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STUDIES ON OBTAINING IONIC THERMOPLASTIC ELASTOMERS BASED ON MALEINIZED STYRENE-BUTADIENE BLOCK-COPOLYMERS

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ABSTRACT. This article presents the process of obtaining ionic thermoplastic elastomers based on maleinized styrene-butadiene block-copolymers (SBS-g-AM) by melt mixing. The following were studied influence of the amount of maleic anhydride, mixing time and degree of neutralization on physico-mechanical properties of blends based on SBS-g-AM rubber.

Keywords: *styrene-butadiene block copolymer, maleic anhydride, ionic thermoplastic elastomers, physico-mechanical properties*

INTRODUCTION

Styrene copolymers with diolefins such as: styrene-co-butadiene, random (SBR) and block (SBS) deserve similar industrial interest in the field of elastomers and thermoplastic elastomers and have been subjected to studies aimed at introducing functional groups, allowing a better interaction particularly with other polymers and inorganic fillers [1-2]. This can be done by modification of conventional polymers by grafting and graft-(co) polymerization techniques. Several researchers [3-7] have documented graft copolymerization reactions initiated by chemical treatment, photo-irradiation, high-energy radiation technique, etc. as a versatile means to modify polymers.

Maleic anhydride (AM) is a strong hydrophilic monomer. If it is grafted onto polymers they will carry a denser distribution of carbonyl or free carboxylic groups. These reactive groups can also serve as sites for further macromolecular reactions of copolymers and grafted polymers, especially for compatibilization of immiscible polymers and preparation of various reactive blends with higher engineering performance and controlled morphology and

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mechanical properties [8-9]. In the last decade, grafting of AM onto various thermoplastic polymers (predominantly polyolefins) and preparation of high performance engineering materials and nanocomposites by using reactive extruder systems and in situ compatibilization of polymer blends have been significantly developed, some results of which are employed in commercial applications [9].

The grafting of styrene-butadiene block copolymers with maleic anhydride occurs by radical mechanism. In literature are presented both the grafting mechanism and the influence of reaction conditions: concentration, structure, and position of the grafted anhydride, depending on the used method (solution, melt state and solid state), and the temperature, pressure, concentration, solvent, additive, etc. [10-11].

Iancu L. et al. [10] studied the functionalization reaction of the styrene-butadiene block copolymers with maleic anhydride was carried out in butyl acetate solution using 2, 2'-azo-bis-isobutyronitrile as initiator.

Passaglia et al. [12] studied the functionalization of polystyrene (PS) block in styrene-b-(ethylene-co-1-butene)-b-styrene (SEBS) triblock copolymer with AM and diethyl maleate (DEM). According to the authors, grafting of AM onto a-PS can be accomplished through a radical process, although the reaction mechanism is not clarity. The bulk functionalization of SEBS triblock copolymer with DEM or AM and dicumyl peroxide as initiator was carried out in a Brabender mixer. They established that the functionalization takes place with a very large preference at the aliphatic carbons of the polyolefin block. Moreover occurrence of degradation and chain extension reactions gives a functionalized product with a molecular weight distribution larger than 1.

A. Kurbanova et al. [13] have shown that functionalization of PS by grafting reaction can be carried out either via the polymer backbone in the case of radical initiators or through the side phenyl rings using cationic catalysts. They chemically modified PS with AM by use of certain cationic catalysts of Lewis acid type ($AlCl_3$, $TiCl_4$, $ZnCl_2$, $FeCl_3$, $SnCl_4$ etc.) in chloroform at 0-30°C.

Rocetti L and Banzi V [14] have shown that the grafting of maleic anhydride onto unsaturated olefinic polymers (such as ethylene-propylene-ethylidenen-1,3,-butadiene terpolymer etc.) can be carried out by mass polymerization, without encountering the above drawbacks, by allowing the reaction to take place in the presence of catalysts being compounds of metals of group VIII of the periodic system (in particular Rh and Ru), wherein the reaction mixture is heated at temperatures of from about 120°C to about 350°C.

