

CHARACTERIZATION OF SOME MICROSTRUCTURED POLYMER BLENDS BY MECHANICAL TESTS AND ATR-FTIR SPECTROMETRY

Zenovia Moldovan*, Florica Ionescu**, Ioana Vasilescu***,
Simona Lițescu* and G.L. Radu***

abstract: In our study, a series of thermoplastic vulcanizate blends based on ethylene propylene diene terpolymer (EPDM) rubber and high-density polyethylene (HDPE), have been prepared by using different chemical systems of vulcanization. The obtained microstructured polymer blends have been characterized by physical-mechanical tests and by Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometry. The dynamic mechanical analysis correlated with ATR-FTIR spectral characteristics reveals that semi-EV and EV systems containing as cure agents sulfur and two accelerators (Tetramethylthiuram disulfide (TH) and 2-Mercaptobenzo-thiazole (M)) show improved properties as against conventional cure systems.

key words: polymer blends, mechanical tests, ATR-FTIR spectrometry

Introduction

Microstructured polymer blends represents one of the most interesting field of research in material science. In this context, the appearance of thermoplastic elastomers (TPEs) in the 1950s [1] provided a new dimension to the field of polymer science and technology. Numerous literature data are available on this subject [2÷5], especially on thermoplastic vulcanizates (TPVs) or dynamic vulcanizates (DV), according to ASTM D5046 [6]. Morphologically, TPVs are characterized by the presence of finely dispersed crosslinked rubber particles distributed in a continuous thermoplastic matrix [7,8]. If the rubber particles are sufficiently vulcanized, the physical and chemical properties of the blend are generally improved. For our study, ternary polyethylene, ethylene-propylene-diene terpolymer, additives (HDPE-EPDM-additives) composites have been prepared. Also, a tentative explanation is given which tries to help to understand better the relations between structure and properties of the composites containing HDPE, EPDM and polymer additives. For this purpose, a correlation between ATR-FTIR spectra and physical-mechanical properties of the obtained thermoplastic elastomers was proposed.

* Department of Analytical Chemistry, University of Bucharest, 90-92 road Panduri, Bucharest, Romania, e-mail:z_moldovan@yahoo.com

** Research Development National Institute for Textile and Leather - Division Leather and Footwear Research Institute, 93 Ion Minulescu St., Sect 3, 031215 - Bucharest, Romania

*** University "Politehnica" of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 1 Gheorghe Polizu St., Sect. 1, Cod 011061-Bucharest, Romania

Experimental

Materials

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

The following polymer additives were used: cure accelerators (Tetramethylthiuram disulfide (TH); 2-Mercaptobenzothiazole (M); N-Cyclohexyl benzothiazole-2-sulfenamide (CZ)); crosslinking agent (Sulfur); activators (Zinc oxide and Stearic acid) and antioxidants (Di-lauril-orto-dipropionate (Irganox 1010) and 2,2,4 – Trimethyl-1,2-dihydroquinoline (TMQ)).

Apparatus

Apparatus for physical-mechanical tests

Tensile tests of the samples 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 of the samples was measured by Shore “A” Durometer according to ASTM D412-98.

Apparatus for FTIR measurements

ATR-FTIR measurements were run with a Bruker instrument (model Tensor 27), in the following conditions: wavenumber range: $600\text{--}4000$ cm^{-1} ; aperture setting: 6 mm; scanner velocity: 2.2 kHz; background scan time: 32 sec; sample scan time: 32 sec; resolution: 6 cm^{-1} ; beamsplitter: KBr; angle of incident radiation: 45° . After recording, the ATR-FTIR spectra were converted into transmission FTIR spectra. The plate samples (6 x 6 mm) were simply posed on the sampling stage, in intimate contact with the optical element, a hemicylindrical prism of SeZn (called Internal Reflection Element (IRE)). The incident radiation arrives onto the sample with a certain angle (usually, between 30 and 60°) to the normal of the sample plane. Then, the reflected beam is collected by a mirror, which focuses the reflected radiation onto the detector.

Procedure

Preparation of polymer blends

All the ingredients (the two polymers EPDM and HDPE and the additives) 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. Finally, when mixing ended, the polymer blend was recovered from the mixer and transferred to a two-roll mill at $155 \pm 5^\circ\text{C}$ 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 same pressure. The specimens were die-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 physical-mechanical properties of the prepared thermoplastic vulcanizates, the test specimens were placed in an air-circulating oven at 100°C for 168 h.

