

ВЛИЯНИЕ ПОЛИХЛОРИРОВАННЫХ *n*-АЛКАНОВ НА ХИМИЧЕСКУЮ СТРУКТУРУ, МЕХАНИЧЕСКИЕ И ТЕРМИЧЕСКИЕ СВОЙСТВА БЛОК-СОПОЛИМЕРОВ СТИРОЛА И БУТАДИЕНА

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*Создание новых функциональных материалов на основе модифицированных широко применяемых отечественных бутадиен-стирольных блок-сополимеров позволит получить материалы с повышенной бензостойкостью, термостойкостью, светостойкостью, озоностойкостью, а также улучшенными адгезионными свойствами. Галогенирование термоэластопластов будет способствовать повышению их совместимости с полярными полимерами. В данной работе рассматривалось влияние хлорпарафина на свойства стирол-бутадиен-стирольного блок-сополимера. Хлорпарафины (ХП) представляют собой сложную смесь полихлорированных *n*-алканов и могут быть использованы в качестве галогенсодержащего модификатора термопластичного эластомера для повышения его прочностных и термических свойств. Композиционные материалы на основе стирол-бутадиен-стирольного блок-сополимера (СБС) с различным количеством хлорпарафина были получены с помощью метода растворного смешения. Анализ спектров НПВО/Фурье-ИК исходного СБС и композитов СБС/ХП показал появление новых характеристических полос поглощения на 1260, 1090, 1020 и 800 см⁻¹. С увеличением количества введенного хлорпарафина отношение оптических плотностей между полосой, связанной с колебаниями связи C-Cl, и колебаниями стирольного блока существенно увеличивается. Исследование показало, что количество хлорированного парафина сильно влияет на конкретные свойства исследуемого термоэластопласта. Установлено, что хлорпарафин повышает термостабильность композитов. Температура начала разложения увеличилась до 262 °С (увеличение на 57 °С), а максимальная температура разложения немного повысилась с 463 до 467 °С. Проведена сравнительная оценка влияния концентрации хлорпарафина на химическую структуру и прочностные свойства стирол-бутадиен-стирольных сополимеров. Установлено, что композиты СБС с 5 м.ч. ХП характеризуются улучшенными прочностными свойствами в сравнение с исходным образцом СБС.*

Ключевые слова: стирол-бутадиен-стирольный блок сополимер (СБС) полихлорированные *n*-алканы, хлорированные парафины, ИК-спектроскопия, термогравиметрический анализ, термические свойства, растворное смешение

EFFECTS OF POLYCHLORINATED N-ALKANES ON THE CHEMICAL STRUCTURE, MECHANICAL AND THERMAL PROPERTIES OF THE STYRENE-BUTADIENE STYRENE TRIBLOCK COPOLYMER

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The development of new functional materials based on modified styrene-butadiene block copolymers will enable the creation of materials with improved resistance to gasoline, heat, light, ozone, and enhanced adhesive properties. This study investigates the influence of chlorinated paraffin on the properties of the styrene-butadiene-styrene triblock copolymer. Chlorinated paraffins (CP), complex mixtures of polychlorinated n-alkanes, were used as halogen-containing modifiers for the thermoplastic elastomer to enhance its tensile and adhesive strength and thermal properties. Composite materials based on styrene-butadiene-styrene copolymer (SBS) with various amounts of chlorinated paraffin were prepared using a solution mixing method. The analysis of the ATR/FT-IR spectra of neat SBS and SBS/CP revealed the appearance of new characteristic absorption bands at 1260, 1090, 1020, and 800 cm⁻¹. The study determined that the amount of chlorinated paraffin strongly influenced specific properties of the examined TPE. It was observed that chlorinated paraffin improved the thermal stability of the composites. The onset temperature of degradation increased to 262 °C (a rise of 57 °C), while the maximum degradation temperature slightly increased from 463 to 467 °C. The impact of the concentration of chlorinated paraffin on the chemical structure and tensile properties was evaluated and compared to those of neat styrene-butadiene-styrene. It was estimated that SBS composites with 5 ppm. CPs are characterized by improved strength properties in comparison with the original SBS sample.

Keywords: styrene-butadiene-styrene triblock copolymer (SBS), polychlorinated n-alkanes, chlorinated paraffin, FT-IR spectroscopy, thermogravimetric analysis, thermal properties, solution mixing

Для цитирования:

Сухарева К.В., Булучевская А.Д., Беседина В.О., Грошева Ю.В., Люсова Л.Р., Попов А.А. Влияние полихлорированных *n*-алканов на химическую структуру, механические и термические свойства блок-сополимеров стирола и бутадиена. *Изв. вузов. Химия и хим. технология*. 2024. Т. 67. Вып. 6. С. 100–108. DOI: 10.6060/ivkkt.20246706.6973.

For citation:

Sukhareva K.V., Buluchevskaya A.D., Besedina V.O., Grosheva Yu.V., Lyusova L.R., Popov A.A. Effects of polychlorinated *n*-alkanes on the chemical structure, mechanical and thermal properties of the styrene-butadiene styrene triblock copolymer. *ChemChemTech [Изв. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2024. V. 67. N 6. P. 100–108. DOI: 10.6060/ivkkt.20246706.6973.