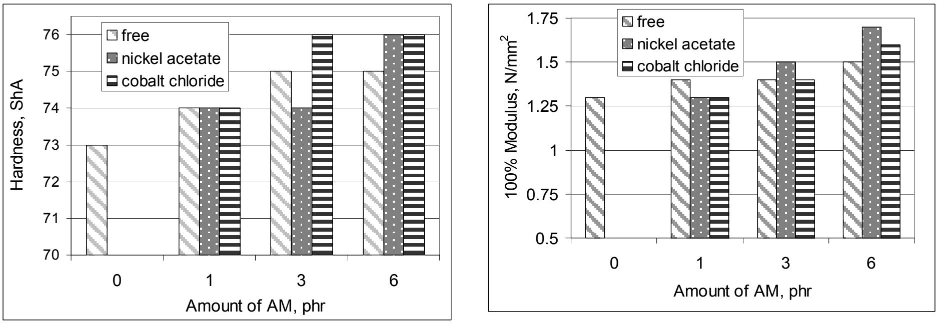
This article presents SBS maleinization by melt mixing the elastomer with AM in the presence of an additive/catalyst. SBS elastomers containing ionizable groups obtained were processed with a metal oxide - ZnO (which can react with the functional groups in the ionizable groups, thus yielding ionic ranges), filler, ionic plasticizer, antioxidants etc. in order to obtain ionic thermoplastic elastomer compounds. The following were studied: influence of the AM amount, of the type and amount of catalyst, and the mixing time after adding AM, on the physico and mechanical properties of blends. Also, the influence of the neutralization degree on physico-mechanical properties of blends based on SBS-g-AM rubber was studied.

RESULTS AND DISCUSSIONS

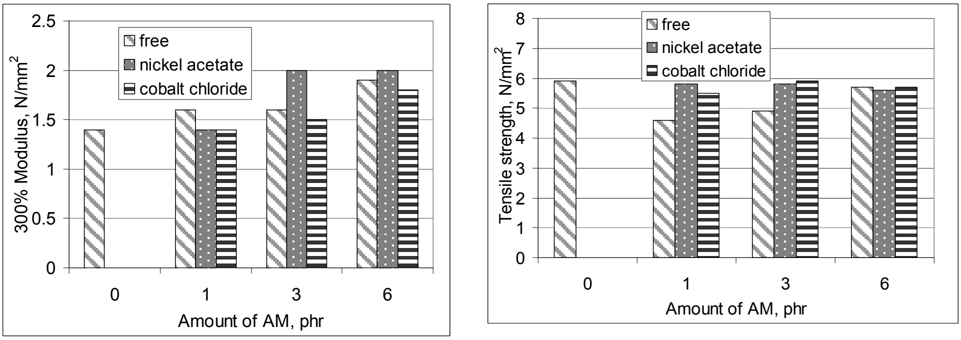
1. Influence of AM amount on the physico-mechanical properties

Figure 1 presents the effect of increasing the amount of AM on physico-mechanical properties of compounds based on SBS-g-AM. Mixing time after adding AM was 5’ and the amount of catalyst was 0.5 phr (parts to 100 parts rubber). It is noticed that upon increasing the amount of AM, hardness and modulus also increase, indicating the growth of ionic groups on the macromolecular chain. Due to the property of groups specific to maleic anhydride existing on the macromolecular chain of reacting with oxides of divalent metals (zinc oxide), ionic bonds form similar to sulphur bridges from vulcanized rubber. This ionic crosslinking has led to an improvement in the value of the module and hardness. Zinc oxide replaces sulphur and vulcanization agents in these blends [15]. Concomitantly, adding ionic groups in SBS leads to a decrease in tensile strength, elongation at break and tear strength. This is explained through the existence of polar bonds COO^- which repel each other, as well as through the change in the polymer structure due to the grafting reaction [10].

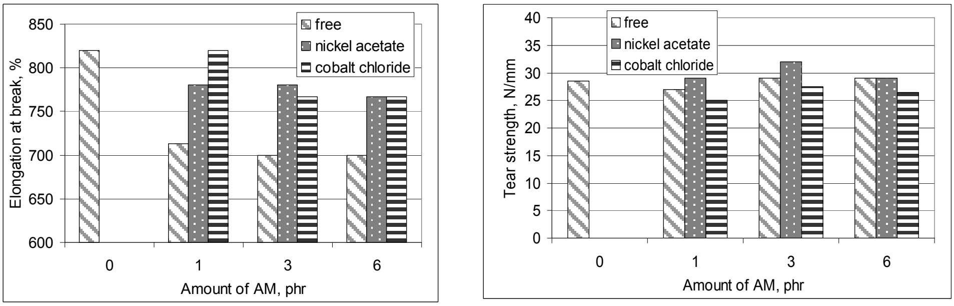
It is noticed that better properties are obtained for blends where additive/nickel acetate or cobalt chloride catalyst were used. As no significant differences of properties of mixtures containing 3 phr AM compared to those containing 6 phr AM were noticed, the next samples were processed using an amount of 3 phr AM.



