Maleinized Linear Styrene-butadiene Block-copolymers

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This paper presents the maleinization study of linear styrene-butadiene block-copolymers carried out in solution by radical mechanism. The vinyl microstructure effect of the polybutadiene block on the kinetics reaction was established and the physical and mechanical properties were correlated with the maleinization degree of the elastomers.

Keywords: styrene-butadiene block-copolymers, maleic anhydride, functionalized block-copolymers

The styrene-butadiene block copolymers (SBS) with predominantly content of diene, show vulcanized rubber properties, at ambient temperature. This behaviour is the result of thermodynamic incompatibility between component blocks, achieving a segregation of dispersed polystyrene blocks, in the form as domains in continuous polybutadiene phase, thus ensuring physical crosslinking of the elastomer at ambient temperature. The styrene butadiene block copolymers show thermoplastics properties at temperature higher than the glass transition of polystyrene phase, so they can be processed in similar conditions to plastics [1-3]. These properties have allowed the use of elastomers in different plastics modification, especially for their poor impact strength improvement [4,-6].

In order to enhance the performance of block copolymers in polar plastics modification we consider the increasing of their compatibility degree, by introducing of polar groups in polydienic block, which is the continuous phase in direct contact with plastomers.

For increasing of SBS polarity post-polymerization modification is used, especially through polymer-analogous reactions like: grafting [7], epoxidation [8], sulphonation [9], halogenation [10], both in solution and by mechanical-chemical grafting directly into the extruder during the modification process [11, 12].

The maleinization is one of the frequently used processes in the modification of elastomers like: natural rubber [13], polyisoprene, polybutadiene, styrene-butadiene block copolymers [14], styrene-isoprene block copolymers [15-17] and in some plastomers functionalization (polystyrene, polyethylene, polypropylene [18, 19]).

The grafting of styrene-butadiene block copolymers with maleic anhydride occurs by radical mechanism [14, 20]. 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. [21].

The maleinized styrene-butadiene block copolymers used in the polyolefin composites improve the impact strength by compatibilizing effect.

Experimental part

The linear styrene-butadiene block copolymers were synthesized by anionic sequential polymerization of the monomers in solution. In order to obtain materials with improved properties SBS was chemical modified by introducing polar functional groups, through radical addition reactions which occur preponderantly at the vinyl double bonds [22].

Two types of linear block copolymers SBS with different vinyl microstructure were used in the maleinization study, whose properties are shown in table 1.

The functionalization reaction of the styrene-butadiene block copolymers with maleic anhydride (MAH) was carried out in butyl acetate solution using 2, 2'-azo-bis-isobutyronitrile (AIBN) as initiator. The plant consisted in a reactor with three necks, equipped with thermometer and stirrer, immersed in an ultrasonic bath for keeping the temperature constant.

The maleinization process in solution was preferable to mechanical-chemical modification because the secondary reactions that could disturb the proper correlations between the maleinization degree and the properties of modified block copolymers can be avoided.

The following parameters: reaction time, anhydride and initiator concentration were studied in the chemical modification of block copolymers with maleic anhydride.

The block-copolymers were dissolved in butyl acetate, at room temperature, then maleic anhydride was added under stirring and when reaction mixture was heated at 75 °C, the initiator (AIBN) was added under stirring and the temperature was kept constant for maximum 8 h.

Table 1
PHYSICO-MECHANICAL PROPERTIES OF STYRENE-BUTADIENE BLOCK COPOLYMERS

Property	SBS 10	SBS 35
Polystyrene content, %	30	29.5
Total molecular weight, g/mol	97,400	152,000
Vinyl content of polybutadiene, wih respect to the polybutadiene block, %	10	35
Tensile strength, MPa	12,8	14.1
Elongation at break, %	680	440
Hardness, °Sh A	66	70