INTRODUCTION

Polymer materials based on styrene and butadiene block copolymers constitute approximately 75%

of the global market for thermoplastic elastomers and over 80% of the domestic market. They find primary use in producing shoe sole materials, anti-corrosion

coatings, waterproofing mastics, and modifying plastics and road bitumens [1]. The most significant application of styrene-butadiene block copolymers is observed in roofing and road asphalt materials. The primary advantage of thermoplastic elastomers (TPEs) over traditional rubber lies in the elimination of the need for vulcanization, complex multi-component formulations, as well as their enhanced ease of processing, secondary processing, and reusability. However, in comparison to rubber, TPEs have drawbacks, including relatively high raw material costs, an inability to be diluted with inexpensive fillers like carbon black, and lower chemical and temperature resistance.

Manufacturers produce adhesives based on these copolymers for various industries such as construction, food and medical product manufacturing, footwear and furniture adhesives, as well as adhesives for different types of tapes. The global market is witnessing a rise in special adhesive grades based on these block copolymers. Replacing polychloroprene with styrene-butadiene thermoplastic elastomers often encounters challenges due to the non-polarity and low adhesive activity of the thermoplastic elastomers. Developing new functional materials based on modified styrene-butadiene block copolymers will enable the production of materials with improved resistance to gasoline, heat, light, ozone, and enhanced adhesive properties.

Among all known types of produced thermoplastic elastomers used as adhesives, butadiene-styrene or divinyl styrene thermoplastic elastomers are the most widely used. Compared to polychloroprene, they have lower tackiness, poorer adhesive properties, and thermal resistance. However, by correctly selecting the bonding technological parameters, the properties of adhesive compositions based on butadiene-styrene TPEs approach the properties of polychloroprene adhesives.

Butadiene-styrene TPEs provide high tensile strength without fillers and vulcanization, exhibit good creep resistance, good compatibility with general-purpose rubbers, and other ingredients. They are technologically efficient when processed through solutions: they do not require plasticization, dissolve with much less time and energy than rubbers, and allow the creation of solutions with low viscosity at a high dry residue content.

Modification of thermoplastic elastomers can be carried out through the introduction of functional additives. Several studies [2, 3] have focused on reinforcing thermoplastic elastomers with carbon fibers. These fibers possess properties such as a high strength-to-weight ratio, excellent wear resistance, and stiffness, which give them an advantage over other materials like metals. The influence of technical carbon on

the electrical conductivity and mechanical properties of thermoplastic elastomers was also investigated [4]. The addition of technical carbon and ethylene glycidyl methacrylate to the thermoplastic elastomer matrix affected electrical conductivity, tensile properties, and impact viscosity. The tensile strength and impact viscosity of the TPE/EGMA blends were significantly improved with the addition of EGMA and modified technical carbon.

In various studies, the use of different metal-containing additives for thermoplastic elastomer modification has been examined. For instance, the inclusion of nano-aluminum oxide powder [5] in a thermoplastic polystyrene matrix is advantageous for improving thermal and mechanical properties. Some additives, particularly those containing silver nanoparticles (AgNp, 0.05%), titanium dioxide (TiO₂, 4.0%) [6], copper nanoparticles [7], as well as zinc oxide with colloidal dispersion of metallic silver adsorbed on fumed silica [8], can exhibit antibacterial properties. Several functionalized nanoparticles can impact the thermal stability of the polymer matrix through specific interactions, barrier mechanisms, or restricted chain mobility [9]. A balance between solid filler particles and elastomer in the polymer matrix creates a multiphase polymer system with optimal mechanical characteristics [10], making it promising for various applications [11]. The use of fillers in polymer compositions with thermoplastic elastomers is driven by key beneficial properties such as improved processability, increased modulus of elasticity, and flame resistance. In compositions requiring flame resistance, aluminum or magnesium hydroxide is often used [12]. Previously, the enhancement of flame resistance in easily ignitable SBS was explored through the chemical modification of the polymer with phosphorus-containing substances. It was found [13] that phosphorus-modified SBS undergoes charring, correlating with the reduced flammability of the modified polymer. The resistance of polymer composites to ultraviolet radiation is often improved by introducing UVA and UV stabilizers into the polymer matrix [14]. The incorporation of fillers can also contribute to improved tribological properties of polymers. Fillers can be metallic or ceramic, which affects the specific electrical resistance of the composites [15]. Adding nanoparticles such as carbon nanotubes, graphene, as well as nanoclays, nanocellulose, metals, and ceramics [16] to the thermoplastic elastomer matrix leads to changes in the structural and functional properties of polymer compositions. Various surface modification approaches can be used to modify the filler dispersion and interface in the polymer matrix. It has been discovered that using hybrid fillers under specific conditions produces a synergistic effect,

resulting in a high modulus of elasticity in nanocomposites [17]. Another common method for modifying thermoplastic elastomers is blending them with other polymers. Block copolymers like styrene-butadiene-styrene are compatible with powdered composites made from impact-resistant polystyrene/ethylene-vinyl acetate copolymer/recycled rubber tire materials [18].

