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Effect of plasticizers on the mechanical and technological properties of styrene-isoprene block copolymer composites under cyclic loading

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Abstract. In various applications, there is a demand for materials with damping properties. One of the promising materials in this respect is polymer composite material based on thermoplastic elastomers. When studying the experience of using thermoplastic elastomers as damping materials, it was found that one of the most promising TPEs for this purpose is block copolymer of the styrene-isoprene-styrene type. In this article, composites based on SIS VECTOR 4111NS and SIS VECTOR 4113NS thermoplastic elastomers with different plasticizer content were tested. The results showed that the composite based on SIS VECTOR 4113NS for the manufacture of damping pads is more promising. It also revealed the optimal amount of plasticizer required for the manufacture of high-quality material with the best mechanical characteristics.

Keywords: polymer composite materials, thermoplastics, vibration absorption, damping materials, styrene-isoprene block copolymer, building structures

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1. Introduction

There has been a growing demand for materials with damping properties, i.e., capable of dissipating the mechanical energy of the system. Damping plays a major role in such areas as electronics, sound insulation, automotive and transportation industry, construction, shipbuilding, household appliances, industrial equipment, firearms, health care, and medical devices, personal protective equipment, and/or sports gear [1-3]. Polymer composite materials show much promise in this regard [4,5].

An example of successful vibration dampers is elastomeric bearing pad, used in the construction of bridges and buildings for over 70 years. Such pads prevent structural damage and reduce repair and maintenance costs [6].

Currently, elastomeric pads are fabricated from natural or synthetic rubbers [7]. However, this type of material is becoming less popular with the recent advent of

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thermoplastic elastomers (TPE), which are a group of materials capable of large reversible deformations during operation, like rubbers, and suitable for recycling, like plastics [8,9]. Using TPE instead of rubbers allows for increasing productivity by 2-4 times, increasing the production outputs by 2-2.5 times; reducing labor and energy costs by 30% (as it is possible to forego blanking, vulcanization, and waste removal); reducing the material consumption of the product by 25-30% (by reducing the specific weight of the material); reducing gas emissions by 10-20 times; ensuring complete waste recycling, and, ultimately, fabricating high-quality products [10,11].

TPE include two large groups of materials: block copolymers (e.g., styrene block copolymers, ester copolymers, thermoplastic polyurethanes, block polyamides) and composites based on a mixture of rubber and thermoplastic (e.g., olefin thermoplastics) [12,13].

Considering the experience of adopting thermoplastic elastomers as damping materials, studies have established that block copolymers of the styrene-isoprene-styrene type are one of the most promising TPE for this purpose [14].

This study aimed to achieve the following goals:

1. Determine the most promising TPE with the best damping properties;
2. Determine the options for fabricating a finished product from this material.

2. Method

Materials. We considered styrene-isoprene-styrene type block copolymers Vector 4111NS and Vector 4113NS (TSRC, Republic of China) and copolymer SKEPT-50 (Nizhnekamskneftekhim, Russia). Vector 4111NS is a linear triblock, and Vector 4113NS is a mixture of linear triblock and diblock, which gives the composition greater softness. Industrial oil I-40 (Gazpromneft, Russia) was used as a softening agent in the compound; the filler combined chalk MICARB (Geocom, Russia), an inert filler with a low price [15], and Newsil 1165 silica (People's Republic of China).

To select the optimal composition for the compound, providing the best combination of technological (recyclability) and operational (damping) properties, the type of thermoplastic elastomer used and the content of industrial oil I-40 were varied, bringing its content to 70 weight parts per 100 weight parts of the polymer [16].

Preparation of compounds. The components were mixed in a Brabender-type micromixer at 180ºC for 20 minutes.

The compositions of model mixtures and their notations are presented in Table 1.

The test specimens were prepared in an injection molding machine at 190ºC.

The notations for the model mixtures correspond to the brand of thermoplastic elastomer (Vector 4111 or Vector 4113) and oil contents (M) in the compound for weight parts per 100 parts of polymer. The mixing modes are presented in Table 2.

The operational properties of the specimens were subsequently assessed; the specimens were molded via an SZS-series thermoplastic testing machine at 190ºC and an injection pressure of 5 atmospheres.

Assessment of operational (rheological) properties. The rheological characteristics, determining the options for subsequent processing by injection molding, were measured for the obtained compounds. The melt flow index (MFI) was evaluated by ASTM D 1238 at a temperature of 190°C and a load of 5 kg with the PTR-Lab-02 device (St. Petersburg, Russia).

