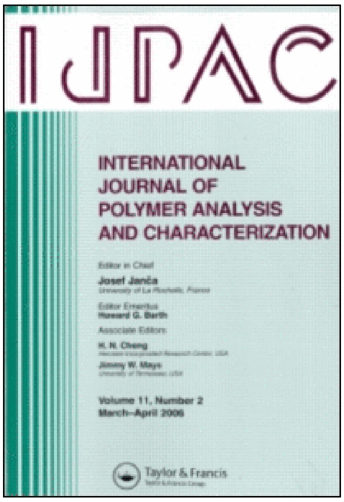


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Composites of High-Density Polyethylene-Elastomer: Analysis by Physico-mechanical Tests and ATR-FTIR Spectrometry

Zenovia Moldovan[a]; Florica Ionescu[b]; Ioana Vasilescu[c]; Simona Liţescu[a]; Laurenţia Alexandrescu[b]
[a] Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest, Bucharest, Romania [b] Research Development National Institute for Textile andLeather—Division Leather and Footwear Research Institute, Bucharest, Romania [c] Department of Analytical Chemistry, Faculty of Chemistry, University "Politehnica" of Bucharest, Bucharest, Romania

To cite this Article Moldovan, Zenovia , Ionescu, Florica , Vasilescu, Ioana , Liţescu, Simona and Alexandrescu, Laurenţia(2009) 'Composites of High-Density Polyethylene-Elastomer: Analysis by Physico-mechanical Tests and ATR-FTIR Spectrometry', International Journal of Polymer Analysis and Characterization, 14: 2, 102 — 114

To link to this Article: DOI: 10.1080/10236660802596664

URL: http://dx.doi.org/10.1080/10236660802596664

International Journal of Polymer Anal. Charact., 14: 102–114, 2009

ISSN: 1023-666X print
DOI: 10.1080/10236660802596664

Composites of High-Density Polyethylene-Elastomer: Analysis by Physico-mechanical Tests and ATR-FTIR Spectrometry

Zenovia Moldovan,[1] Florica Ionescu,[2] Ioana Vasilescu,[3] Simona Liţescu,[1] and Laurenţia Alexandrescu[2]
[1]Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest, Bucharest, Romania
[2]Research Development National Institute for Textile and Leather—Division Leather and Footwear Research Institute, Bucharest, Romania
[3]Department of Analytical Chemistry, Faculty of Chemistry, University "Politehnica" of Bucharest, Bucharest, Romania

Abstract: 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). These blends were obtained in the presence of binary sulfur-free accelerator systems. One of the two components of these energetically active systems was tetramethylthiuram disulfide (TH) and the second was one of the following cure agents: 2-mercaptobenzothiazole (M); N-cyclohexyl benzothiazole-2-sulfenamide (CZ) or 2,2′-dithiobenzothiazole (DM). These properties were correlated with the ATR-FTIR spectra. The samples containing as cure system TH + DM in the weighed ratio 2:1 was found to exhibit better properties, especially tensile strength, modulus 300%, and tear strength.

Submitted 12 August 2008; accepted 14 October 2008.

This work was performed within the framework of the National Program CEEX-Matnantech, Project no. 88/2006.

Correspondence: Zenovia Moldovan, Dept. of Analytical Chemistry, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Blvd., 030018, Sect. 3 – Bucharest, Romania. E-mail: z_moldovan@yahoo.com

Keywords: ATR-FTIR; HDPE-EPDM; Mechanical properties; Thermoplastic vulcanizates

INTRODUCTION

Thermoplastic elastomers (TPEs) are a category of materials prepared by blending rubber component with polyolefin. Research on TPEs based on rubber thermoplastic composites has been on two classes. One consists of simple blends and is commonly designated as thermoplastic elastomeric olefins (TEO).[1] In the other class, the rubber phase is dynamically vulcanized, giving rise to a thermoplastic vulcanizate (TPV) or dynamic vulcanizate (DV).[2] TPVs are characterized by the presence of finely dispersed cross-linked rubber particles distributed in a continuous thermoplastic matrix.[3–5] If the rubber particles are sufficiently vulcanized, the physical and chemical properties of the blend are generally improved. The thermoplastic vulcanizates present improved physical and chemical properties, such as higher values of Shore "A" hardness, modulus 300%, stress at break, tear strength and low value of strain at break, improved high-temperature utility, greater stability of phase morphology in the melt, more reliable thermoplastic processing, and greater resistance to attack by fluids, e.g., hot oils and alkaline and acid solutions.

