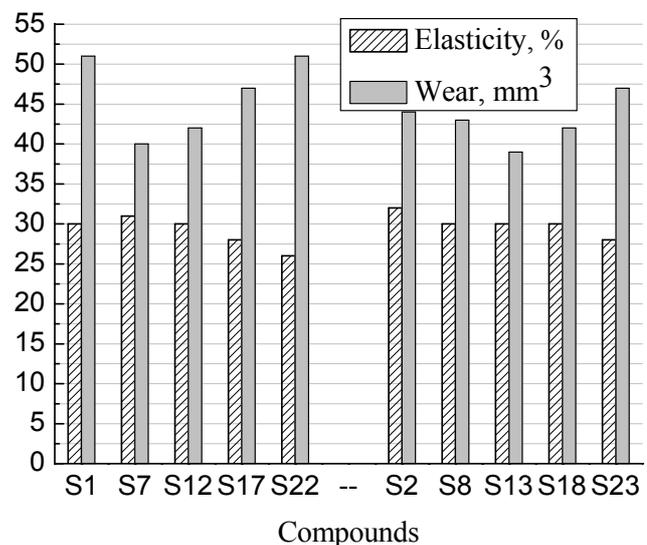

Fig. 5 – Tear strength, N/mm.

Fig. 6 – Elasticity, % and wear, mm³ .

Elasticity and wear. As it is seen in Figure 6, in the almost all the cases a higher value of the elasticity is associated with a lower wear. These results were predictable taking into account that a low elasticity could be a result of the regularity of the polymer chains and vice versa.

The effect of accelerated aging. Generally, the effect of accelerated aging lies in an increase of modulus 300% and stress at break and a decrease of strain at break. This behavior is confirmed by the results in Tables 2 and 3 and consists in the improvement of some physico-mechanical properties of the obtained thermoplastic vulcanizates at high temperature. The effect of accelerated aging should be explained as follows: at high temperature, a physical interaction between many vulcanized elastomer particles takes place; this results in a network of vulcanized elastomer.[16] The substantial change of most of tensile properties may also be an indication of a post-curing process. The effect of accelerated aging shows that the prepared thermoplastic vulcanizates are good candidates for industrial applications at high temperatures.

Table 2

The effect of aging on the physico-mechanical properties of some thermoplastic vulcanizates containing as cure agents S, TH, M, DM obtained by using conventional cure systems

Physico-mechanical parameter	Symbol of polymer blends											
	S1		S2		S7		S8		S12		S13	
	a	b	a	b	a	b	a	b	a	b	a	b
°Shore A Hardness	96	96	95	95	96	96	95	96	96	96	95	94
Elasticity, %	30	32	32	30	31	26	30	28	30	28	30	29
Modulus 300%, N/mm^2	8.4	11.8	8.5	10.7	9.1	10.6	9	10.8	9.3	11.2	8.6	11.8
Stress at break, N/mm^2	13	19.8	13	19.3	12.6	21.1	9.7	18.7	13.1	19.5	14	19
Strain at break, %	640	560	620	553	600	600	647	567	667	567	587	520
Tear strength, N/mm	103.5	96.5	98	96	98.5	102.5	101	92.5	98.5	93	104	98.5

a) – Normal conditions: b) – After accelerated aging

Table 3

The effect of aging on the physico-mechanical properties of some thermoplastic vulcanizates containing as cure agents S, TH, M, DM obtained by using semi-EV and EV cure systems

Physico-mechanical parameter	Symbol of polymer blends							
	Semi-EV systems				EV systems			
	S17		S18		S22		S23	
	a	b	a	b	a	b	a	b
°Shore A hardness	96	96	96	95	96	96	96	96
Elasticity, %	28	26	30	30	26	28	28	34
Modulus 300%, N/mm^2	10.2	10.3	9.5	10.4	9	10.6	9.7	10.4
Stress at break, N/mm^2	16.2	18.7	15	18.7	12.2	19	16	19
Strain at break, %	767	580	580	560	610	560	600	580
Tear strength, N/mm	93	96	106	96.5	101.5	98.5	106.5	105

a) – Normal conditions: b) – After accelerated aging

The ATR technique has given fresh hope for IR spectrometry of polymer materials that do not allow the usual methods of sample preparation. Moreover, the literature data reports ATR-FTIR spectrometry being useful for characterization of the surface of complex polymer blends, taking into account that the IR radiation penetrates into the sample a few nanometers depth. As a matter of fact, in the case of polymer blends characterized by a good incorporation of additives, the presence of the IR characteristic peaks of additives in the surface spectra cannot be detected.[17]

On the basis of this well-documented assumption, the ATR-FTIR spectra recorded for the studied polymer blends gave us the following information:

No absorption bands were detected in the range 4000-3200 cm^{-1} for the samples S18 and S23 (see

Fig. 7b). The vibrations responsible for bands in this region are O-H and N-H stretchings and are characteristic IR spectral bands of primary and secondary amines (*i.e.* the antioxidant TMQ), organic acids (*i.e.* the activator stearic acid) and phenols (*i.e.* the antioxidant Irganox 1010).

Many spectral bands occur in the spectra of the other polymer blends (Figure 7ab). They could be attributed to the polymer additives. For example, in

Figure 7a, spectra of S7 and S22 present a large band at 3420 cm^{-1} characteristic for tertiary amines (characteristic for the cure accelerator DM). In Figure 7b (spectra of samples S2, S8, S13) a weak N-H stretching band may be seen at 3300-3500 cm^{-1}, assigned to secondary aromatic amines and diamines. This band is characteristic for the additives M, DM, TMQ, TH.