Halogenating thermoplastic elastomers will contribute to increasing their compatibility with polar polymers. The chemical modification of elastomers plays a crucial role in enhancing the physical properties of rubbers [19]. Today, the demand for elastomeric materials with specific properties, ensuring performance under extreme conditions, is continually increasing. Among the various types of rubber chemical modification, halogenation reactions are the most common and effective, imparting versatile curing possibilities that enhance adhesion, resistance to aging, and resistance to different chemicals.

The first polymer containing halogens that displays both rubber-like characteristics and the ability to maintain thermoplasticity is plasticized polyvinyl chloride (PVC) [20]. However, authentic thermoplastic elastomers consist of PVC combined with cross-linked or elastomeric polymers. The pioneering example of such a material involves blending PVC with acrylonitrile-butadiene rubber. Furthermore, polyvinyl chloride demonstrates compatibility with other elastomers, including copolyester elastomers, as well as thermoplastic polyurethanes (TPUs). Chemical post-modification of styrene-butadiene copolymers is possible through hydrochlorination and Stieglitz etherification reactions to obtain alkynyl-functionalized styrene-butadiene copolymers [21].

The introduction of halogen-containing adhesion promoters affects the adhesion and bond strength in adhesive joints, the low values of which are the main disadvantages of adhesive compositions based on SBS. Adhesion promoters based on chlorine-containing compounds also affect resistance to aggressive environments and thermal stability. Thus, within the scope of this study, the effect of introducing a chlorine-containing modifier (chlorinated paraffin) on the changes in SBS properties for the creation of adhesive compositions was examined.

MATERIALS AND METHODS

The radial styrene-butadiene styrene triblock copolymer (SBS) was used as the polymer matrix. SBS (grade SBS R 3000A) was supplied by Sibur, Russia. (styrene/butadiene ratio of 30/70, MFR <1 g/10 min (200 °C, 5 kg). SBS R 3000A is commonly used for bitumen and plastic modification, shoe compounds, rubber goods, and protective coatings.

Industrial chlorinated paraffins (CP) are a complex mixture of polychlorinated n-alkanes that differ in chain length composition and degree of chlorination. Technical CP mixtures (CP-66T) (AO Kaustik, Volgograd, Russia) with a chlorine content of 69.5 ± 0.1 wt.%, yellow-tinged and partly clotted powder. CPs are produced by chlorination of alkane mixtures, which leads to complex products of thousands of homologs and congeners. CP-66T product has on average one Cl substituent on almost every carbon atom. According to the alkane chain length, CP-66 T was classified as long-chain chlorinated paraffins. The mean carbon formula of CP ($\text{CH}_{1.30}\text{Cl}_{0.82}$) indicates the approximate mean number of chlorine/hydrogen atoms per carbon atom. Based on the mean carbon formula, 1 g of CP contains 0.695 g of Cl.

SBS/CP composites were prepared by incorporating various amounts (2, 5, 10 and 15 phr) of chlorinated paraffin using the solution blending compounding method according to the recipe from Table 1. The SBS/CP solutions were cast into a glass Petri dish. The solvent was then evaporated at room temperature until a constant weight was obtained.

Table 1
Formulation of chlorine chlorinated paraffin and thermoplastic elastomer solutions
Таблица 1. Рецептура растворов хлорированных парафинов и термоэластопласта

	Mass parts per 100 mass parts of TPE (phr)			Total
	SBS	Toluene	CP	
SBS-0	100	695	0	795
Mass Percentage (w.%)	12.58	87.42	0	100%
SBS-2	100	695	2	797
Mass Percentage (w.%)	12.55	87.20	0.25	100%
SBS-5	100	695	5	800
Mass Percentage (w.%)	12.50	86.88	0.62	100%
SBS-10	100	695	10	805
Mass Percentage (w.%)	12.42	86.34	1.24	100%
SBS-15	100	695	15	810
Mass Percentage (w.%)	12.35	85.80	1.85	100%

For the study of the bond strength of the adhesive joint based on SBS, the basic adhesive formulation was chosen, which is presented in Table 2.

The examination of tensile properties was conducted using a GOTECH testing machine (Turkey) at a testing rate of 500 mm/min. Samples were prepared in the form of strips measuring 7 cm×1 cm. Each data point was confirmed with five measurements.

The processes of thermo-oxidative degradation were investigated using the method of thermo-

gravimetric analysis (TGA) on the TG50 Mettler Toledo instrument (Switzerland) with microbalances M3 under an air flow rate of 200 ml/min in dynamic mode at a rate of 10 °C/min in the temperature range from 25 to 800 °C. The obtained thermograms were processed using Mettler TC 11 software.