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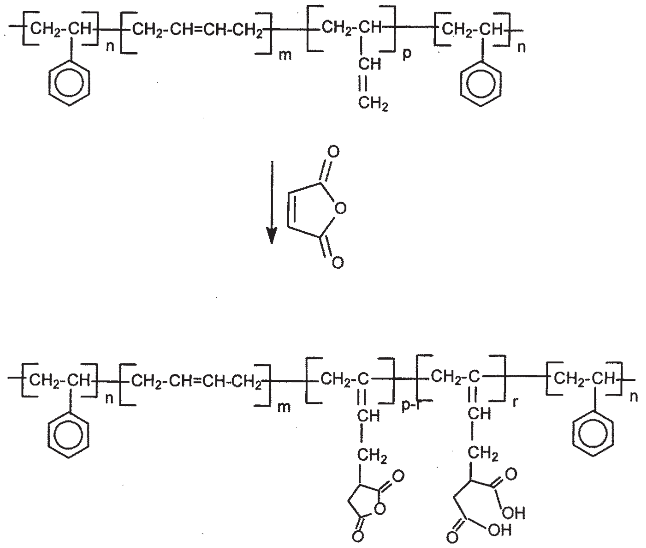

Fig. 1. The reaction scheme of SBS maleinization

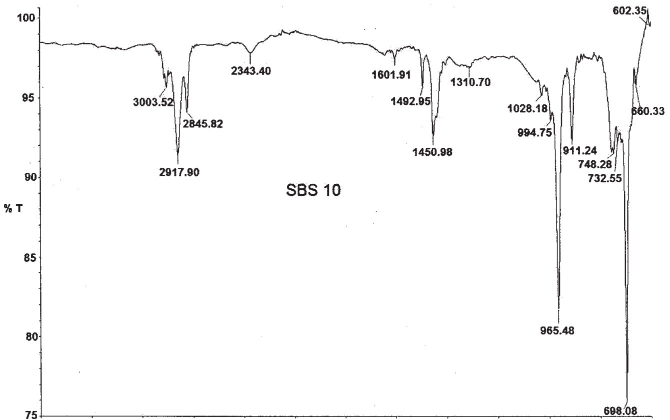

Fig. 2. FT-IR spectra of styrene-butadiene block copolymer with 10% vinyl (SBS 10)

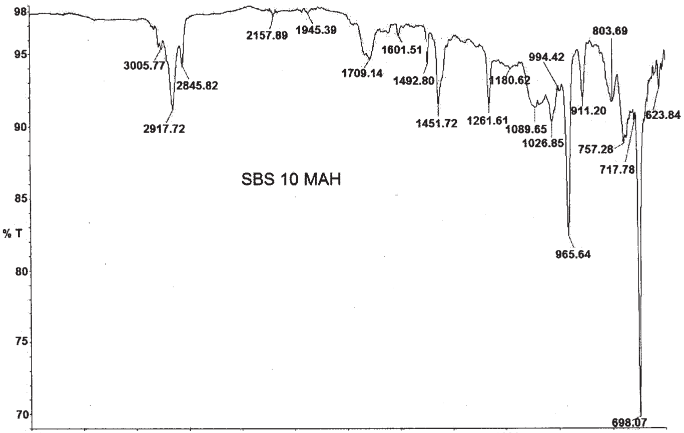

Fig. 3. FT-IR spectra of maleinized styrene-butadiene block copolymer (SBS 10 MAH)

The unreacted maleic anhydride was removed by precipitation in isopropanol and dissolving in butyl acetate. The procedure was repeated three times for a more advanced removal.

At the end of reaction was dosed amount of 1% (with respect to elastomer) of 2,6-di-tert-butyl-4-methylphenol (TOPANOL OC), in order to stabilize against thermal-oxidative degradation and finally the polymers were precipitated in isopropyl alcohol and dried in an oven under reduced pressure, at a temperature not exceeding 60 °C.