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 physical-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 in weight) EPDM:HDPE:ZnO:Stearic acid:TMQ:Irganox 1010 = 50:50:5:0.4:1:1. The cure agents are variable and are given in Table 1.

Table 1. Cure agents in formulation of some microstructured polymer blends (parts in weight).

Cure system Cure agents	Symbol of polymer samples									
	Conventional cure system						Semi-EV system*		EV system*	
	S2	S3	S8	S9	S13	S14	S18	S19	S23	S24
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	
CZ		0.5		1		0.3		0.7		0.8

EV system = Efficient vulcanization system. Semi-EV system = Semi-efficient vulcanization system

Shore “A” Durometer Hardness

The value of Shore “A” Durometer is the measure of elastic modulus of the polymer blend, which is often measured indirectly 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 it can be seen in Fig. 1, the values of this parameter were not significantly different for all investigated compounds; the loading with cure agents and the presence of HDPE gives a great hardness of the cured compounds.

Stress at 300% (Modulus) and tensile strength (stress-at-break)

The stress values at 300% strain 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 total sum of chemical and physical crosslinks, such as chain entanglements [9]. As it is shown in Fig. 2, the value of modulus at 300% is higher for the compounds S8, S18, S19 and S23. The stress-at-break values for all polymer composites are shown in Fig. 3. The highest tensile strength corresponds to the compounds S18, S23 and S24. As the literature data

reported, the tensile strength depends on the compatibility of EPDM phase and HDPE phase of TPV [10], which is evident in the case of the mentioned samples. The other compounds, i.e., S2, S3, S8, S9 showed lower and nearly equal tensile strength values. This suggests that using conventional cure systems of compounding did not hinder the strain crystallization behavior of these samples. Overall, the cure conditions obtained by using semi EV and EV systems always results in higher tensile values.



Fig. 1 Shore A Durometer Hardness

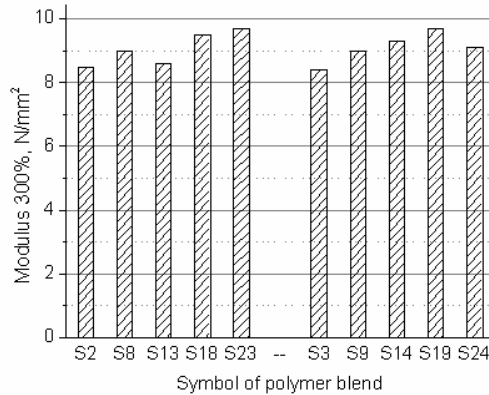


Fig. 2 Stress at 300% and 500% strain (modulus)

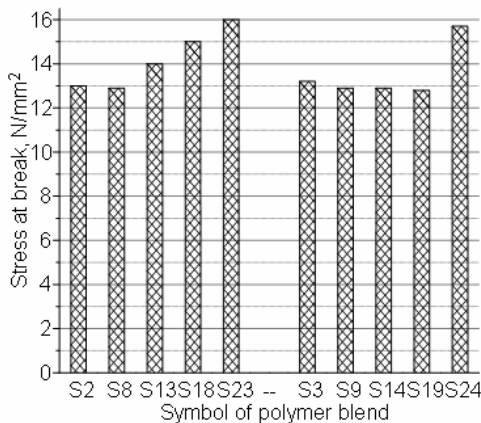


Fig. 3 Stress at break, N/mm²

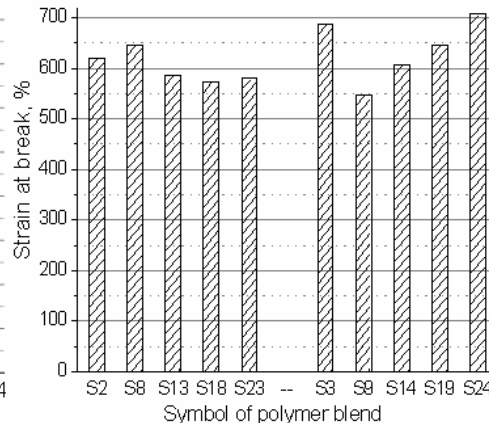


Fig. 4 Strain at break, %

Strain at break (Elongation, %)

Strain at maximum elongation, i.e., the extensibility of the studied composites is illustrated in Fig. 4. It is known that the extensibility of the polymer blend decreases with the increases of crosslinking [11]. In the same time, a high crosslink makes the compound stiff and it loses its extensibility and strength (which is confirmed from its elongation, % value).