Table 2
Formulation of adhesive composition based on SBS
Таблица 2. Рецепттура клевого состава на основе СБС

Ingredients	Dry residue per 100 parts by weight of polymer	Concentration (%)
SBS	100	9.2
Petroleum resin	40	3.7
Glycerol ester of rosin	20	1.84
Dibutyl phthalate	3	0.26
Methylene chloride	924	85
Total	1087	100

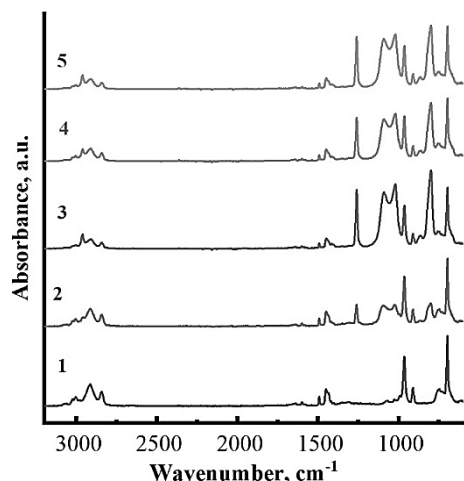


Fig. 1. ATR-FTIR spectra of original SBS and SBS/CP composites with different amount of chlorinated paraffins in the wavelength range of 3200–600 cm^{-1} : 1 – SBS, 2 – SBS-2, 3 – SBS-5, 4 – SBS-10

Рис. 1. ИК спектры (метод НПВО) исходного образца СБС и композитов СБС/ХП с различным содержанием хлорированного парафина в диапазоне волновых чисел 3000–600 cm^{-1} : 1 – СБС, 2 – СБС-2, 3 – СБС-5, 4 – СБС-10

The chemical composition of SBS/CP composites was studied using an FT-IR Lumos BRUKER (Berlin, Germany) spectrometer at a temperature of (22 ± 2) °C in the range of wavenumbers of $4000 \leq \nu \leq 600 \text{ cm}^{-1}$ using the ATR method (diamond crystal).

The determination of the adhesive bond strength based on the modified SBS was carried out in accordance with GOST 6768-75 – Method for determining the bond strength between layers during delamination. For the test, substrates were cut in the form of a rectangle measuring 12×2 cm from shoe rubber based

on SKMS-30 (GOST 7926-75 – Rubber for the sole of shoes). The rubber substrates were glued with a glue solution, which was applied as a thin layer to the sanded and degreased surface. All samples after bonding were subjected to rolling with a roller and kept under a press for 7 days.

RESULTS AND DISCUSSION

Infrared attenuated total reflectance spectroscopy (ATR-FTIR) analysis allows for the study of the chemical structure of polymer surfaces. Fig. 1 and 2 show the ATR-FTIR spectra of neat SBS and SBS-2, SBS-5, SBS-10 and SBS-15.

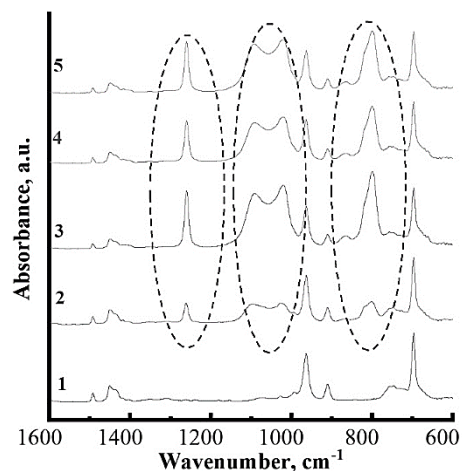


Fig. 2. ATR-FTIR spectra of original SBS and SBS/CP composites with different amount of chlorinated paraffins in the wavelength range 1600–600 cm^{-1}

Рис. 2. ИК спектры (метод НПВО) исходного образца СБС и композитов СБС/ХП с различным содержанием хлорированного парафина в диапазоне волновых чисел 1600–600 cm^{-1} : 1 – СБС, 2 – СБС-2, 3 – СБС-5, 4 – СБС-10

Infrared attenuation of total reflectance spectroscopy (ATR-FTIR) analysis enables the examination of the chemical structure of polymer surfaces. Fig. 1 and 2 display the ATR-FTIR spectra of neat SBS as well as SBS-2, SBS-5, SBS-10, and SBS-15. The ATR/FT-IR spectra of both neat SBS and SBS/CP samples exhibit similar elastomer absorption bands. The FT-IR spectra of SBS block copolymers with varying amounts of chlorinated paraffins reveal distinct elastomer absorption bands: 690 cm^{-1} for polystyrene, 730 cm^{-1} for cis-1,4 bonds of polybutadiene, 910 cm^{-1} for vinyl bonds, and 965 cm^{-1} for trans-1,4 bonds of polybutadiene. Furthermore, specific bands corresponding to polar groups were observed, particularly the characteristic absorptions at 800 cm^{-1} corresponding to the C–Cl bond, as depicted in Fig. 2. C–Cl absorbances are commonly found within the range of 600–800 cm^{-1} [22, 23]. C–O stretching vibrations usually occur within the range of 1260–1000 cm^{-1} . Fourier

transform infrared spectroscopy studies revealed a doublet band in the interval of 1090-1020 cm^{-1} , attributed to the vinyl acetate C–O stretching vibration. This absorption spectrum was observed for all SBS samples with chlorinated paraffins. The peak near 1265 cm^{-1} in the ATR/FT-IR data represents the –C–O single bond vibration of the –C–OH group. Table 3 presents the optical densities of the vibrational bands in the SBS and SBS/CP samples.

