

Obtaining a Binary System Based on Styrene–Butadiene–Styrene Polymer using Carbon Nanotubes and Determination of the Flow Index of the Composition Melt.

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ABSTRACT

This work is devoted to the preparation and investigation of a composite based on styrene–butadiene–styrene (SBS) polymer using carbon nanotubes. Nanocomposites based on styrene–butadiene–styrene polymer (SBS) and carbon nanotubes were prepared by the emulsion mixing method, while the vulcanization process was carried out in accordance with standard test methods used for SBS evaluation.

The incorporation of carbon nanotubes (CNTs) into the rubber compound improved the compatibility of the components, and the resulting nanocomposite exhibited high thermal stability. The nanomaterial enhanced the process ability of SBS rubber–based composites. Compared with rubber reinforced solely with carbon black, the use of nanomaterials led to a 27% increase in stress at 100% permanent elongation. In addition, partial replacement of carbon black resulted in an increase in the elongation at break of the vulcanization from 424.5% to 554.0%.

The mechanical properties of the obtained rubbers demonstrated that they can be regulated by

Keywords: Styrene–butadiene–styrene rubber, carbon black, CNT, modification, vulcanization, rheology.

INTRODUCTION

Styrene–Butadiene–Styrene (SBS) is a triblock copolymer belonging to the class of thermoplastic elastomers, and it is one of the most important materials combining both elastic and thermoplastic properties [1–4]. Its structure consists of a linear PS–PB–PS block chain, where polystyrene (PS) blocks are located at both ends and a polybutadiene (PB) segment is positioned in the middle. This unique architecture provides SBS with rubber-like elasticity as well as thermal form stability. The polybutadiene segment imparts flexibility and elongation capability, while the polystyrene domains act as rigid phases that ensure mechanical strength. Consequently, SBS behaves as an elastomer under ambient conditions, whereas upon heating it softens like a thermoplastic and becomes moldable [5–11].

METHOD

Preparation and Mixing Technology of SBS-CNT Composites

For the preparation of the nanocomposites, multi-walled carbon nanotubes (MWCNTs) were first dispersed in a predetermined amount of toluene and subjected to ultra-sonication in a Bandelin Sonora Super RK106 ultrasonic bath for 6 hours. This step was intended to reduce nanotube agglomeration and to ensure good dispersion within the solvent. Subsequently, SBS polymer was added to the dispersion at a defined ratio (5.5 mL of toluene per 1 g of SBS) and mechanically stirred until complete dissolution was achieved. The resulting homogeneous solution

was cast as a thin layer onto a clean glass surface and allowed to evaporate at room temperature, yielding thin, elastic, and homogeneous composite films.

The distribution and morphology of MWCNTs within the SBS matrix were examined using scanning electron microscopy (SEM, Philips X230 FEG) based on both surface and fracture images. Prior to SEM analysis, the samples were cryogenically fractured in liquid nitrogen and subsequently gold-coated by sputter deposition to prevent surface charge accumulation and to enhance image quality.

The electrical conductivity and resistance of the composites were measured using a Kiteley 487 automated Pico ammeter/voltage source. During the measurements, the applied voltage was varied from -10 V to $+10\text{ V}$. Based on the obtained current–voltage (I – V) characteristics, the electrical resistance (R) was determined, after which the volume resistivity (ρ) was calculated using the following equation:

$$\rho = RLA \quad (1)$$

RESULTS OF EXPERIMENTAL RESEARCH

Study of rheological properties

Determination of the melt flow index (MFI) of polymer composite systems is of great importance for establishing their processing parameters. Taking these considerations into account, a composite based on SBS + CNT was prepared according to the formulation given below (Table 1).

Table 1. Formulation of the CNT-based composite.

Names of Components	Sample K-1 Component amount, gr	Sample K-2 Component amount, gr	Sample K-3 Component amount, gr	Sample K-4 Component amount, gr	Sample K-5 Component amount, gr
Styrene–butadiene–styrene rubber	100	100	100	100	100
Carbon Nanotube	1	2	3	4	5
Total	101	102	103	104	105

The binary mixture was prepared in an extruder at a temperature of $190\text{ }^{\circ}\text{C}$ for 3 minutes.