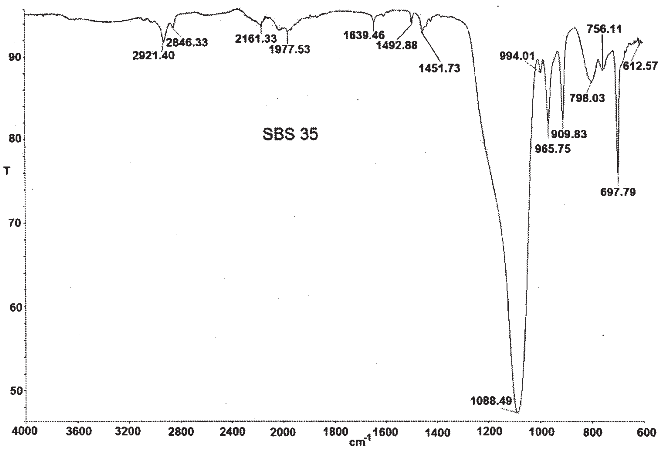

Fig. 4. FT-IR spectra of styrene-butadiene block copolymer with 35% vinyl (SBS 35)

Figure 1 shows the scheme of the SBS maleinization reaction [23].

The initial and maleinized SBS molecular weight was determined by gel permeation chromatography (GPC). The physico-mechanical properties were determined on polymer films obtained by centrifugal casting from toluene solution using a FPZ 100 Dynamometer, with an elongation rate of 500 mm/min, according to the specific characterization requirements of styrene-diene block copolymers.

The maleinization degree of SBS block-copolymers was investigated by Fourier Transform Infrared Spectroscopy (FT-IR) on a Perkin Elmer Spectrum GX device, equipped with ATR, in normal conditions [21].

The DMA characterization was carried out on a TA Instruments DMA-Q 800 apparatus, according to ASTM D 4065 standard, at 1 Hz frequency, a temperature range of -120-180°C with a heating rate of 3 °C/min, in air.

Results and discussions

The maleinization of SBS block copolymers was carried out at 75 ° C, the reaction time being varied between 1 to 8 h, using the following formulation: 100 g SBS was dissolved in 1 L butyl acetate then 2,5-5 g maleic anhydride was introduced next 2-7,5 g AIBN.

Figures 2-5 show the FT-IR spectra of SBS and maleinized SBS.

The FT-IR spectra of maleinized block copolymers SBS have revealed the elastomers absorption bands (figs. 3 and 5):

- 690 cm^{-1} for polystyrene;
- 730 cm^{-1} for cis-1,4 bonds of polybutadiene;
- 910 cm^{-1} for vinyl bonds (type 1,2);
- 965 cm^{-1} for trans-1,4 bonds of polybutadiene.

There were also visible the polar groups specific bands, especially noticing the appearance of the characteristic absorptions of carboxyl and carbonyl groups, as can be seen in figures 3 and 5.

Introducing of maleic groups in styrene-butadiene block copolymers leads to an increase in glass transition temperature for polybutadiene phase by macromolecular chain stiffening, as can be seen from table 2.

The glass transition temperature decreases for polystyrene phase indicates a less advanced separation of these domains from the polybutadiene matrix. This morphological change is a consequence of increasing the two phases compatibility due to maleic groups presence in the elastomeric block.

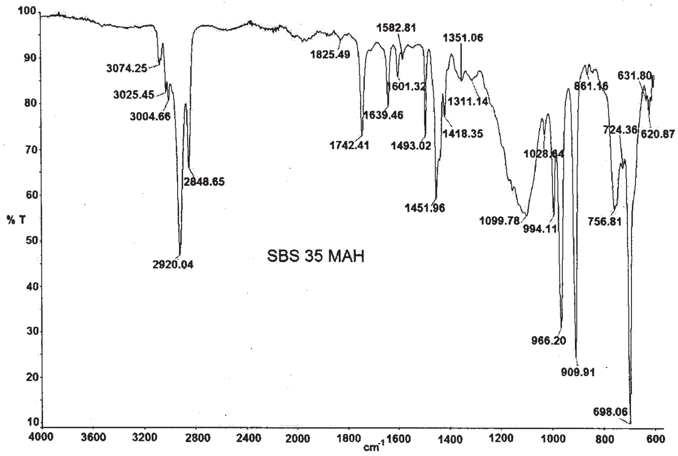

Fig. 5. FT-IR spectra of maleinized styrene-butadiene block copolymer (SBS 35 MAH)