Table 3

Relative density of absorption bands in ATR/FT-IR spectra of original SBS and SBS/CP composites

Таблица 3. Относительная плотность полос поглощения в спектрах НПВО/ИК-Фурье исходного СБС и композитов СБС/ХП

Absorbance	Sample				
Wavenumber (cm^{-1})	SBS	SBS-2	SBS-5	SBS-10	SBS-15
A_{697} / A_{964}	1.4	1.4	1.4	1.4	1.4
A_{800} / A_{690}	-	0.18	1.01	1.26	1.6
A_{1260} / A_{1450}	-	1.42	3.55	5.46	7.95

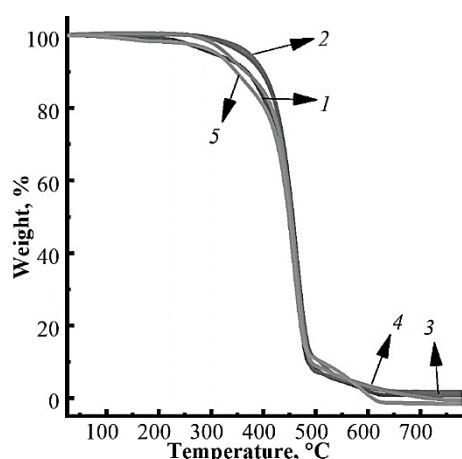


Fig. 3. TG curves of SBS/CP composites: SBS (curve 1), SBS-2 (curve 2), SBS-5 (curve 3), SBS-10 (curve 4), SBS-15 (curve 5)
Рис. 3. ТГ кривые композитов СБС/ХП: СБС (кривая 1), СБС-2 (кривая 2), СБС-5 (кривая 3), СБС-10 (кривая 4), СБС-15 (кривая 5)

The absorption intensity ratio of the band at 697 cm^{-1} to the band at 964 cm^{-1} remains consistent across all SBS samples. In comparison to the spectra of pure SBS, the peak identified at 800 cm^{-1} corresponds to the characteristic frequency of C–Cl vibration. As the amount of introduced chlorinated paraffin increases, the ratio of optical densities between the band associated with C–Cl bonding vibrations and the vibrations of the styrene block significantly increases. An increase in the absorption bands ratio of 1260/1450 cm^{-1} indicates a higher quantity of oxygen-containing groups in the composite samples as the amount of in-

roduced chlorinated paraffin increases. The appearance of these oxygen-containing functional groups suggests that oxygen became incorporated into the polymer chains due to the modification process.

The TGA mass loss curves are presented in Fig. 3. For each composite material, the mass loss factors are determined, including T_5 , T_{10} , T_{50} (temperature at 5%, 10%, and 50% weight loss, respectively), and T_{max} (temperature of the maximal rate of decomposition). The measurement data are further summarized in Table 4.

Table 4

Data on the analysis of TG curves of thermal oxidative degradation of SBS/CP and the original SBS sample

Таблица 4. Данные по анализу ТГ кривых термоокислительной деструкции эластомерных композитов СБС/ХП и исходного образца СБС

Sample	ITD	T_{max}	$T_5/^\circ\text{C}$	$T_{10}/^\circ\text{C}$	$T_{50}/^\circ\text{C}$
SBS	205	463	309	372	453
SBS-2	262	467	376	403	460
SBS-5	255	467	365	399	459
SBS-10	248	466	332	370	457
SBS-15	222	460	314	350	451

The decomposition process of SBS/CP composites consists of one major stage. Thermal analysis has indicated that the presence of polychlorinated n-alkanes affects the thermal properties of the SBS/CP composites. The thermal degradation mechanism of SBS involves two primary processes: chain scission and crosslinking [24]. In the block copolymer exposed to atmospheric air, initial thermo-oxidative degradation occurs through the attack on unsaturated bonds in polybutadiene. SBS can be completely pyrolyzed in air. The SBS/CP blend systems exhibit better thermal stability than neat SBS due to a higher thermal degradation temperature. As observed in the TG plots, the onset and maximum decomposition temperatures shift to higher values after the addition of the polychlorinated n-alkanes. The T_5 and T_{50} values of SBS-2 are higher than those of pure SBS. This is likely due to interactions between SBS and chlorinated paraffin. Polychlorinated n-alkanes shield SBS from degradation at higher temperatures, resulting in an improvement in the thermal stability of SBS composites. Under oxidative degradation conditions, the onset temperature of degradation increased to 262 $^\circ\text{C}$ (an increment of 57 $^\circ\text{C}$), while the maximum degradation temperature underwent a slight change (from 463 to 467 $^\circ\text{C}$).

The relationship between the thermal stability of the four polymers and the content of polychlorinated n-alkanes is best characterized by T_5 , which represents the temperature at which 5% mass loss occurs. Table

4 illustrates that, for SBS-0, T_{10} is 309 °C, while for SBS-2, T_5 is 376 °C. SBS samples with higher chlorine content are more likely to release HCl at the experimental temperature. Chlorine can create additional stable crosslinks between the polymer chains in the butadiene block, playing a significant role in enhancing the thermal stability of the elastomeric materials.