(a) Hardness (b) 100% Modulus



(c) 300% Modulus (d) Tensile strength



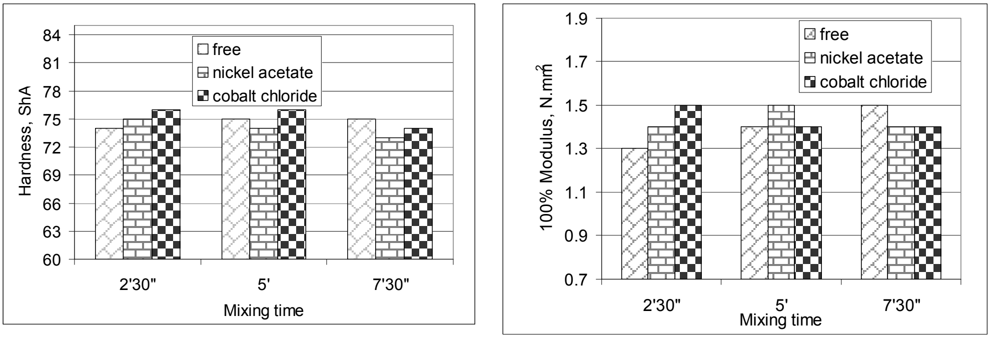
(e) Elongation at break (f) Tear strength

Figure 1. Influence of AM amount on physico-mechanical properties*

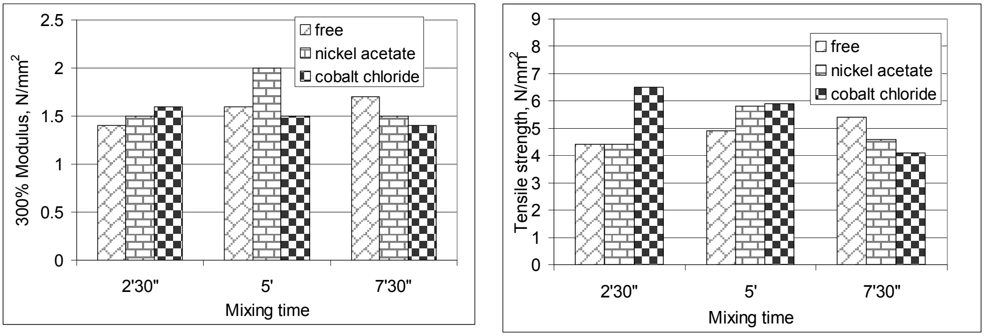
*The unit “**phr”** is “parts to 100 parts rubber” which is a weight measurement relative to the amount of rubber in the formulation.

2. Influence of mixing time after adding AM on the physico-mechanical properties

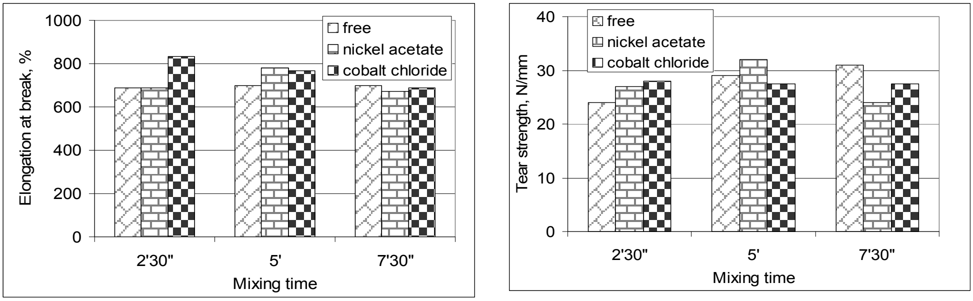
In order to determine the influence of mixing time after adding AM, blends were made in which 3 phr AM and 0.5 phr catalyst were added. In this case, better physico-mechanical properties are obtained for blends containing catalyst, particularly based on cobalt chloride, which, even after 2’30”, have led to blends with very good values for hardness, modulus, tensile strength and elongation at break. The best characteristics were obtained after mixing for 5’.



