The Morphology Influence of Styrene-Diene Block Copolymers Reinforced with Bentonite

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This paper presents the effect of reinforcement for styrene-butadiene and styrene-isoprene block copolymers with bentonite in correlation with morphology biphasic thermoplastic elastomers.

Keywords: SBS, SIS, bentonite, reinforced composite.

The styrene-diene block copolymers, due to the sequential structure of the component blocks show a special combination of physical and mechanical properties: elasticity, toughness, flexibility at low temperatures, relatively high temperature strength, good processability and reprocessability. These characteristics recommend them for industrial uses where require with high mechanical properties and a wide range of operating temperature variation [1, 2].

Reinforcement styrene-diene block copolymers with mineral fillers composites aims at obtaining more suitable properties in different fields of use. Mainly, reinforcement with mineral fillers leads to improved breaking strength at higher temperatures than the ambient and reduce contracting of extruded composites in injection molds [3-8]. The presence inorganic fillers in styrene-diene block copolymers reduce flammability and change electrical properties, tribological and acoustic of composites [1, 9-12]. It should be stressed that the reinforcement of styrene-diene block copolymers with mineral fillers has an important economic effect by reducing the cost price of composites.

Reinforcing effect is influenced on the one hand by the nature mineral fillers and on the other hand, if used as such or additive and not least, by reinforced material particle size [1, 8, 10, 13-17]. The additivation aims to increase the degree of dispersion and bentonite adherence to continuous phase diene block copolymers.

Reinforcement styrene-diene block copolymers are made by dispersing the mineral filler which is distributed preponderantly in diene phase and the nature of polydiene block influences the modification degree of physical and mechanical properties of composites.

The paper shows the influence of morphology styrene-diene block copolymers on the effect of reinforcing them with bentonite.

Experimental part

The reinforcing study was performed using two thermoplastic elastomers, one star styrene-butadiene (SBS) and linear styrene-isoprene (SIS) block copolymers, whose physical and mechanical properties are shown in table 1.

Block copolymers have been synthesized via anionic sequential polymerization of monomers in a solution of cyclohexane, the reaction being initiated with n-butyl lithium [18-20]. After the synthesis of block copolymers were stabilized with 1% 2, 6-di-tert-butyl-4-methylphenol (TOPANOL CA) directly to the cyclohexane solution in which the polymerization took place. The separation from the solution of the block copolymers was performed by stripping with hot water and water vapor, and finally polymers were dried in an oven under reduced pressure at a temperature of 60^0 C.

Molecular weight of the polymers and building-blocks collected during the various stages of the synthesis was determined by gel permeation chromatography (GPC). Physical and mechanical properties were determined on films with a thickness of about 1 mm obtained by centrifugal casting at temperatures not exceeding 60^0 C in toluene solution, in accordance with the requirements of standardized characterization of styrene-diene block copolymers.

Reinforcement of block copolymers was performed with bentonite Chioar Valley with a content of over 60% montmorillonite with interlamelar space of 15.1 Å.

After grinding, bentonite particle size presented the following composition: sieve residue:

$$R_{1,0}=0\ \%;\ R_{0,5}=0,2\ \%;\ R_{0,063}=65,8\ \%;\ R_{0,04}=97,1\ \%;\ R_{0,025}=100\ \%.$$

Reinforcement has been achieved by dosage in steps of 5 % bentonite, between 0 -30 % of the 20 % toluene solutions of styrene-diene block copolymers.

Desolvation was carried out by centrifugal casting at a temperature of 60^0 C, the solution of the polymer with bentonite being added in small portions in long time to avoid the formation of a gradient of reinforcement in the film thickness.

The use of toluene as solvent from composites obtaining as the reason, that toluene is a nonselective solvent for polystyrene, polybutadiene and polyisoprene blocks respectively [21] thus avoiding morphologic changes for biphasic structure styrene-diene block copolymers that could disrupt the interpretation effect reinforcement of polymers.

The tensile properties of the composites were measured by means of a FPZ 100 dynamometer at a stretching speed of 500 mm/min on stamped specimens from composite films according to SR EN ISO 527-96.