Many studies have been focused on microstructured polymer blends obtained by melt cross-linking with native sulfur-free systems.[6] As related in the cited review, the use of binary accelerator systems is an aspect of vulcanization that has been generating an increased interest in recent years. A number of popular accelerator combinations have been investigated and found mutual activation in many of them. The synergistic activity of two or more accelerators arises from the interaction of the accelerators to form new intermediate compounds that again actively take part in the vulcanization reaction leading to enhancement of cross-link density and the rate of vulcanization reaction. The aim of our study was to investigate some thermoplastic vulcanizates based on high-density polyethylene (HDPE)/ethylene propylene diene terpolymer (EPDM) blends and containing binary systems of energetically active accelerators as cure agents. The optimum formulation (deduced from the resulting physico-mechanical properties) was used to prepare a series of blends under different technological conditions. Also, a correlation between their mechanical properties and IR spectra (obtained by applying the ATR technique) was proposed. A correlation between ATR-FTIR spectra and physico-mechanical properties of the obtained thermoplastic elastomers was proposed.

EXPERIMENTAL SECTION

Materials

The two polymers used were ethylene propylene diene terpolymer (EPDM elastomer, Nordell IP 3745P, DuPont) and high-density polyethylene (HDPE B084, Petro-Midia, Romania), in the ratio 1:1 by weight.

In addition to the polymers, the other ingredients were: cure accelerators (tetramethylthiuram disulfide (TH), 2-mercaptobenzothiazole (M), diphenylguanidine (D), 2,2′-dithiobenzothiazole (DM)), activators (zinc oxide, stearic acid), and antioxidants (di-lauril-orto-dipropionate (Irganox 1010), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ)).

Apparatus

Apparatus for Physico-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 $500 \pm 5\,\text{mm/min}$. Hardness of the samples was measured using a Shore type "A" Durometer (Zwik Model) according to ASTM D412-98.

Apparatus for FT-IR Measurements

Attenuated total reflectance-Fourier transform-infrared (ATR-FTIR) measurements were run with a Bruker instrument (model Tensor 27), in the following conditions: wave number range: $600–4000\,\text{cm}^{-1}$; aperture setting: 6 mm; scanner velocity: 2.2 kHz; background scan time: 32 s; sample scan time: 32 s; resolution: $6\,\text{cm}^{-1}$; beam splitter: KBr; angle of incident radiation: 45°. After recording, the ATR-FTIR spectra were converted into transmission FT-IR spectra. The plate samples (6×6 mm) were simply posed on the sampling stage, in intimate contact with the optical element, a hemicylindrical prism of SeZn (called the internal reflection element (IRE)). The incident radiation arrives on the sample with a certain angle (usually, between 30° and 60°) to the normal of the sample plane, and the reflected beam is collected by a mirror that focuses the reflected radiation onto the detector.

Procedure

Preparation of Polymer Blends

The blends were prepared by melt-mixing the ingredients, the two polymers (EPDM and HDPE) and the additives, in a laboratory cam mixer (Brabender Plasti-Corder PLE-60), at 180°C for about 7–8 min. A constant rotor (cam type) speed of 80 rpm was applied. Finally, once homogeneous mixing was assured, 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 thickness. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 h of storage at room temperature. All experiments were made at room temperature. Fifteen compositions of EPDM/HDPE blends were prepared by using various systems of accelerators in different ratios.

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.

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 formulas. All polymer samples have the same ratios (parts by weight) EPDM:HDPE:ZnO:stearic acid:TMQ: Irganox 1010 = 50:50:5:0.4:1:1 and different ratios of cure agents. Various cure systems are given in Table I.

Shore "A" Durometer Hardness

The value of a 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 can be seen in Figure 1, the values of this parameter were not significantly different for all investigated compounds; the loading with cure agents and the presence of HDPE give a great deal of hardness to the cured compounds.