Table 2
GLASS TRANSITION TEMPERATURES OF BLOCK COPOLYMERS, FROM THE DMA DETERMINATIONS

Polymer	SBS 10	SBS 10 with 0,5 %MAH	SBS 35	SBS 35 with 0,5 %MAH
Tg polybutadiene phase	-73	-65	-55	-49
Tg polystyrene phase	103	98	92	86

The research aimed the obtaining of some block copolymers with maximum 1% maleic groups, being avoided accentuated modifications in mechanical properties of SBS elastomers, changes which could limit their field of application.

As expected, the increasing of maleinization degree with reaction time and initiator concentration was confirmed by the reaction kinetics study of styrene-butadiene block copolymers modified with maleic anhydride (fig. 6).

The preferential enchaining in 1, 2 butadiene position (SBS 35) facilitates the maleinization reaction, in accordance with the mechanism presented in figure 1,

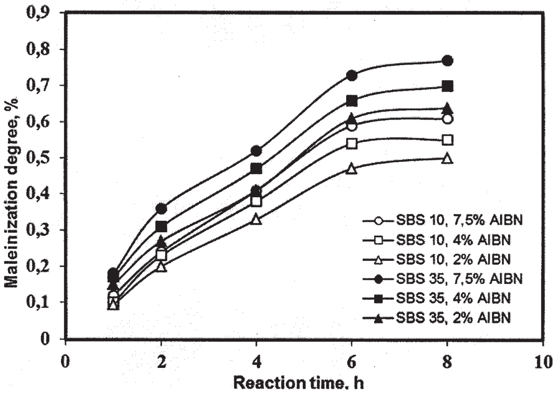

Fig. 6. Variation of maleinized degree depending on reaction time and AIBN concentration

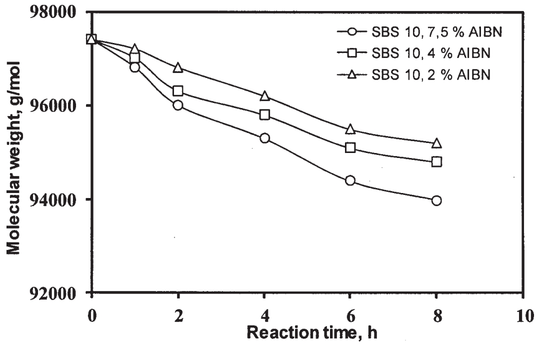

Fig. 7. Variation of molecular weight of maleinized block-copolymers with 10% vinyl depending on reaction time and AIBN concentration

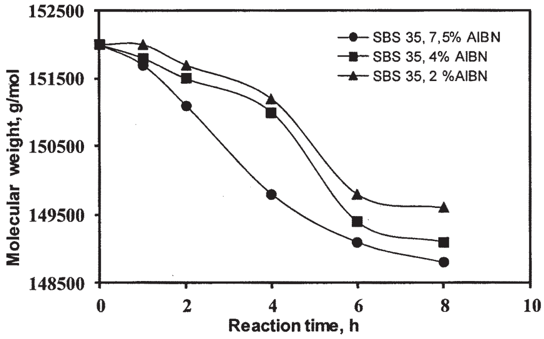

Fig. 8. Variation of molecular weight of maleinized block-copolymers with 35% vinyl depending on reaction time and AIBN concentration