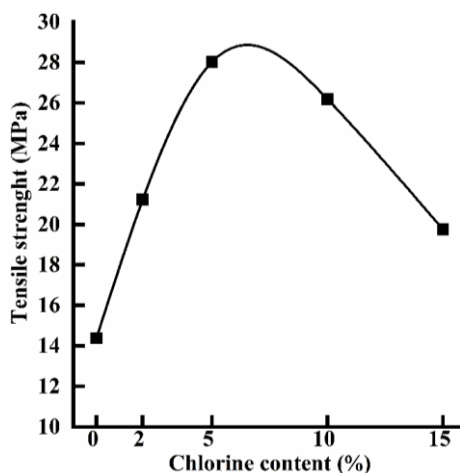


Fig. 4. Effect of chlorinated paraffin content on tensile strength of SBS/CP composites

Рис. 4. Влияние содержания хлорированного парафина на прочность композитов СБС/ХП

As the content of polychlorinated n-alkanes increases, the tensile strength of SBS/CP composites also increases. The highest tensile strength value of 28 MPa was achieved when the chlorine content was 5 phr, which was twice as high as that of pure SBS (14.2 MPa). From Fig. 4, it is evident that the tensile strength of films made from chlorinated SBS initially increases from the SBS-0 sample to SBS-5, and then gradually decreases from SBS-5 to SBS-15. This leads to the conclusion that the highest tensile strength is found in samples made from styrene-butadiene TPE with low chlorine content. The optimal result is observed in SBS-5. The lowest strength values are observed in the original thermoplastic elastomer. An increase in the amount of introduced polychlorinated n-alkanes beyond 5 phr likely leads to an accumulation of excess chlorinated paraffin in the sample, which acts as a plasticizer for the elastomer and consequently reduces the strength properties of the rubber.

The modified SBS presented in the work is considered for use in the adhesive industry. In this regard, the influence of the amount of chlorinated paraffin introduced into the SBS matrix on the adhesive characteristics of the adhesive composition based on it was studied. Fig. 5 shows a graph of the dependence of the bond strength of the adhesive joint on the amount of modifier.

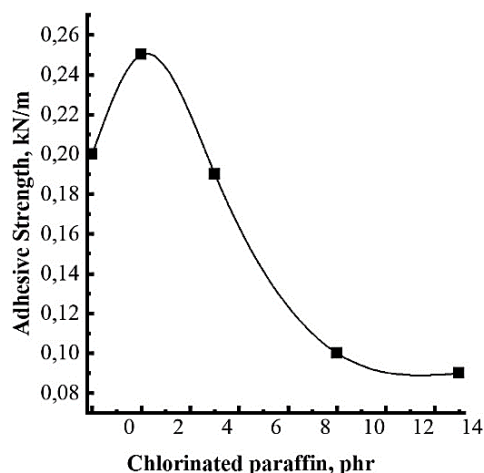


Fig. 5. Effect of chlorinated paraffin content on adhesive strength of SBS/CP composites

Рис.5. Влияние содержания хлорированного парафина на прочность связи композитов СБС/ХП

From the results presented in Fig. 5, the adhesive strength of solutions made from chlorinated SBS initially increases with the introduction of chlorinated paraffin from the SBS-0 sample to SBS-5 by 45% (from 0.20 kN/m to 0.29 kN/m), and then sharply decreases from SBS-5 to SBS-20.

A small amount of introduced chloroparaffin acts as an additive, imparting additional functionality (polarity property) to the polymer and enhancing its adhesive characteristics. Polar additives containing active functional groups, such as synthetic resins with polar groups, are introduced into rubbers and latexes to increase the bond strength when adhering to various substrates [25, 26]. Introducing new halogen-containing polar groups into the elastomer matrix allows the adhesive based on it to interact with both non-polar rubber (SKMS) and some polar additives included in the formulation.

However, an increase in its quantity beyond 5 wt.% leads to the accumulation of low-molecular-weight chloroparaffin within the polymer matrix. This modifier functions similarly to a surfactant, adsorbing at the adhesive interface between the adhesive and rubber and obstructing adhesion. Similar patterns were observed in the work [27] which demonstrated that small additions of surfactants up to 1% (mixtures of paraffinic emulsifiers with fatty acid derivatives), introduced into the adhesive composition formulations, exert a modifying effect on adhesion characteristics. However, exceeding the permissible concentration limit of surfactants leads to changes in the surface tension of the adhesive film and a decrease in adhesive strength.