The results illustrated in Fig. 4 seem to confirm this assumption. The effect of crosslink density on the extensibility is evident in the case of the compound noted S9, S18 and S23, which have the lower values of Elongation. On the other hand, on the basis of data given in

Table 1, we observe the following ratios cure accelerators/sulfur: 0.75 for the conventional cure systems S2, S3, S8, S9 and 0.4 for S13, S14; 1.85 for the semi-EV cure systems S18, S19; 6.34 for EV cure systems S22, S23. So, even the conventional systems have higher sulfur loading, more efficient seem to be the semi-EV and EV cure systems S18 and S23 respectively, which contains 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 S2, S3, S8, S14), which have higher values of strain at break. Also, in high loading of sulfur (it is the case of the mentioned systems S2, S3, S8, S14), most of links are dangling and do not contribute towards the strength of the compounds. 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 in terms of providing the mobility to align the chains upon deformation; as a result, the strain at break is lower. On the other hand, the semi EV and EV-cure systems containing the accelerators TH+M seems to be more efficient than those containing TH+CZ. This could be a consequence of the delayed action of CZ (see the value of Elongation for S18, S23, comparatively with S19, S24).

Tear behavior

The tear strength values for the compounded polymer blends are presented in Fig. 5.

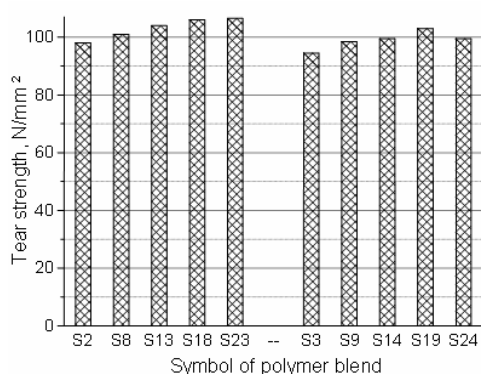


Fig. 5 Tear strength, N/mm^2

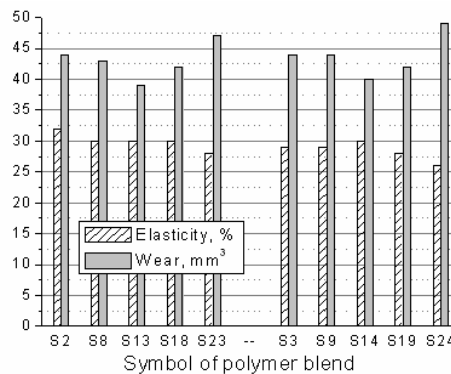


Fig. 6 Elasticity, % and wear, mm^3

As we can see, the tearing strength values were influenced on the kind of sample. As a confirmation of this assumption, the literature data reported that tear strength values completely depends on the type of sample itself, filler type and test conditions [9,11,12]. We observe that the compounds S18, S23 have higher tear strength values than the others. This behavior could be explained by the strain crystallization property in the mentioned compounds.

Elasticity and wear

As we observe in Fig. 6, in the almost all cases, a higher value of the elasticity is confirmed by a lower wear. These results were predictable taking into account that a low elasticity could be a result of regularity of the polymer chains and vice versa.

The effect of accelerated aging

Generally, an increase of modulus 300% and stress at break and a decrease of strain at break were observed (see Tables 2 and 3). This represents an improvement of some physical-mechanical properties of the obtained thermoplastic vulcanizates at high temperature. This behavior should be explained as follows: at high temperature, a physical interaction between many of vulcanized rubber particles takes place, this resulting in a network of vulcanized elastomer [13]. Also, the substantial change on most of tensile properties may 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 to be used at high temperature.