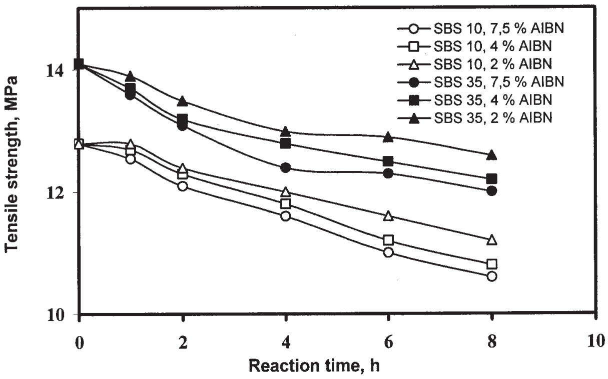

Fig. 9. Variation of tensile strength of maleinized block-copolymers depending on reaction time and AIBN concentration

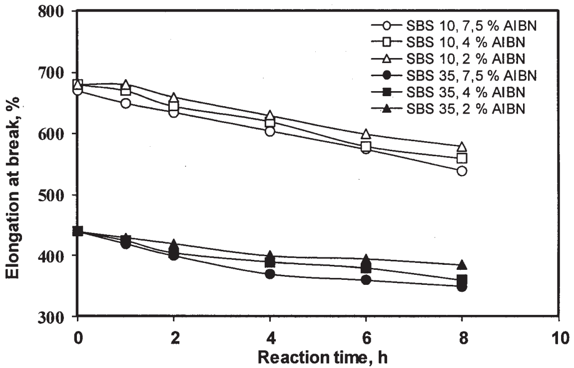

Fig. 10. Variation of elongation at break of maleinized block-copolymers depending on reaction time and AIBN concentration

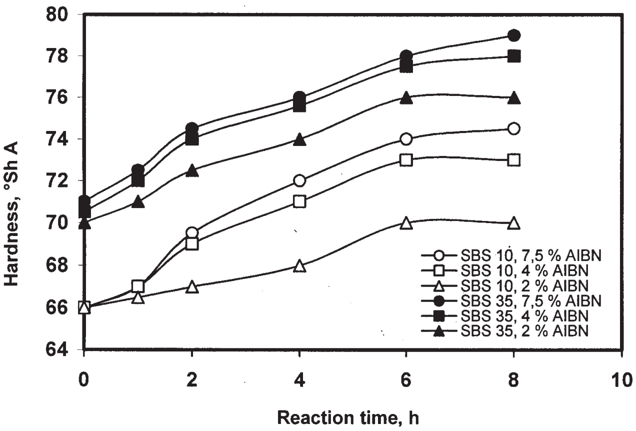

Fig. 11. Variation of hardness of maleinized block-copolymers depending on reaction time and AIBN concentration

leading to higher increase of reaction rate and therefore significantly increase of maleinization degree.

From the kinetic study was found that AIBN scission rate is not dependent of its concentration in the system and after 6 h, the reaction rate is limited due to initiator consumption.

In the used synthesis conditions, the number of macromolecular chain scission reaction is low, but a correlation between the decrease of molecular weight and the initiator concentration can be observed, as shown in figures 7 and 8.

The polar groups presence in polybutadiene chain disturb the block copolymers morphology, by modifying the phases separation degree (evidenced by higher glass transition temperatures) and by decreasing the entanglement, which leads to tensile strength and elongation at break diminution for maleinized elastomers (figs. 9 and 10).

Introducing of polar groups in polybutadiene chain leads to its stiffening, the phenomenon being evidenced by hardness increase of the modified block copolymers in correlation with the maleinization degree, as can be seen in figure 11.

Conclusions

The modification study of the styrene-butadiene block copolymers by radical grafting in solution, emphasized the favourable effect of increasing the vinyl microstructure proportion in polybutadiene block, manifested by a higher reaction rate and maleinization degree. This observation is an additional argument that sustains the reaction mechanism, which indicates the preferentially free radicals attack to the 1, 2 double bond of polybutadiene.

The influence of the maleinization degree on physical and mechanical properties of modified styrene-butadiene block copolymers in correlation with their vinyl microstructure was established.

Finally, we can conclude that dramatic variations of physical-mechanical properties are not produced to a maleinization degree up to maximum 1 %. Therefore the current field of application of block copolymers is not affected, moreover this can be extended by a more efficient modification of polar polymers.

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