CONCLUSION

The results demonstrate that chlorinated paraffin can effectively serve as a modifier for the styrene-butadiene-styrene triblock copolymer. The structure and morphology of composite materials were examined using Fourier-transform infrared spectroscopy (FTIR) in ATR mode. In comparison to neat SBS, new absorption bands were observed at 1260, 1090, 1020, and 800 cm^{-1} . The appearance of characteristic absorptions at 800 cm^{-1} was attributed to the C–Cl bond. A doublet band ranging from 1090 to 1020 cm^{-1} was assigned to the vinyl acetate C–O stretching vibration. The peak around 1260 cm^{-1} corresponds to the –C–O single bond vibration of the –C–OH group. Thermal analysis in an oxygen atmosphere showed that the inclusion of chlorinated paraffin caused an increase in the thermal stability of the tested SBS/CP compositions. The tensile properties of the composite materials increased with an increase in mass fraction of chlorinated paraffins up to 5 phr. However, an increase in the amount of polychlorinated n-alkanes introduced beyond 5 phr led to a drop in tensile properties. This drop could be attributed to the accumulation of excess chlorinated paraffin in the sample, acting as a plasticizer for the elastomer and consequently reducing the strength properties of the rubber. The adhesive strength of solutions made from chlorinated SBS initially increases with the introduction of chlorinated paraffin from the SBS-0 sample to SBS-5 by 45% (from 0.20 kN/m to 0.29 kN/m), and then sharply decreases from SBS-5 to SBS-20.

The study revealed that polychlorinated n-alkanes in the amount of 2-5 phr can be successfully used in composite materials based on SBS.

ACKNOWLEDGMENTS

The work was carried out using the equipment of the Center of Shared Usage «New Materials and Technologies» of Emanuel Institute of Biochemical Physics, Joint Research Center of Plekhanov Russian University of Economics.

This study was financed by a grant from the Plekhanov Russian University of Economics.

Работа выполнена с использованием оборудования Центра коллективного пользования «Новые материалы и технологии» Института биохимической физики им. Эмануэля Объединенного научного центра Российского экономического университета имени Плеханова. Исследование выполнено за счет гранта Российского экономического университета имени Плеханова.

CONFLICT OF INTERESTS

The authors declare the absence a conflict of interest warranting disclosure in this article.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

ЛИТЕРАТУРА
REFERENCES

1. **Гувалов А.А., Мамедов А.Д., Кахраманов Н.Т.** Влияние модификаторов на свойства битума и асфальтобетона. *Изв. вузов. Химия и хим. технология*. 2021. Т. 64. Вып. 10. С. 98-104. **Guvalov A.A., Mamedov A.D., Kakhramanov N.T.** Влияние модификаторов на свойства битума и асфальтобетона. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2021. Т. 64. Вып. 10. С. 98-104. DOI: 10.6060/ivkkt.20216410.6383.
2. **Gopinath S., Radhakrishnan N.P., Mathew S.** Study on thermal and mechanical properties of SBS/PCL based thermo-responsive shape memory polymer nanocomposite actuator. *Mater. Today: Proc.* 2020. V. 24. P. 1742–1748. DOI: 10.1016/j.matpr.2020.03.598.
3. **Alshammari B.A., Alsuhybani M.S., Almushaikeh A.M.** Comprehensive review of the properties and modifications of carbon fiber-reinforced thermoplastic composites. *Polymers*. 2021. V. 13(15). 2474. DOI: 10.3390/polym13152474.
4. **Yasar M., Bayram G., Celebi H.** Effect of carbon black and/or elastomer on thermoplastic elastomer-based blends and composites. *AIP Conf. Proc.* 2015. V. 1664. 120003. DOI: 10.1063/1.4918493.
5. **Chen C.-M., Chang H.-L., Lee C.-Y.** The dynamic properties at elevated temperature of the thermoplastic polystyrene matrix modified with nano-alumina powder and thermoplastic elastomer. *Polymers*. 2022. V. 14(16). 3319. DOI: 10.3390/polym14163319.
6. **Tomacheski D., Pittol M., Simões D.N.** Influence of natural ageing on mechanical, thermal and antimicrobial properties of thermoplastic elastomers containing silver nanoparticles and titanium dioxide. *Polym. Bull.* 2018. V. 75(9). P. 3917–3934. DOI: 10.1007/s00289-017-2245-2.
7. **Ribeiro V. F., Simões D.N., Pittol M.** Effect of copper nanoparticles on the properties of SEBS/PP compounds. *Polym. Testing*. 2017. V. 63. P. 204–209. DOI: 10.1016/j.polymertesting.2017.07.033.
8. **Marchini L.G., Parra, D.F., Rangari V.K.** Incorporation of silver nanoparticles in zinc oxide matrix in polyester thermoplastic elastomer (TPE-E) aiming antibacterial activity. *Magnesium Technol.* 2019. P. 79–88. DOI: 10.1007/978-3-030-05749-7_9.
9. **Król-Morkisz K., Pielichowska K.** Thermal decomposition of polymer nanocomposites with functionalized nanoparticles. *Polymer Composites with Functionalized Nanoparticles*. Elsevier. 2019. P. 405–435. DOI: 10.1016/B978-0-12-814064-2.00013-5.
10. **Ez-Zahraoui S., Sabir S., Berchane S.** Toughening effect of thermoplastic polyurethane elastomer on the properties of fly a reinforced polypropylene-based composites. *Polym. Comp.* 2023. V. 44 (3). P. 1534–1545. DOI: 10.1002/pc.27186.
11. **Кахраманов Н.Т., Гасанова А.А., Аллахвердиева Х.В., Мустафаева Ф.А., Абдалова С.Р.** Физико-механические свойства композитов на основе полиэтилена низкой плотности и термозолы бытовых отходов. *Изв. вузов. Химия и хим. технология*. 2022. Т. 65. Вып. 8. С. 125-133.