(a) Hardness (b) 100% Modulus



(c) 300% Modulus (d) Tensile strength



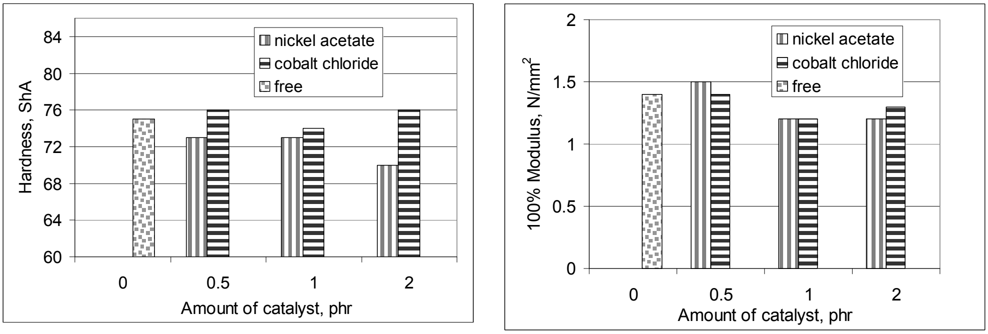
(e) Elongation at break (f) Tear strength

Figure 2. Influence of mixing time after adding AM on physico-mechnaical properties

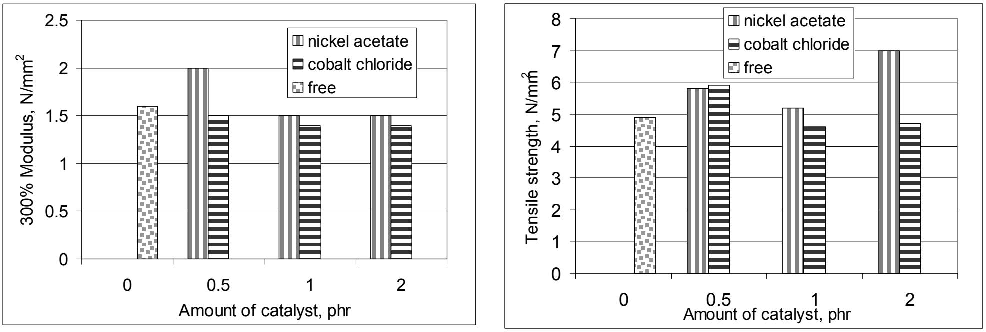
3.3. Influence of the catalyst amount on physico-mechanical properties

In order to determine the influence of catalyst amount on physico-mechanical properties, mixtures were made containing 3 phr AM, and the time after adding AM was 5’.

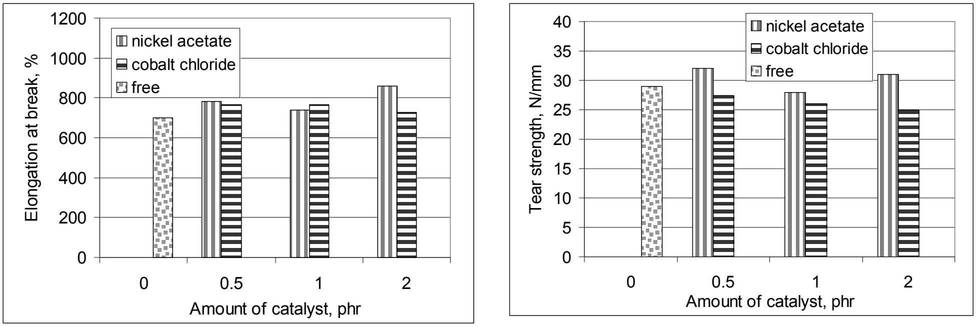
It can be noticed that, upon the significant increase of catalyst amount, no similar improvement of physico-mechanical properties occurs. Based on results presented in Figure 3 and in Figures 1 and 2, the mixture containing 0.5 phr cobalt chloride and 3 phr AM, mixing time 5’ after adding AM, was selected.



(a) Hardness (b) 100% Modulus



(c) 300% Modulus (d) Tensile strength



(e) Elongation at break (f) Tear strength

Figure 3. Influence of catalyst amount on physico-mechanical properties

3.4. Influence of the crosslinking degree on SBS-g-AM ionic thermoplastic elastomer characteristics

Table 1 presents formulations and characteristics for the polymer blends based on chemically unmodified SBS (M0 and M1) and blends where SBS elastomer was chemically modified by adding 3 phr AM in the presence of 0.5 phr cobalt chloride, mixing time after adding AM was 5'.

Comparing characteristics of blends where SBS is not modified (M0 and M1) with those having a similar composition, where SBS-g-AM was used (A0 and A2), it can be noticed that, as a result of the maleinization reaction, hardness decreased very much (by 10-13°ShA) and tensile strength and elongation at break also decreased. This can be due to the chemical modification of SBS through maleinization, which led to a change in the packing degree of macromolecules, changing the structure of the elastomer. This has also been reported by other researchers [10].