Assessment of operational properties. Mechanical tensile tests were carried out using an Autograph AG-X 5 kN tensile testing machine by Shimadzu (Kyoto, Japan) at room temperature and a travel speed of 500 mm/min for dumbbell-shaped specimens (Fig. 1) in accordance with GOST 270-75 [17].

Table 1. Compositions of the studied compounds

Ingredient	Content, weight parts per 100 weight parts of polymer									
	SIS VECTOR 4111NS					SIS VECTOR 4113NS				
	V4111 M30	V4111 M40	V4111 M50	V4111 M60	V4111 M70	V4113 M30	V4113 M40	V4113 M50	V4113 M60	V4113 M70
SKEPT-50	20	20	20	20	20	20	20	20	20	20
SIS Vector 4111NS (18% Styrene)	80	80	80	80	80	-	-	-	-	-
SIS Vector 4113NS (15% Styrene)	-	-	-	-	-	80	80	80	80	80
MICARB chalk	40	40	40	40	40	40	40	40	40	40
Newsil 1165 silica	30	30	30	30	30	30	30	30	30	30
I-40 industrial oil	30	40	50	60	70	30	40	50	60	70
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Total	202.5	212.5	222.5	232.5	242.5	202.5	212.5	222.5	232.5	242.5

Table 2. Compound preparation conditions

Ingredient	Time, min	Speed, rpm	Temperature, °C
Stage 1			
SKEPT-50 and thermoplastic elastomer	3–5	60	180
30% oil/filler	3–5		
30% oil/filler	3–5		
30% oil/filler	3–5		
Stage 2			
Stage 1 mixture	5–7	60	180

Intermittent cyclic tensile tests at 100% elongation were carried out with the Autograph AG–X 5 kN machine by Shimadzu (Kyoto, Japan) at a travel speed of 500 mm/min for dumbbell-shaped specimens (Fig. 1). Figure 2 shows a schematic diagram of the loading-unloading cycle and the resulting hysteresis loop, with arrows indicating the unloading and reloading sequences. The dissipated energy, or hysteresis energy loss, WD, corresponds to the area enclosed in this hysteresis loop, while the area under the lower curve (corresponding to unloading) of the hysteresis loop represents the stored elastic energy, WE. Specific dissipated and elastic energies were determined by dividing WD and WE by the initial volume of the specimen. The specific damping capacity is the ratio of the energy dissipated in five cycles to the elastic or potential energy accumulated in this cycle [19], and was found from:

$$\Psi = W_D / W_E. \quad (1)$$

Fig. 1. Dumbbell-shaped specimens for testing

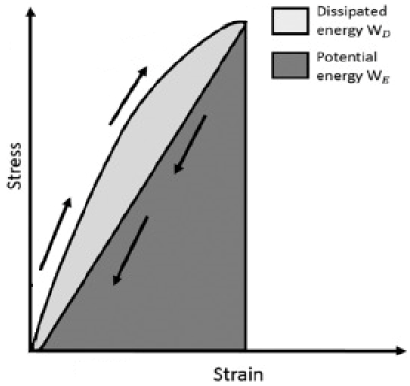

Fig. 2. Schematic diagram of an unloading-loading cycle showing the amount of dissipated energy and elastic energy. The graph is constructed based on the data from Ref. [18]

This characteristic reflects the damping capacity of the material, i.e., indicates how effectively the material dissipates directed kinetic energy. The greater the ratio of the scattered energy in the material to the potential energy stored in it, the more effectively the material absorbs vibrations.

The ultimate tensile strength was determined by the formula:

$$R_S = Q_{max}/A, \tag{2}$$

where Q_{max} is the maximum load, and A is the cross-sectional area.

Ultimate tensile strength serves as a measure for estimating the seismic or other loads that the material can withstand before tensile failure.

The equivalent stiffness was calculated by the formula:

$$E_{100} = \sigma_{100}/\varepsilon_{100}\ , \tag{3}$$

where σ_{100} is the stress at 100% elongation, ε_{100} = 1 – 100% elongation.

The equivalent stiffness serves as a measure for comparing the stiffness of the material at the same elongation. The higher E100, the stiffer the material. This means that the material can absorb a greater load at the same elongation.

Shore A hardness was measured with a durometer in accordance with GOST 263-75 [20].

This characteristic allows estimating the magnitude of the vertical load that the material can withstand before failure. Shore A hardness is important because the material developed is to be used as a damping pad.

3. Results and discussion

Technological properties. The compound's suitability for injection molding can be estimated from the magnitude of MFI.