For the binary mixtures, the flow time of the composite melts through a 2 mm capillary over a fixed distance ($S = 0.002\text{ cm}$) was determined (in seconds) at different temperatures (150, 170, 190, and $210\text{ }^{\circ}\text{C}$) under four different applied loads. The obtained results are presented in Table 2.

Table 2. Time required for the flow of the melts of the SBS/CNT binary system (in seconds)

145°C				
Loads	G_1	G_2	G_3	G_4
Samples				
K-1	43.18	10.92	8.47	5.29
	40.12	18.85	7.74	4.62
	41.35	11.24	8.09	4.95
K2	44.86	13.78	9.61	6.67
	46.12	13.45	10.38	6.15
	45.58	13.22	9.97	6.34
K3	47.32	16.71	13.18	8.76
	48.05	13.64	13.64	7.94
	47.61	13.41	13.41	8.33

K4	49.42 53.18 51.09	17.94 16.86 17.85	14.48 14.91 14.65	8.18 9.48 8.83
165°C				
K1	31.02 29.85 30.21	8.62 9.19 8.41	6.23 5.48 5.79	2.41 3.28 2.89
K2	31.58 31.12 30.89	9.15 9.57 9.31	6.74 5.48 6.35	3.21 3.15 3.18
K3	33.42 33.65 33.29	11.08 8.42 9.74	7.29 7.48 7.36	3.81 4.08 3.96
K4	33.89 31.05 32.41	9.62 10.15 9.88	7.58 7.76 7.69	4.23 4.36 4.29
185°C				
K1	19.92 19.15 19.48	6.48 6.01 6.24	4.79 4.23 4.51	1.74 2.04 1.88
K2	21.54 18.72 20.05	6.64 5.98 6.29	4.45 4.20 4.33	1.72 1.54 1.62
K3	20.56 18.74 19.52	4.51 4.65 4.58	5.17 6.59 5.92	2.27 3.25 2.78
K4	23.94 22.45 23.08	6.47 6.02 6.25	5.63 6.98 6.31	3.24 3.46 3.35

The applied loads were, respectively: G1 = 11.75 kg, G2 = 20.85 kg, G3 = 26.85 kg, and G4 = 34.85 kg. The pressure generated on the sample surfaces due to the applied loads was calculated primarily using the following equation (2).

$$P = \frac{G}{\pi D^2} = \frac{G}{\frac{3.14 \cdot (0.954)^2}{4}} = \frac{G}{0.7144} \quad (2)$$

$$P_1 = \frac{G_1}{0.8321} = \frac{11.75}{0.8321} = 16,9701946 \text{ kg/sm}^2$$

$$P_3 = \frac{G_3}{0.8321} = \frac{26.85}{0.8321} = 32,267756 \text{ kg/sm}^2$$

$$P_2 = \frac{G_2}{0.8321} = \frac{20.85}{0.8321} = 25,0570844 \text{ kg/sm}^2$$

$$P_4 = \frac{G_4}{0.8321} = \frac{34.85}{0.8321} = 41,881985 \text{ kg/sm}^2$$

After modification of the SBS polymer with carbon nanotubes, the prepared samples were extruded through a capillary. For this purpose, the shear stress was calculated (Equation (3)).

$$\tau = \frac{P \cdot r}{2l} = \frac{P \cdot 0.05}{2 \cdot 0.8} \quad (3)$$

Here, P is the pressure generated on the sample surface as a result of the applied loads; τ is the shear stress; r is the radius of the capillary used; and l is the length of the capillary. The calculations were performed as follows:

$$T_1 = \frac{P_1 \cdot 0,05}{1,6} = \frac{16,9701946 \cdot 0,05}{1,6} = 0,530318 \frac{kq}{sm^2} \cdot 9,806 \cdot 10^4 = 5,20029833 \cdot 10^4 Pa$$