Table I. Energetically active systems of accelerators in formulation of some microstructured polymer blends (parts by weight)

Binary cure system	Cure agents			
	TH	CZ	M	DM
AB1	2	1		
AB2	1	1		
AB3	0.5	0.5		
AB4	2		1	
AB5	1		1	
AB6	0.5		0.5	
AB7	2			1
AB8	1			1
AB9	0.5			0.5

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 cross-links, such as chain entanglements.[5] As shown in Figure 2, the value of modulus at 300% is higher for compounds AB1, AB4, and AB7, for which the ratio (parts by weight) of the two accelerators is 2:1. The stress at 300%

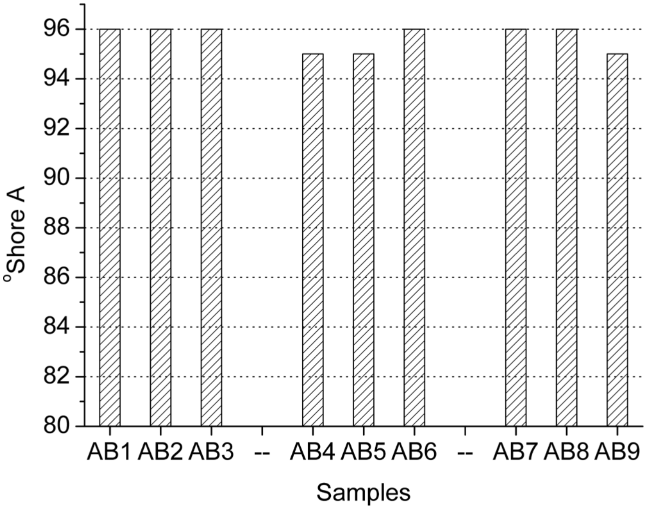


Figure 1. Shore "A" hardness.

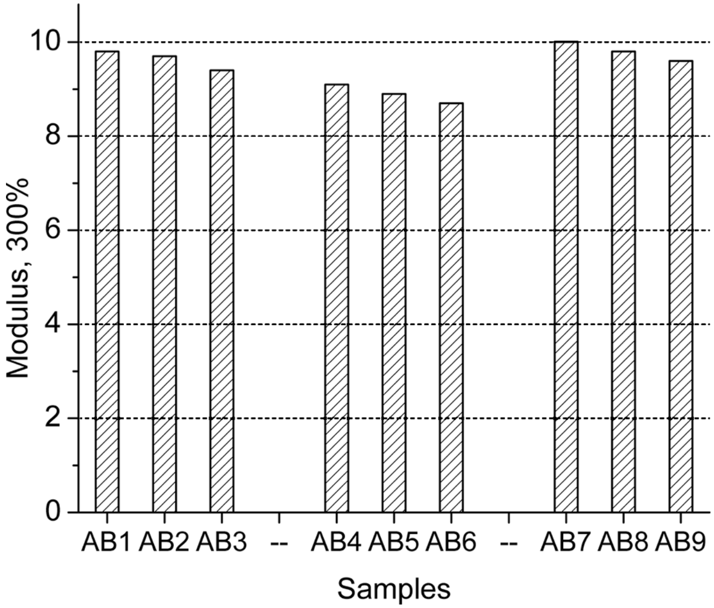


Figure 2. Stress at 300% strain (modulus).

strain reached the highest value when the system of cure accelerators contained TH and DM. The stress-at-break values for all polymer composites are shown in Figure 3. The highest tensile strength corresponds to the compounds AB1, AB4, and AB7 (the first ones of each of the three series of the investigated samples), with a maximum value in the case of sample AB7. As the literature data reported, the tensile strength depends on the compatibility of EPDM phase and HDPE phase of TPV,[7] which is evident in the case of the mentioned samples. The other compounds (especially AB3, AB5, and AB9) showed lower tensile strength values. This suggests that the use of the two accelerators of the cure system in the ratios (parts by weight) 1/1 and 0.5/0.5 did not hinder the strain crystallization behavior of the last mentioned samples. The cure conditions obtained by using the two accelerators in the ratio 2:1 (parts by weight) always result in higher tensile values (especially by using TH+DM as binary cure system).