- Kakhramanov N.T., Hasanova A.A., Allahverdiyeva K.V.** Физико-механические свойства композитов на основе полиэтилена низкой плотности и термозолы бытовых отходов. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2022. Т. 65. Вып. 8. С. 125–133. DOI: 10.6060/ivkkt.20226508.6583.
12. **Rothon R., DeArmitt C.** Fillers (Including Fiber Reinforcements). *Brydson's Plastics Materials*. Elsevier. 2017. P. 169–204. DOI: 10.1016/B978-0-323-35824-8.00008-6.
 13. **Chernyy S., Ullah S., Jomaas G.** Modification of poly(styrene-block-butadiene-block-styrene) [SBS] with phosphorus containing fire retardants. *Eur. Polym. J.* 2015. V. 70. P. 136–146. DOI: 10.1016/j.eurpolymj.2015.07.015.
 14. **Ching Y.C., Gunathilake T.U., Ching K.Y.** Effects of high temperature and ultraviolet radiation on polymer composites. Durability and Life Prediction in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites. Elsevier. 2019. P. 407–426. DOI: 10.1016/B978-0-08-102290-0.00018-0.
 15. **Brostow W., Lobland H., Hnatchuk N.** Improvement of scratch and wear resistance of polymers by fillers including nanofillers. *Nanomaterials*. 2017. V. 7 (3). P. 66. DOI: 10.3390/nano7030066.
 16. **Peponi L., Puglia D., Torre L.** Processing of nanostructured polymers and advanced polymeric based nanocomposites. *Mater. Sci. Eng.: R: Rep.* 2014. V. 85. P. 1–46. DOI: 10.1016/j.mser.2014.08.002.
 17. **Dubey K.A., Hassan P.A., Bhardwaj Y.K.** High performance polymer nanocomposites for structural applications. *Mater. Under Extreme Conditions*. 2017. P. 159–194. DOI: 10.1016/B978-0-12-801300-7.00005-X.
 18. **Wang Z., Zhang Y., Du F.** Thermoplastic elastomer based on high impact polystyrene/ethylene-vinyl acetate copolymer/waste ground rubber tire powder composites compatibilized by styrene-butadiene-styrene block copolymer. *Mater. Chem. Phys.* 2012. V. 136(2–3). P. 1124–1129. DOI: 10.1016/j.matchemphys.2012.08.063.
 19. **Sukhareva K.V., Sukharev N.R., Levina I.I.** Solvent swelling-induced halogenation of butyl rubber using polychlorinated n-alkanes: structure and properties. *Polymers*. 2023. V. 15(20). P. 4137. DOI: 10.3390/polym15204137.
 20. **Drobny J.** Thermoplastic elastomers based on halogen-containing polyolefins. *Handbook of Thermoplastic Elastomers*. 2007. P. 201–214. DOI: 10.1016/B978-0-81551549-4.50009-8.
 21. **Wittenberg E., Abetz V.** New post modification route for styrene butadiene copolymers leading to supramolecular hydrogen bonded networks - synthesis and thermodynamic analysis of complexation. *Polymer (Guildf)*. 2017. V. 121. P. 304–311. DOI: 10.1016/j.polymer.2017.06.001.
 22. **Ashok N., Balachandran M., Lawrence F.** EPDM-chlorobutyl rubber blends in γ -radiation and hydrocarbon environment: mechanical, transport, and ageing behavior. *J. Appl. Polym. Sci.* 2017. V. 134 (33). P. 45195. DOI:10.1002/app.45195.
 23. **Pazur R.J., Petrov I.** The thermo-oxidation of chlorinated and brominated isobutylene-co-isoprene polymers: activation energies and reactions from room temperature to 100 °C. *Polym. Degrad. Stabil.* 2015. V. 121. P. 311–320. DOI: 10.1016/j.polymdegradstab.2015.09.023.
 24. **Su T.-T., Jiang H., Gong H.** Thermal stabilities and thermal degradation kinetics of a styrene-butadiene-styrene star block copolymer. *Polym.-Plast. Technol. Eng.* 2009. V. 48(5). P. 535–541. DOI: 10.1080/03602550902824341.
 25. **Zhang J., Luo H., Zhou X.** Epoxy resin adhesives: modification and applications. *Epoxy-Based Composites*. IntechOpen. 2022. DOI: 10.5772/intechopen.101971.
 26. **Chudzik J., Bieliński D.M., Demchuk Y.** Influence of modified epoxy dian resin on properties of nitrile-butadiene rubber (NBR). *Materials*. 2022. V. 15(8). P. 2766. DOI: 10.3390/ma15082766.
 27. **Kozorez M.D., Kotova S.V., Lyusova L.R.** The role of surfactants in adhesives based on nitrile rubbers. *Kauchuk Rezina/Adhesion*. 2023. V. 82. N 4. P. 186–190. DOI:10.47664/0022-9466-2023-82-4-186-190.

Поступила в редакцию 20.09.2023

Принята к опубликованию 13.11.2023

Received 20.09.2023

Accepted 13.11.2023