$$T_2 = \frac{P_2 \cdot 0,05}{1,6} = \frac{25,0570844 \cdot 0,05}{1,6} = 0,783656 \frac{kq}{sm^2} \cdot 9,806 \cdot 10^4 = 7,68453 \cdot 10^4 Pa$$

$$T_3 = \frac{P_3 \cdot 0,05}{1,6} = \frac{32,267756 \cdot 0,05}{1,6} = 1,008365 \frac{kq}{sm^2} \cdot 9,806 \cdot 10^4 = 9,888027 \cdot 10^4 Pa$$

$$T_4 = \frac{P_4 \cdot 0,05}{1,6} = \frac{41,881985 \cdot 0,05}{1,6} = 2,094095 \frac{kq}{sm^2} \cdot 9,806 \cdot 10^4 = 120,5346955 \cdot 10^4 Pa$$

To calculate the volumetric flow rate of the melts of the composites modified with carbon nanotubes at different compositions, Equation (4) was used.

$$Q = \frac{S}{t} \times \frac{\pi D^2}{4} = \frac{0,02}{t} \times \frac{3,14 \times (0,954)^2}{4} = \frac{0,014288}{t} \quad (4)$$

The values calculated based on the given equation and their decimal logarithms are presented in Table 3.

Table 3. Calculated volumetric flow rate (Q) values of the SBS+CNT composite (cm³/s)

145°C				
Samples	G1	G2	G3	G4
K1	0,0003625	0,0013289	0,0018426	0,0030184
K2	0,0003341	0,0011423	0,0015089	0,0023547
K3	0,0003184	0,0009628	0,0011297	0,0018126
K4	0,0002961	0,0008796	0,0010364	0,0017068
165°C				
K1	0,0004986	0,0017894	0,0025867	0,0053182
K2	0,0004862	0,0016128	0,0023795	0,0047429
K3	0,0004528	0,0015489	0,0020696	0,0038247
K4	0,0004685	0,0015297	0,0019823	0,0035069
185°C				
K1	0,0007765	0,0024158	0,0033486	0,0080943
K2	0,0007569	0,0023947	0,0034972	0,0093986
K3	0,0007751	0,0032864	0,0025698	0,0054681
K4	0,0006589	0,0024183	0,0023875	0,0044862

In this study, the volumetric flow rate of the composite (log Q) was calculated, and the obtained results are presented in Table 4.

Table 4. Calculated volumetric flow rate of the SBS/CNT mixture (log Q values).

150°C				
Samples	G1	G2	G3	G4
K1	-3.4682	-2.9014	-2.7586	-2.5449
K2	-3.5039	-2.9687	-2.8468	-2.6543
K3	-3.5261	-3.0395	-2.9756	-2.7698
K4	-3.5586	-3.0859	-3.0134	-2.7957
170°C				
K1	-3.3296	-2.7718	-2.6119	-2.2974

K2	-3.3403	-2.8169	-2.6487	-2.3476
K3	-3.3728	-2.8334	-2.7105	-2.4419
K4	-3.3871	-2.8398	-2.7282	-2.4806
190°C				
K1	-3.1354	-2.6298	-2.4986	-2.0345
K2	-3.1471	-2.6431	-2.5098	-2.0492
K3	-3.1665	-2.6649	-2.6147	-2.2853
K4	-3.2098	-2.6895	-2.6446	-2.3719

Based on the calculations corresponding to the data presented in the tables, the $\log \dot{\gamma}$ - $\log \tau$ dependence (shear rate and shear stress) for the SBS/CNT binary system at 150 °C, 170 °C, and 190 °C was constructed, and the resulting curves are shown in Figures 1, 2, and 3.

RESULTS

To improve the photo stability of SBS-based composites, 3–5 parts by weight of carbon nanotubes (CNTs) were added. These additives enhance the stability of the material under solar radiation, ensuring long-term durability.

The results show that nanomaterials such as CNTs and carbon black scatter and reflect UV radiation, preventing its penetration into the polymer structure and reducing macromolecular degradation. Their combined use increases surface area and improves resistance to photo degradation.

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