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 extensibility of

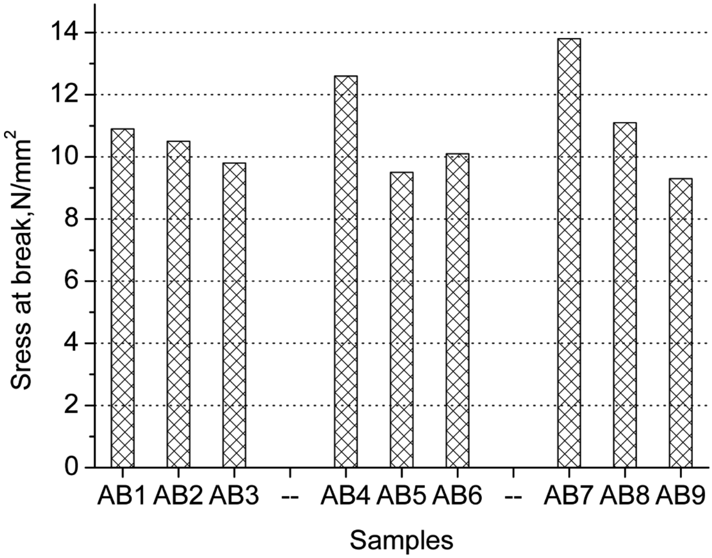


Figure 3. Stress at break, N/mm^2.

the polymer blend decreases with the increase of cross-linking.[8] At the same time, a high cross-link makes the compound stiff, and it loses its extensibility and strength (which is confirmed from its elongation, % value).

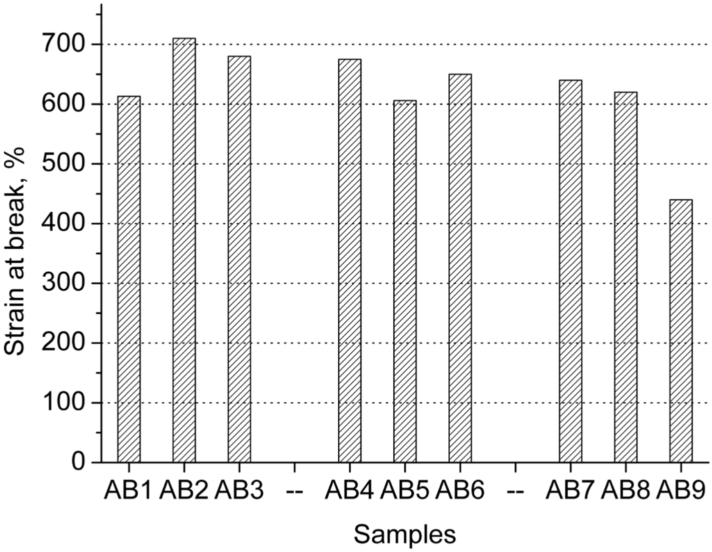


Figure 4. Strain at break, %.

As we observe in Figure 4, the compounds AB2, AB3, and AB4 have higher values of extensibility. On the other hand, the highly cross-linked compounds cannot crystallize easily because of the immobility of the network structure. Thus, too many cross-link junctions will hinder the structural regularity needed for the crystallization. This seems to be the case of samples AB1, AB5, and especially AB9, which have the lower values of elongation. Some cross-linking could be beneficial in terms of providing the mobility to align the chains upon deformation. We assume that this behavior should be attributed to the other samples, such as AB6, AB7, and AB8, that have moderate values of strain at break.

Tear Behavior

The literature data reported that tear strength values completely depend on the type of sample itself, filler type, and test conditions.[8,9] The tear strength values for the compounded polymer blends are presented in Figure 5. We observe that the compounds AB7 and AB9 have higher tear strength values than the others. This behavior could be explained by the strain crystallization property in the mentioned compounds.