Molding failed in specimens V4111M20, V4111M25, V4113M20, and V4113M25 shown in Fig. 3. The low oil content in the specimens (20 and 25 weight parts) did not allow producing of high-quality specimens by injection molding. High-quality specimens were produced from mixtures with the oil contents of 30, 40, 50, 60, and 70 weight parts (Fig. 4). The results obtained are consistent with the data on MFI (Fig. 5).

Thus, we found that the compounds suitable for molding using a thermoplastic machine under a pressure of 5 atmospheres are those with MFI over 30 g/10 min, which is the minimum value required. Specimens acceptable for testing can be obtained at this MFI.

Fig. 3. Specimens 1 and 2 with the oil contents of 20 and 25 weight parts, respectively, for SIS VECTOR 4111NS

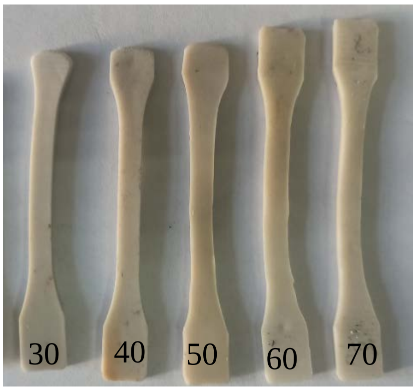

Fig. 4. Specimens with the oil contents of 30, 40, 50, 60, and 70 weight parts for SIS VECTOR 4111NS

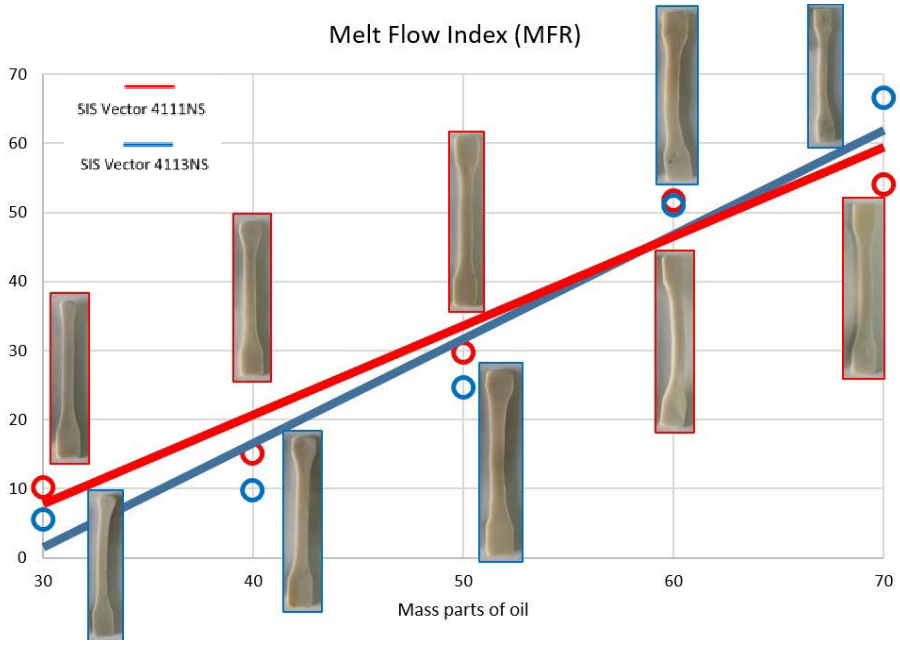

Fig. 5. MFI of compounds as a function of oil contents (for 30, 40, 50, 60, and 70 weight parts)

Monotonic tensile testing. Comparing materials based on SIS VECTOR 4111NS and SIS VECTOR 4113 NS, we can observe that equivalent stiffness, strength and hardness are higher in the material based on SIS 4111NS (Figs. 6-8). The elongation is higher in the material based on SIS 4113NS (Fig. 9).

In addition, the mechanical characteristics of materials vary depending on the oil content in the mixture, with a similar dependence observed for both materials [17]. It can be seen from the graphs that increasing the oil content produces a decrease in the following mechanical characteristics: equivalent stiffness, strength, and Shore A hardness. The elongation at break first increases with increasing oil content but then decreases as well. It can be concluded that the material has optimal mechanical properties at an oil content of 50 weight parts per 100 weight parts of polymer.