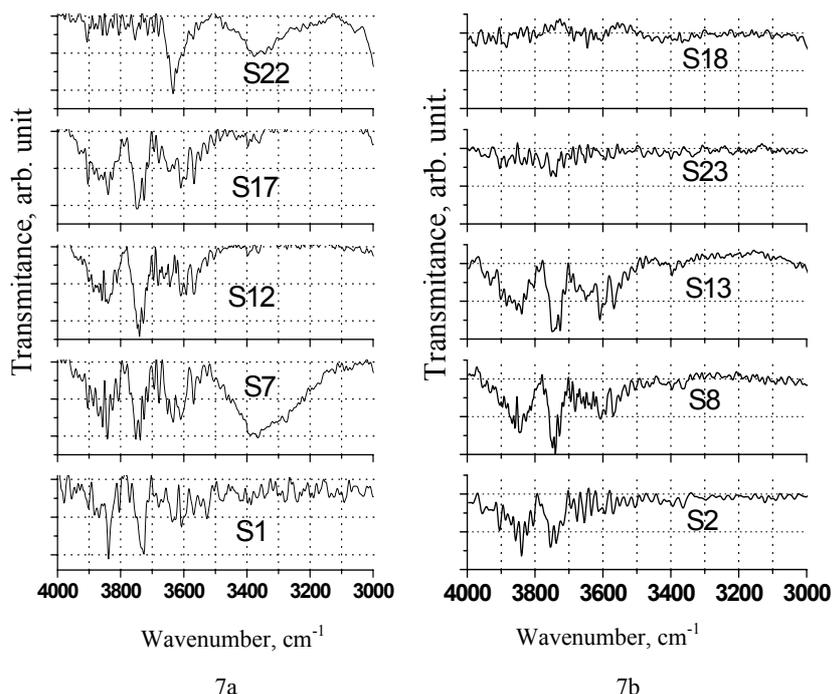7a   7b

Fig. 7a,b – FTIR spectra of some polymer composites.

On the basis of these spectral information we assume that the activator (stearic acid), the antioxidant (Irganox 1010) and the cure accelerators are completely incorporated in the polymer blends S18 and S23, because in the spectra of these samples do not occur the bands characteristic for these additives. This confirms the compatibility of the ingredients (polymers and additives).

The assignment of the IR bands was carried out according to literature data.[18]

EXPERIMENTAL

Materials. All composites contain the same polymers: the EPDM elastomer (Nordell IP 3745P) and the high density polyethilene (HDPE B084, Petro-Midia), in the ratio 1:1.

In addition to the polymers, other additives were used, as follows: cure accelerators: 2-mercaptobenzothiazole (M); 2,2'–

dithiobenzothiazole (DM); tetramethylthiuram disulfide (TH); crosslinking agent: sulfur (S); activators: zinc oxide and stearic acid; antioxidants: di-lauril-orto-dipropionate (Irganox 1010) and 2,2,4–trimethyl-1,2-dihydroquinoline (TMQ).

Preparation of thermoplastic elastomers. All the ingredients were mechanically melt-mixed in a Brabender Plasti-Corder PLE-60 at 180°C for 7-8 minutes. A constant rotor (cam type) speed of 80 rpm was applied. Then, the polymer blend was recovered from the mixer and transferred to a two-roll mill at 155 ± 5°C and 24 rpm. The compound was then compression-molded (using an electrically heated hydraulic press at 190°C under 20 MPa pressure) to achieve a sheet of about 2 mm thick. The sheet was then cooled down to room temperature under the same pressure. The specimens were cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

Aging experiments. In order to investigate the effect of lab aging conditions on the physico-mechanical properties of the prepared thermoplastic vulcanizates, the test specimens were placed in an air-circulating oven at 100°C for 168 h.

Apparatus for physico-mechanical tests. Tensile tests were carried out according to ASTM D412-98 using a Zwick Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness was measured using Shore "A" durometer according to ASTM D412-98.

Apparatus for FTIR measurements. The attenuated total reflection Fourier Transform IR (ATR-FTIR) method was chosen for spectral characterization of the prepared polymer blends. The plate samples (6 x 6 mm) were simply posed on the sampling stage, in intimate contact with the optical element, a hemi-cylindrical prism of SeZn (colled Internal Reflection Element (IRE)). ATR-FTIR measurements were run with a Bruker instrument (model Tensor 27), in the following conditions: wavenumber range: 600-4000 cm^{-1}; apperture setting: 6 mm; scanner velocity: 2.2 KHz; background scan time: 32 sec; sample scan time: 32 sec; resolution: 6 cm^{-1}; beamspliter: KBr; angle of incident radiation: 45°.

CONCLUSIONS

The optimum values of the main physico-mechanical parameters, characteristic for thermoplastic vulcanizates (high values of $^{\circ}$Shore A hardness, 300% modulus, stress at break, tear strength and low values of strain at break or elasticity) were obtained in the case of semi-EV and EV systems S18 and S23 respectively. Thus, by using as cure agents sulfur and the two accelerators M and TH (in the ratio cure accelerators/S = 1.9, in the case of sample S18 and 6.34 in the case of sample S23), we have obtained the best thermoplastic vulcanizates. The compatibility of the polymer phases in the case of S18 semi-EV system and S23 EV system was confirmed by their physico-mechanical properties and correlated with IR spectra. Both physico-mechanical and ATR-FTIR techniques allowed understanding the structure of the prepared chemical microstructured systems.

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