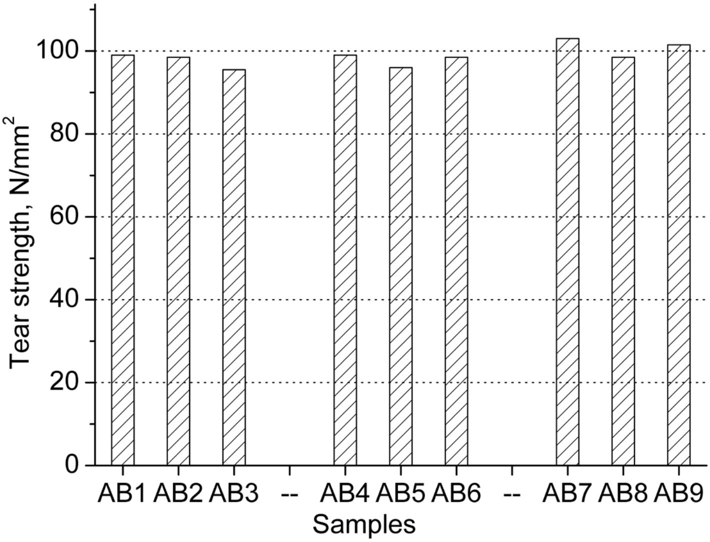


Figure 5. Tear strength, N/mm^2.

Table II. Different technological procedures applied to compounds having the formulation of sample AB7

Symbol of polymer blend	Constant parameter Rotor (cam type) speed, rpm	Variable parameter Time on curing level, min
AB7	80	1
AB7_T1		2
AB7_T2		3

	Time on curing level, min	Rotor (cam type) speed, rpm
AB7	1	80
AB7_R2		100
AB7_R3		120

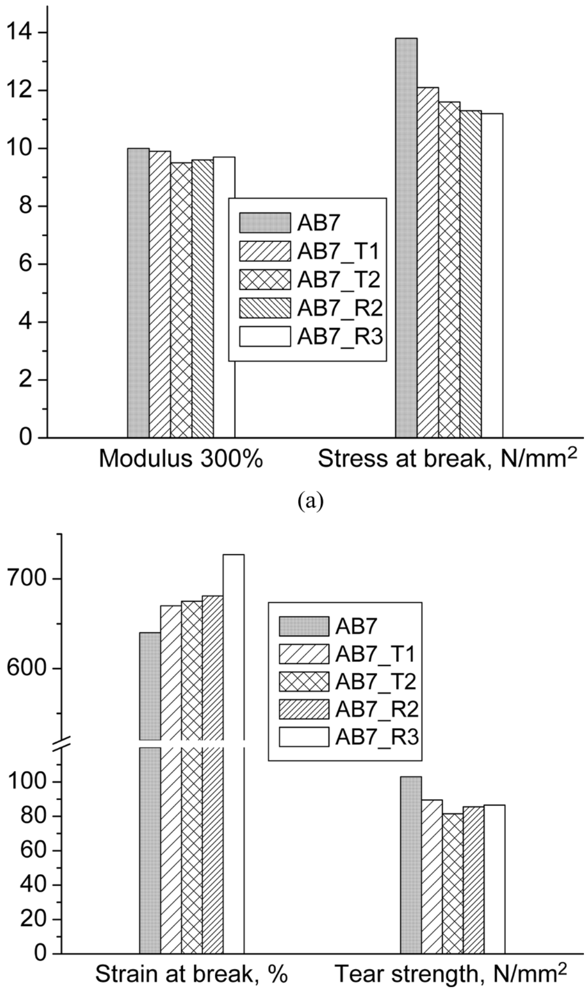
Effect of Technological Conditions

On the basis of the obtained results presented above, we have found that sample AB7 seems to have the optimum values of almost all physico-mechanical properties. For this reason, using the same formulation of sample AB7, different technological procedures were applied, as depicted in Table II.

The comparative results of the physico-mechanical properties of the samples described in Table II are illustrated in Figure 6. The optimal values of tear strength, stress at break, modulus 300%, and strain at break correspond to sample AB7 (obtained by applying a rotor speed of 80 rpm and one minute on curing level).

Effect of Accelerated Aging

The samples AB7 obtained under different technological conditions were tested after aging. The comparative results of the physico-mechanical properties are presented in Table III. An increase of modulus 300% and stress at break and a decrease of strain at break were observed, which represents an improvement of some physico-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 the vulcanized rubber particles takes place, and it results in a network of vulcanized elastomer.[10] Consequently, the substantial change of the most of tensile properties may be an indication of a post-curing process. The effect of the accelerated aging shows that the prepared thermoplastic vulcanizates are good candidates for industrial applications to be used at high temperature.