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Crt. no.	Property	SBS	SIS
1.	Polystyrene content, %	31.8	30.4
2.	Total molecular weight, g/mol	190,000	123,500
3.	Polystyrene block molecular weight, g/mol	15,650	18,800
4.	Polybutadiene block molecular weight, g/mol	128,200	-
5.	Polyisoprene block molecular weight, g/mol	-	85,900
6.	Yield, MPa	5.22	-
7.	Modulus at 300 %, MPa	4.7	3.5
8.	Tensile strength, MPa	22.2	13.8
9.	Elongation at break, %	810	1380
10.	Remanent elongation, %	10	14.3
11.	Hardness, ^{0}Sh A	68	51
12.	T_g of the polybutadiene phase, ^{0}C	- 78	-
13.	T_g of the polyisoprene phase, ^{0}C	-	-64
14.	T_g of the polystyrene phase, ^{0}C	87	91

Tabel 1
THE PHYSICO-MECANICAL PROPERTIES OF THE STYRENE-DIENE BLOCK-COPOLYMERS

Results and discussions

The styrene-diene block copolymers with 30-35 % polystyrene content, shows polystyrene domains with cylindrical morphology having dimensions of 10-100 nm arranged in a hexagonal network [22-29]. Polystyrene domains dispersed in the continuous polydiene elastomers phase realize physical crosslinking, which ensures crosslinking the utmost performance values of physical and mechanical properties of block copolymers [30].

From the data presented in table 1, we find that the physical and mechanical properties of styrene-isoprene block copolymer (SIS) differ significantly from those of styrene-butadiene block copolymer (SBS), although the degree of crosslinking of the elastomeric phase is basically similar, it provided the same weight polystyrene phase.

If we take into account that molecular entanglements between contact points, where for polybutadiene is about 6.000 g / mol and 12.000 to 16.000 g / mol and in the case of polyisoprene [31-34], we find a higher degree of packing polybutadiene phase (about 21 contacts polybutadiene chain compared with 6-7 polyisoprene chain).

In conclusion, the degree of crosslinking total polybutadiene phase is superior polyisoprene phase, which gives SBS block copolymers superior tensile strength and elongation at break respectively lower compared with the values presented SIS block copolymer.

Higher hardness of SBS block copolymer is partially a consequence of all packaging greater degree of polybutadiene chains.

Elongation at break and higher remanente elongation of SIS block copolymer attest the greater mobility polyisoprene chains, confirming the total degree of crosslinking less in the case of this elastomer.

As can be seen from table 1, when block copolymers are subjected stretching effort, only SBS block copolymer shows yield. The high value of yields indicate a significant less advanced amount of separation from polystyrene chains in the polybutadiene phase, while the lack of yield in the case of SIS block copolymer certifies more advanced polystyrene domains segregation from polyisoprene phase. The degree of segregation more advanced phases in the case SIS block copolymer is due to higher incompatibility between the polystyrene and polyisoprene compared to the incompatibility of polystyrene with polybutadiene.

The minimum molecular weight of the polystyrene blocks to the polybutadiene phase segregation occurs is 5,000-6,000 g/mol and 10,000-12,000 g/mol in the polybutadiene phase, which confirms pronounced degree of incompatibility between the polystyrene and polyisoprene [35, 36].

The glass transition temperature (Tg) of the polystyrene phase of SBS block copolymer is smaler than in SIS block copolymer (table 1), which mentions that in areas polystyrene chains of the first polymer polybutadiene is there.

These comparative variations in physical and mechanical properties corresponding to the two styrene-diene block copolymers is due to the existence of an interphase stage of different sizes in the separation matrix of polystyrene polydiene domains [24, 37-41].

Bentonite introduced in SBS block copolymer is preferentially distributed in polybutadiene phase due to adhesive more pronounced in the diene phase than polystyrene, behaviour characteristic of montmorillonite fillers, which have not undergone particle surface activation. The first dose (5%) bentonite present in the matrix polybutadiene leads to accentuated decrease interphase area, the phenomenon is evidenced by subtracting the yield, as can be seen from figure 1.