Analyzing the data in Table 1 it is noticed that upon adding ZnO in the blend containing chemically unmodified SBS (blend M0 compared to M1), no substantial change occurs in the physico-mechanical properties. In contrast, for blends containing SBS-g-AM (A0 compared to A1, A2, A3), it is noticed that upon increasing the amount of ZnO, hardness, 100% modulus and 300% modulus increase, while tensile strength and elongation at break increase up to a maximum and then decrease. This is due to ionic crosslinks forming between zinc ions and COO^- groups of SBS-g-AM, upon increasing the neutralization degree of ionic groups in SBS-g-AM [15].

Table 1. Formulations and characteristics for the polymer blends based on SBS and SBS-g-AM

Ingredients / Mixture symbol	M0	M1	A0	A1	A2	A3
SBS	100	100				
SBS-g-AM		**0**	100	100	100	**100**
ZnO		5		2	5	10
Stearine		0.5		0.2	0.5	1
Irganox 1010		0.5		0.5	0.5	0.5
Properties						
Hardness ,°ShA	70	69	57	59	59	61
100 % Modulus, N/mm^2	1.1	0.7	0.9	1	1	1.2
300 % Modulus, N/mm^2	1.3	1.2	1.3	1.9	2	**2**
Tensile strength, N/mm^2	8.7	8.2	4	4.5	6.4	4.9
Elongation at break, %	890	900	620	620	680	540

Samples M0 and A0 were processed in order to be subjected to FTIR spectrophotometric analyses according to the work method presented in chapter 2. FTIR spectra are presented in Figures 4 and 5. Analysis of these spectra shows that the band at 875.6 cm^{-1}, determined by the deformation vibration of CH bond in the aromatic ring, is more prominent for the SBS-g-AM spectrum and can indicate the fact that AM substituted a hydrogen atom in the meta position. The band at 1421 cm^{-1} highlights the existence of COOH group, namely vC=O and δOH coupled bonds. This band overlaps with the band specific to the vibration of δCH2 bond, as well as with the one specific to double bonds in the aromatic ring.

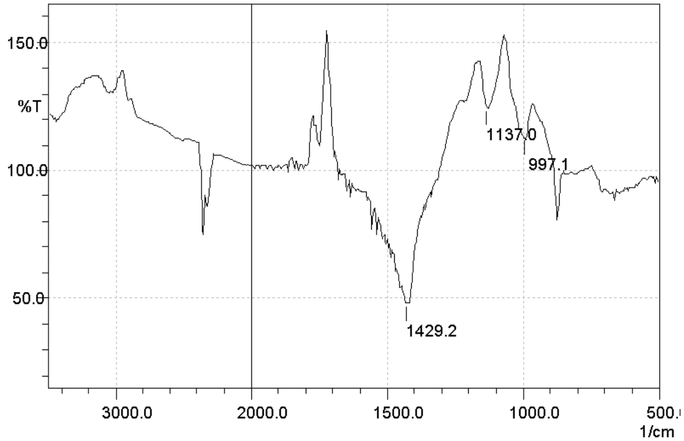


Figure 4. FT-IR spectra of styrene-butadiene block copolymer Calprene 484 (sample M0)

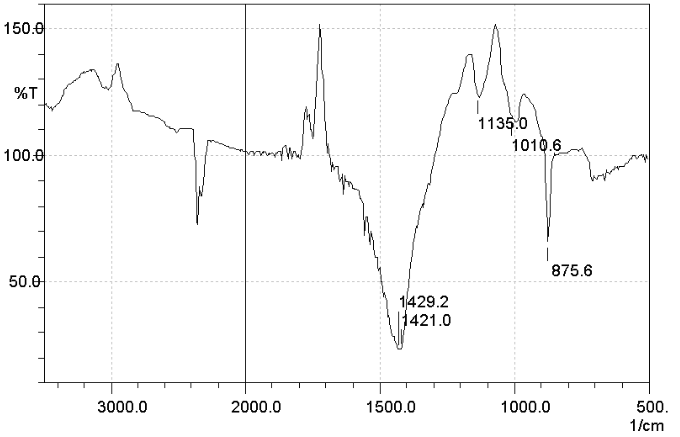


Figure 5. FT-IR spectra of maleinized styrene-butadiene block copolymer (sample A0)

CONCLUSIONS

As a result of the conducted study, it can be concluded that SBS was maleinized by melt mixing the elastomer with AM in the presence of an additive/catalyst. The influence of AM amount, of the type and amount of catalyst and of the mixing time after adding AM on the physico-mechanical properties of blends was studied and optimal working parameters were established in order to obtain desired characteristics.