(a)

(b)

Figure 6. Physico-mechanical properties of sample AB7 obtained in different technological conditions.

ATR-FTIR Spectra

The ATR-FTIR method was chosen for the spectral characterization of the mentioned polymer blends. This technique is of considerable value when studying physical properties of the materials known as difficult samples, such as polymer composites.[11] The great advantage of using the ATR technique is that no sample preparation is required. Taking into

Table III. Effect of accelerated aging on the physico-mechanical properties of thermoplastic vulcanizates containing as energetically active systems of accelerators TH+DM (in the ratio 2:1, parts by weight) and obtained in different technological conditions

Physico-mechanical parameter	Symbol of polymer blend									
	AB7		AB7_T1		AB7_T2		AB7_R2		AB7_R3	
	NC	AA	NC	AA	NC	AA	NC	AA	NC	AA
Shore "A" hardness	96	96	96	96	96	95	96	97	96	96
Modulus 300%	10.0	11.0	9.9	10.5	9.5	10.0	9.6	10.8	9.7	10.0
Stress at break, N/mm^2	13.8	16.3	12.1	14.8	11.6	17.1	11.3	15.9	11.2	18.2
Strain at break, %	640	600	670	585	675	607	681	611	727	660
Tear strength, N/mm	103	111.5	89.5	92.5	81.5	98.5	85.5	96.5	86.5	105

NC: normal conditions, AA: after accelerated aging.

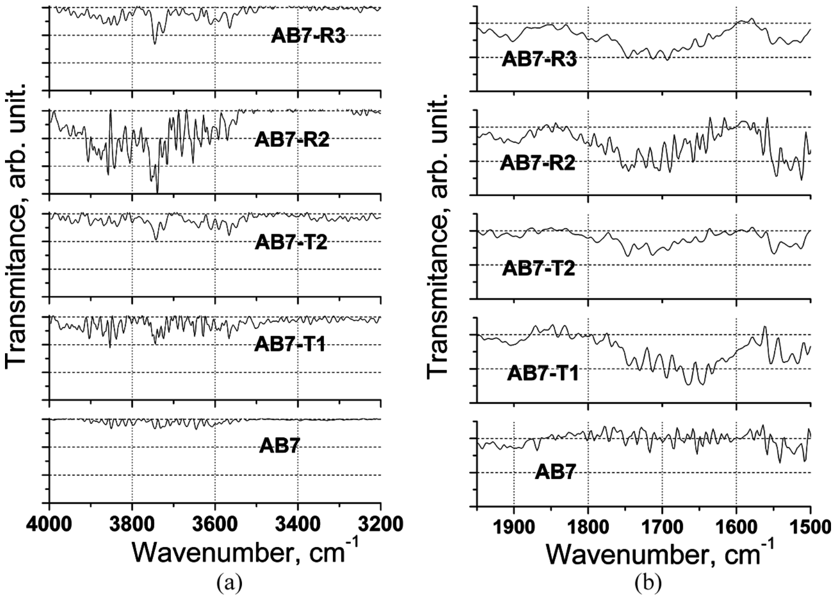
account that the IR radiation penetrates into the sample to a few nanometers' depth, it must be assumed that the information obtained is characteristic for the surface of the sample. As a matter of fact, in the case of polymer blends characterized by a good incorporation of the additives, the presence of the IR characteristic peaks of additives in the surface spectra cannot be detected.[12] 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 sample AB7 and weak signals for samples AB7_T1 and AB7_T2 (see Figure 7(a)). The vibrations responsible for bands in this region are O-H and N-H stretching and are characteristic IR signals of the primary and secondary amines, organic acids, and phenols (these bands could be attributed to stearic acid, Irganox 1010, Flektol H, and TH).

The C = O group of the saturated aliphatic carboxylic acids absorbs at around 1740 cm^{-1} . This band is present in the IR spectra recorded for almost all investigated samples, except the spectrum of sample AB7 (see Figure 7(b)).

Thus, the absorption bands in the region 1870–1550 cm^{-1} could be assigned to C = O stretching vibration (characteristic for amides, like DM, and carboxylic acids, like stearic acid).