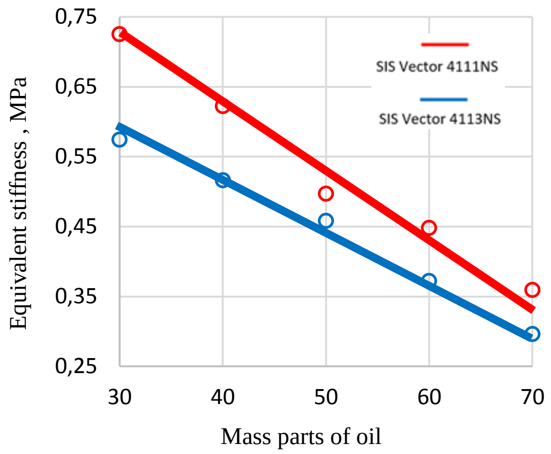

Fig. 6. Effect of oil content on equivalent stiffness of the compound

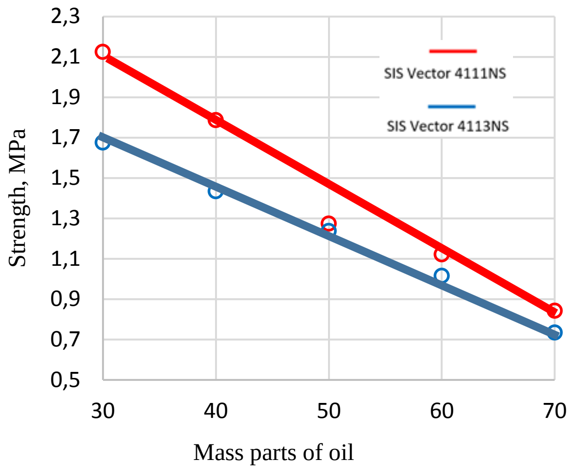

Fig. 7. Effect of oil content on strength characteristics of the compound

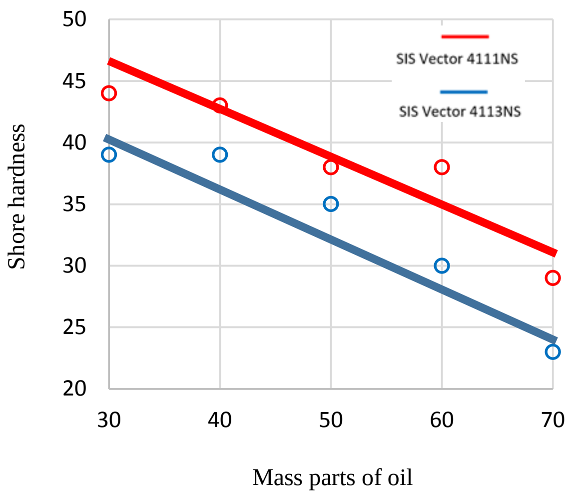

Fig. 8. Effect of oil content on the Shore hardness of the compound

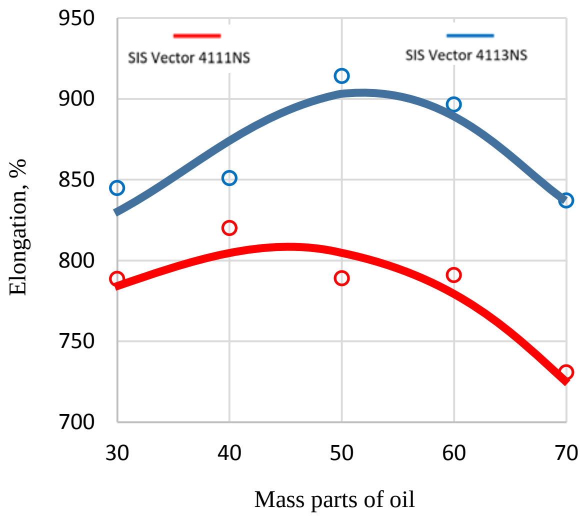

Fig. 9. Effect of oil content on maximum elongation of the compound

Repeated cyclic tensile tests. The cyclic tensile responses of the compounds are shown in Fig. 10. A large hysteresis loop occurs between the first loading-unloading cycle, while much smaller loops can be observed for subsequent loading cycles. Moreover, a constant deformation of 20% appears after the first loading-unloading cycle, which practically does not increase with subsequent cycles. This suggests that all fractures within the composite structure mainly occur in the first cycle. The nature of hysteresis has not changed in different brands of thermoplastic elastomers.

Comparing materials based on SIS Vector 4111NS and SIS VECTOR 4113NS with different weight parts of oil, we can conclude that the specific damping capacity is better for the material based on SIS VECTOR 4113NS, and oil content has little effect on the damping capacity (Fig. 11).