The new types of thermoplastic elastomers can be processed by specific techniques for thermoplastic materials, thus removing the vulcanization stage involving high power expenditure and release of noxious products, improved characteristics of these materials can be assured.

The potential users of the new rubber materials will be economic operators processing rubber and plastics, footwear and car component manufactures etc.

EXPERIMENTAL

SBS maleinization was performed by melt mixing SBS with AM in the presence of an additive/catalyst. Mixing was performed in Plasticorder Brabender PLV 330 at 100 rpm and temperature of 180°C to allow the elastomer to melt. After elastomer melting, the catalyst was added, and then the maleic anhydride. We monitored the influence of AM amount, of the type/amount of catalyst and of the reaction time after adding AM on the physico-mechanical properties of ionic thermoplastic elastomer compounds obtained.

The following materials were used in the study to obtain SBS-g-AM:

1,3-Butadiene-styrene block polymer Calprene 484 (melt flow index at 190ºC, 5kg, 7.5 g/10’, volatile matter, 0.4%, oil, 31.5 %, total styrene (on polymer), 44 %, density 0.95 g/cm^3).

Two types of additives/catalysts were used: (a) *cobalt chloride hexahydratate* - $CoCl_2 \times 6H_2O$ - Lewis acids, molar mass 237,93 g/mol, density 1.924 g/cm^3, appearance - pink monoclinic crystals, soluble in: water, ethyl alcohol, diethyl ether, acetone. (b) *nickel acetate tetrahydrate* $(CH_3COO)_2Ni \times 4H_2O$, molar mass 248.86 g/mol, density 1.79 g/cm^3, appearance – green crystals.

Maleic anhydride - $C_2H_2(CO)_2O$, molar mass 98.06 g/mol, appearance - white crystals, density 1.48 g/cm^3, melting point 52.8ºC; boiling point 202ºC.

In order to analyze the efficiency of the method of SBS chemical modification (through maleinization) on the physico-mechanical properties, ionic thermoplastic elastomer compounds were developed using SBS elastomers chemically modified by grafting with maleic anhydride (SBS-g-AM).

They were obtained by adding: neutralizing agent of ionic groups - zinc oxide (zinc oxide content 99.2%, humidity 0.15%, free zinc 0.14%), stearophanic acid (titre fatty acids 59, mineral acids absence), ionic plasticizer- zinc stearate; (Zn content 11%, melting point 127°C), as active filler precipitated silica Ultrasil VN 30 and antioxidant Irganox 1010 - pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate. Blends were developed on Plasticorder Brabender PLV 30. The process variables were: temperature: 170°C and rotational speed: 100 rpm.

The blends were homogenized on an electrically heated laboratory roller mill. The optimum process variables were: temperature: 150-160°C and friction coefficient: 1:1.1. The distance between the rolls was of 2 mm for 1’, it decreased to 0.2 mm for 3’ and then increased to 2 mm for 1’ and the mixture was taken off the roller mill in a sheet.

Samples used in tests for physico-mechanical characterization were made by means of a laboratory electrical press at a temperature of 170°C and 150 MPa, pre-heating time 2', modeling time 5' and room temperature cooling time 2'.

Mechanical properties of samples were measured on a Schopper tensile tester with a nominal rate of the traverse of the moving grip of 460 mm/min. Modulus at 100% and 300% strain, tensile strength and elongation at break tests were carried out according to the conditions described in ISO 37/2012, on dumb-bell shaped specimens of Type 2. Tearing strength tests were carried out using angular test pieces (type II) according to SR EN 12771/2003. Hardness of materials was measured using the Shore A scale, by using a hardener tester according to ISO 7619-1/2011.

AM grafting on the SBS macromolecular chain was highlighted by FTIR spectroscopy. In order to do this: (a) the polymer was dissolved in toluene ($\varphi = 0.866$ g/cm^3) at room temperature (approximately 5 hours), (b) the polymer was precipitated with acetone ($\varphi = 0.790$ g/cm^3), (c) the precipitate was filtered and washed with acetone several times; (d) the precipitate was dried to eliminate traces of solvents and then used in FTIR spectroscopic analysis. A Schimadzu 8900 device was used for this, range: 4000 - 400 cm^{-1}, resolution 2 cm^{-1}.

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