In the same context, the N-C = S groups, characteristic for the cure agents such as thiazoles (i.e., DM), give an absorption band in the region 1570–1500 cm^{-1}. This band, with variable intensities, is present in almost



(a) (b)

Figure 7. IR spectra of sample AB7 (by applying ATR technique) obtained in different technological conditions.

all spectra, except that of AB7. Thus, the absence of the spectral bands attributed to the polymer additives in the spectra of this sample should be correlated with their good incorporation in the mentioned blend.

On the basis of this spectral information, we assume that the activator (stearic acid), the antioxidant (Irganox 1010), and the cure accelerators are completely incorporated in the polymer blend AB7, because in the spectrum of this sample (recorded by the ATR technique) the bands characteristic for its corresponding polymer additives do not occur. The assignment of the IR bands was carried out according to literature data.[13]

CONCLUSION

The optimum values of the main physico-mechanical parameters, characteristic for thermoplastic vulcanizates (high values of Shore "A" hardness, 300% modulus, stress at break, tear strength, and low value of strain at break), were seen in the case of sample AB7, obtained by applying a rotor speed of 80 rpm and one minute on curing level. By using the two accelerators TH and DM as cure agents (in the ratio = 2:1, parts by weight), under the mentioned technological conditions, we obtained the best thermoplastic vulcanizate. Both physico-mechanical and ATR-FTIR techniques allow understanding the structure of the prepared chemical microstructured systems. The compatibility of the polymer phases in the case of sample AB7 was confirmed by its physico-mechanical properties and correlated with IR spectra.

REFERENCES

[1] American Society for Testing and Materials. ASTM D 5593-99: Standard Classification for Thermoplastic Elastomers-Olefinic (TEO).

[2] American Society for Testing and Materials. ASTM D 5046-98: Standard specification for Fully Crosslinked Elastomeric Alloys.

[3] Legge, N. R., G. Holden, and H. E. Schroeder, ed. (1987). *Thermoplastic Elastomers: A Comprehensive Review*. Munich: Hanser Publishers.

[4] Jha, A., and K. Bhowmick. (1997). Interaction on mechanical and dynamic mechanical thermal properties. *Rubber Chem. Technol.* **70**, 798–814.

[5] Patel, J. D., M. Maiti, K. Naskar, and A. K. Bhowmick. (2005). Novel styrenic thermoplastic elastomers from blends with special reference to compatibilization and dynamic vulcanization. *Rubber Chem. Technol.* **78**, 893–909.

[6] Santhosh, A. A., J. Kurauvilla, and T. Sabu. (2005). Recent developments in crosslinking of elastomers. *Rubber Chem. Technol.* **78**, 458–488.

[7] Mishra, J. K., and I. M. Chang-Sik Ha. (2005). Structure-property relationship of thermoplastic vulcanizate (PV)/layered silicate nanocomposites prepared using maleic anhydride modified polypropylene as compatibilizer. *Rubber Chem. Technol.* **78**, 42–53.

[8] Hamed, G. R., and N. Rattanasom. (2002). Effect of crosslink density on cut growth in gum natural rubber vulcanizates. *Rubber Chem. Technol.* **75**, 323–332.

[9] De, D., and A. N. Gent. (1996). Tear strength of carbon-black-filled compounds. *Rubber Chem. Technol.* **69**, 834–850.

[10] Coran, A. Y., and R. P. Patel. (1996). Thermoplastic elastomers based on dynamically vulcanized elastomer-thermoplastic blends. In *Thermoplastic Elastomers*, 2nd ed., G. Holden, N. R. Legge, R. P. Quirk, and H. E. Schroeder, ed., ch. 7, 153–190. Munich: Hanser/Gardner.

[11] Harrick, N. J. (1987). *Internal Reflection Spectroscopy*. Ossining, N.Y.: Harrick Scientific Corp.

[12] Jawhari, T., L. Quintanilla, and J. M. Pastor. (1994). A comparison of specular reflection and PA-FTIR techniques in the analysis of annealed injection-molded polyamide 6,6. *J. Appl. Polym. Sci.* **51**, 463–471.

[13] Socrates, G. (2001). *Infrared and Raman Characteristics Group Frequencies: Tables and Charts*. New York: John Wiley.