Table 2. The effect of aging on the physical-mechanical properties of some thermoplastic vulcanizates

Physical-mechanical parameter	Symbol of polymer blend									
	S2		S8		S13		S18		S23	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
°Shore A Hardness	95	95	95	96	95	94	96	95	96	96
Elasticity, %	32	30	30	28	30	29	30	30	28	34
Modulus 300%	8.5	10.7	9	10.8	8.6	11.8	9.5	10.4	9.7	10.4
Tensile strength, N/mm ²	13	19.3	9.7	18.7	14	19	15	18.7	16	19
Strain at break, %	620	553	647	567	587	520	580	560	600	580
Tear strength, N/mm	98	96	101	92.5	104	98.5	106	96.5	106.5	105

Table 3. The effect of aging on the physical-mechanical properties of some thermoplastic vulcanizates

Physical-mechanical parameter	Symbol of polymer blend									
	S3		S9		S14		S19		S24	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
°Shore A Hardness	96	94	95	95	96	94	96	96	96	96
Elasticity, %	29	28	29	32	30	30	28	28	26	28
Modulus 300%	8.4	10.3	9	10.8	9.3	15.7	9.7	12.1	9.1	10.2
Tensile strength, N/mm ²	13.2	19.3	12.9	18.4	12.6	17.4	12.8	18.8	15.7	18.5
Strain at break, %	687	573	547	540	607	520	647	547	707	600
Tear strength, N/mm	94.5	94	98.5	96	99.5	88	103	77.5	99.5	88

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

ATR-FTIR spectra

The Attenuated total reflectance-Fourier Transform IR (ATR-FTIR) method was chosen for spectral characterization of the prepared polymer blends. This, because the mentioned

technique is of considerable value when studying physical properties of materials known as difficult samples such as polymer composites [14]. The ATR-FTIR technique allows the analysis of specimens with minimum sample preparation without solvent casting, grinding or pressing, as in the case in the transmission experiments.

Taking into account that the IR radiation penetrates into the sample a few nanometers depth, it must be précised that the information obtained is characteristic for the surface of the sample and the great advantage of using ATR technique is that no sample preparation was required. The ATR-FTIR spectra recorded for the studied polymer blends gave us the following informations:

1. All the investigated samples has the specific strong bands in their IR spectra near 2925 and 2853 cm^{-1} , which are due to the asymmetric and symmetric stretching frequency of the C-H group (which stems from $-\text{CH}_2-$ bonds in EPDM and HDPE polymers), a medium band located at $1430\text{-}1470\text{ cm}^{-1}$, attributed to deformation frequency of the same methylene groups and a weak peak at 720 cm^{-1} (also, for $-\text{CH}_2$).
2. No absorption bands were detected in the range $4000\text{-}3200\text{ cm}^{-1}$ for the samples S18, S23 and very weak signals for the samples S19, S24 (see Fig. 7a and 8a). The vibrations responsible for bands in this region are O-H and N-H stretching and are characteristic IR signals of primary and secondary amines, organic acids and phenols.

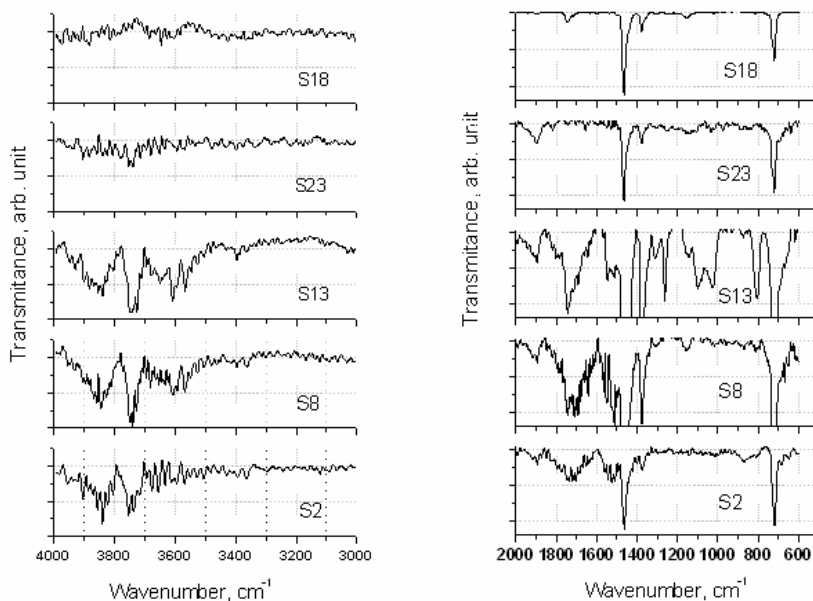


Fig. 7 a, b IR Spectra of some polymer blends

Considering these spectral informations, we assume that the activator (Stearic acid) and the antioxidant (Irganox 1010) are completely incorporated in the polymer blends S18 and S23 and almost complete in samples S19 and S23.