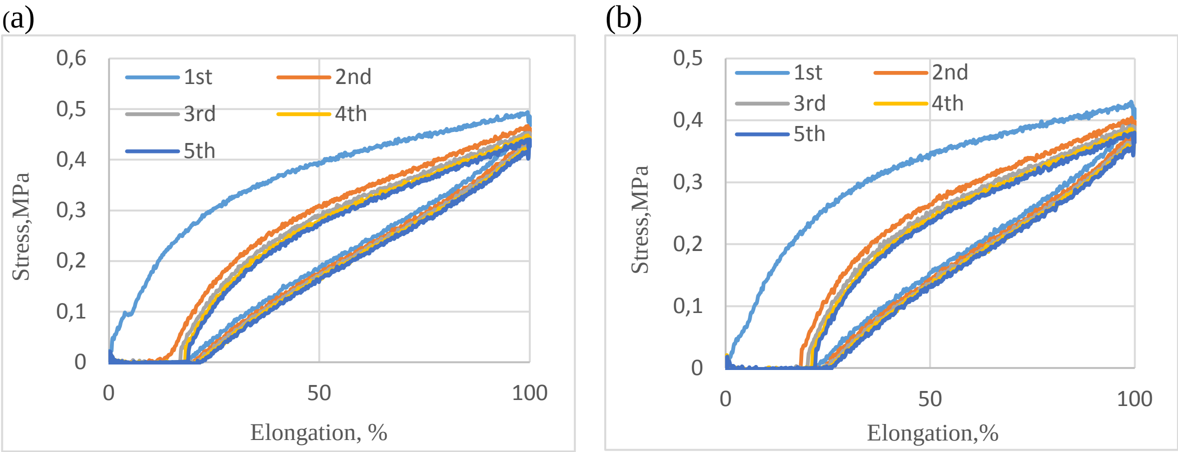

Fig. 10. Standard cyclic tensile reactions of composites based on SIS VECTOR 4111NS (a) and based on SIS VECTOR 4113NS (b), respectively

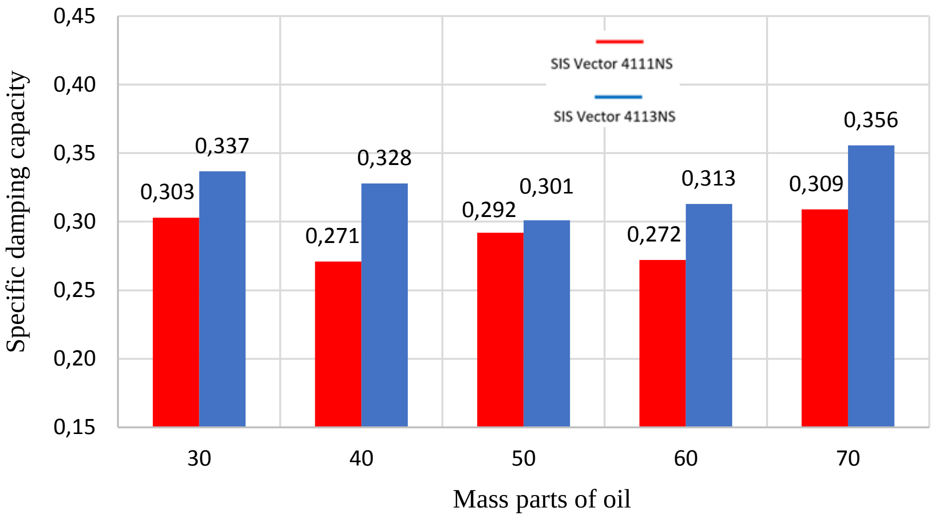

Fig. 11. Specific damping capacity for SIS VECTOR 4111NS and SIS VECTOR 4113NS

4. Conclusion

To summarize, we have obtained the following results:

1. SIS 4113NS shows the greatest promise for manufacturing damping pads because it has the best damping properties; the optimal amount of oil for the compound based on it is 50 weight parts of oil per 100 weight parts of polymer. Materials with such ratios of oil and block copolymer exhibit sufficiently high mechanical properties, while specimens can still be produced by injection molding. Increasing the oil content leads to a decrease in the mechanical characteristics of the material.

2. The MFI for obtaining a product by injection molding using an SZS-series thermoplastic testing machine at a temperature of 190°C and an injection pressure of 5 atmospheres had to be at least 30 g in 10 min. This melt flow rate is the minimum required.

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