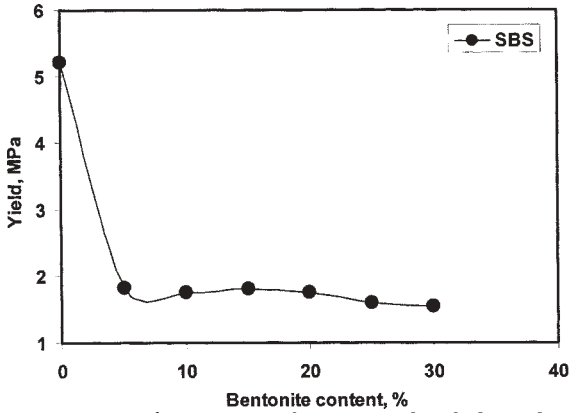

Fig. 1. Variation of composites elongation at break depending on bentonite content

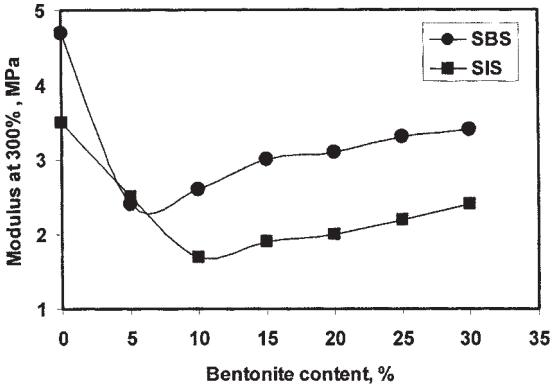

Fig. 2. Variation of composites modulus at 30% depending on bentonite content

Increasing dosage of bentonite does not lead to complete separation of polystyrene phase from polybutadiene, the composites presenting a small yield throughout the field of reinforcement.

The importance reducing of the interphase area caused by the presence of bentonite in styrene-diene block copolymers at the first dosages (5-10%), has the effect of increasing mobility of polydiene chain and therefore decreases elongation modulus 300% [17, 42], as it can be seen in figure 2.

Further increasing the dosage of bentonite, produce decreased mobility elastomeric chains by reducing interchain contact and manifests strongly reinforcing effect [43-47], characterized by increasing 300% elongation modulus (fig. 2), low tensile strength (fig. 3), elongation to break (fig. 4), and the remanent elongation increase (fig. 5) of the composite of the two block copolymers.

Higher values of the 300 % elongation modulus, tensile strength all the reinforcing area, and respectively lower elongation at break of SBS composites compared with those of SIS composites are superior due to entanglement polybutadiene phase as mentioned above.

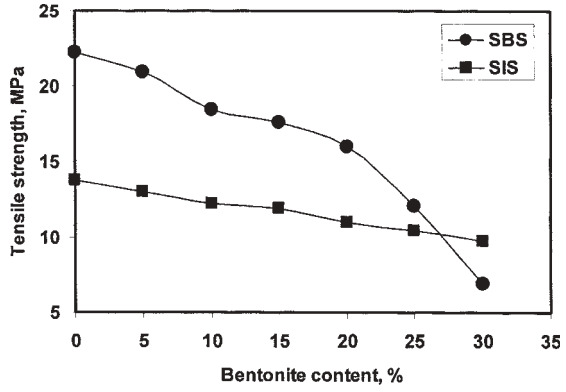

Fig. 3. Variation of composites tensile strength depending on bentonite content

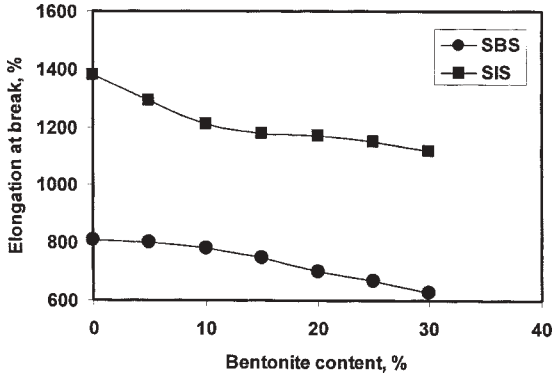

Fig. 4. Variation of composites elongation at break depending on bentonite content

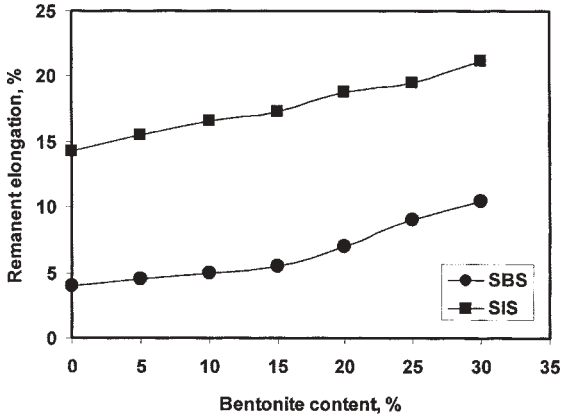

Fig. 5. Variation of composites remanent elongation depending on bentonite content