3. The same assumption should be considered in the case of the other polymer additives. Thus, the C=O group of saturated aliphatic carboxylic acids absorbs very strong in the

region $1740\text{-}1700\text{ cm}^{-1}$. These bands are presented in the IR spectra recorded for almost all investigated samples, except the spectrum of sample S23. In the spectrum of S18, the mentioned absorption band is very weak. On the same context, the N-C=S groups, characteristic for the cure agents as thiazoles (i.e., M) and sulphenamides (i.e. CZ), give IR absorption bands in the regions $1570\text{-}1395\text{ cm}^{-1}$, $1420\text{-}1266\text{ cm}^{-1}$ and a weak band at $1140\text{-}940\text{ cm}^{-1}$. The two mentioned bands, with variable intensities are present in almost all spectra, except that of S23 and S18. So, the absence in the spectra of these samples of the spectral bands attributed to the polymer additives, should be correlated with their good incorporation in the mentioned blends (see Fig. 7*b* and 8*b*).

We mention that the spectra in Figs. 7*a,b* and 8*a,b* are enlarged twenty times as against the recorded spectra.

The assignment of the IR bands was carried out according to literature data [15].

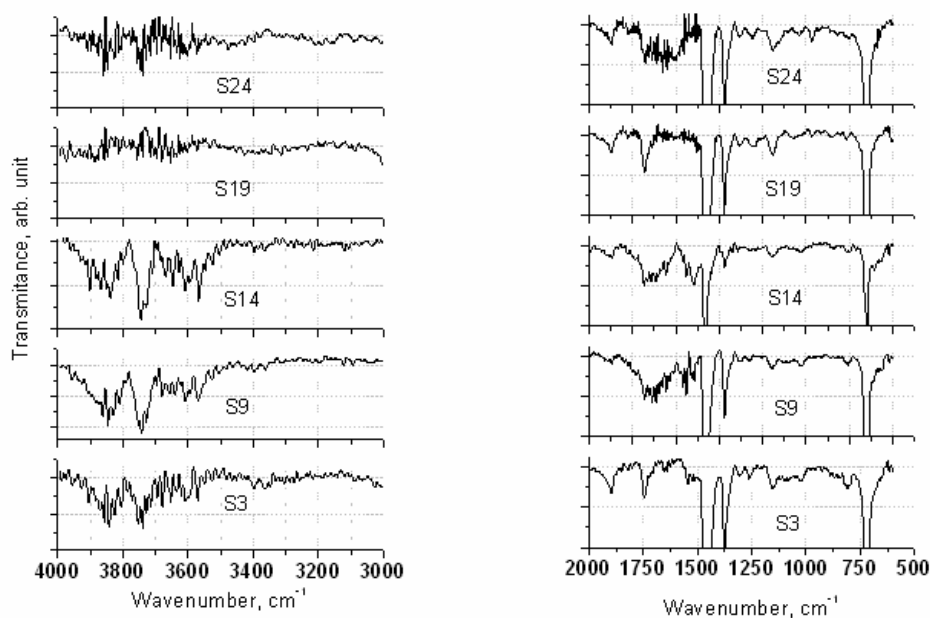


Fig. 8 a,b IR Spectra of some polymer blends

Conclusion

The overall results can be considered important. The optimum values of the main physical-mechanical parameters, characteristic for thermoplastic vulcanizates (high values of °Shore A hardness, 300% modulus, stress at break, tear strength and low values of strain at break, elasticity), were obtained in the case of semi-EV and EV systems S18 and S23 respectively. So, by using as cure agents sulfur and the two cure agents M and TH (in the ratio cure accelerators/S = 1.85, in the case of sample S18 and 6.34, in the case of sample S23), we

have obtained the best thermoplastic vulcanizates. This was confirmed both by the ATR-FTIR analysis and physical-mechanical tests.

Further research

In a continuation of these experiments, many other thermoplastic vulcanizates are in work and they will be analyzed and proposed for industrial applications.

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