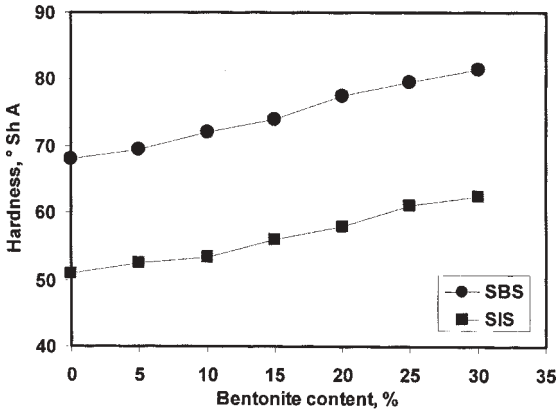

Fig. 6. Variation of composites hardness depending on bentonite content

Sharp decrease tensile strength SBS composites with increasing reinforcement indicate a lower bentonite adhesion to polybutadiene matrix compared polyisoprene matrix [14]. Consequently, when the composite material is subjected stretching, deformation destructive effort will be taken with a growing share of polybutadiene chains with increasing bentonite content and thus tensile strength will drop more pronounced.

Lower adherence of the bentonite to polybutadiene block is confirmed by the significantly higher values of composites SBS remanent elongation, deformation of the material being lesser extent reversible.

SBS and SIS composites hardness (fig. 6) shows a relatively uniform growth, following the simple rule charging an elastic material with a hard material, and does not notice a significant influence of this property on the nature of the elastomeric block.

To highlight more clearly the composite material destruction resistance, breaking strength can be reported in section specimen, the property so determined is called the real breaking resistance (σ_T).

Real breaking resistance is calculated according to the following formula:

$$\sigma_T = {}^{273}\!/_{293}\,\sigma_b \cdot \lambda_b \qquad (1)$$

where :

σ_T - real breaking resistance

σ_b – tensile strength

λ_b - elongation at break.

From figure 7 it can be see that real breaking resistance of SIS composites shows higher values than SBS composites throughout the bentonite reinforcement area, order reversed in comparison with varying tensile strength (fig. 3).

Again notice a greater reduction in the real breaking resistance in the case SBS composites compared to the

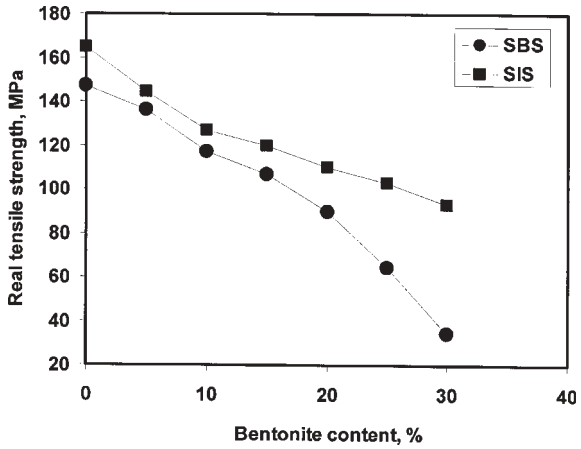

Fig. 7. Variation of composites real tensile strength depending on bentonite content

SIS, as shown above explanation, the variation analysis in the same way tensile strength.

The greater mobility of polyisoprene chains, because of higher molecular weight entanglements of points and interphase superior adherence with bentonite of polyisoprene block allows a more uniform takeover and a more balanced distribution of destructive effort, when the composite material is subjected stretching, and so real breaking resistance of the SIS composite is superior to SBS composites.

The wide range of values physical and mechanical properties of the composites presented SBS and SIS block copolymers charged with bentonite, allows to easily choose the degree of reinforcement for composites with properties most appropriate to different uses.

Conclusions

The study has highlighted reinforcement effect of bentonite SBS and SIS block copolymers.

Reinforcing mechanism is influenced both biphasic morphology of block copolymers and different degrees of bentonite adhesion of polybutadiene and polyisoprene phase.

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