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Effect of plasticizers of different polarity on dynamic mechanical properties of butyl rubber

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ABSTRACT

The article presents the results of studies of the influence of the concentration of three types of plasticizers with different percentages on the dynamic mechanical properties of mixtures based on elastomer: butyl rubber (BR) / industrial oil, BR/chlorinated paraffin, BR/dioctyl phthalate. Plasticizers were taken in a ratio of 20 to 40% by volume. The leading research methods were a comparative analysis of the temperature-frequency dependence of the loss tangent and the elastic modulus, obtained by the method of dynamic mechanical analysis (DMA). The developed compositions of the composite material were tested by IR spectroscopy. It has been established that in order to obtain self-adhesive composite materials with high damping properties, a plasticizer-industrial oil with a minimum content of 40 % should be used. Based on the conducted studies, it was proved that when plasticizers of various types and polarities are introduced into butyl rubber, the properties of the compositions change depending on the concentration of the plasticizer, the molecular structure and the forces of intermolecular interaction. It was revealed by infrared spectroscopy that no chemical interaction occurs in the polymer matrix of butyl rubber, on the grounds that the influence of the components on the intensity or magnitude of the peak is not traced.

KEYWORDS

elastic modulus • mechanical loss $\tan \delta$ • temperature • butyl rubber (BR) • plasticizers • industrial oil (IO) chlorinated paraffin (CP) • dioctyl phthalate (DOP)

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Introduction

Increased levels of harmful noises and vibrations can have undesirable effects on humans and structures in general. Using materials with high damping properties is an effective method for reducing noise and vibration. Analysis of different vibration-damping materials indicates that the highest damping characteristics are found in materials containing polymers [1–3], which can undergo significant reversible deformations at low stresses [4]. Vibration absorption (damping) is a method for reducing vibration by inducing internal friction processes in the structure, dissipating vibration energy by irreversibly transforming it into heat during deformation occurring in materials [5]. The measure of vibration damping is the mechanical loss tangent ($\tan \delta$), which is a characteristic of the lag between strain and stress, damping materials must meet the requirement that $\tan \delta > 0.3$ [6–8].

As a rule, rubbers are used as a basis for composite materials with vibration-damping properties [7,9–12] since their glass transition temperature lies in the region of negative temperatures. The properties of polymer composite materials are also influenced by plasticizing additives introduced into the polymer to reduce the glass transition temperature, to expand the temperature range of the highly elastic state of the polymer and to improve machinability. Esters of aliphatic and aromatic carboxylic acids, polyesters, epoxidized compounds, synthetic and vegetable oils are most commonly used [13]. Various types of oils are commonly used as plasticizers for composite vibration-damping materials based on BR [14,15].

The mechanism of plasticization is considered in [3,5,16], finding the main factors influencing the plasticizing efficiency: the amount of plasticizer introduced into the polymer, the chemical structure of the polymer and plasticizer, their thermodynamic compatibility, volume, shape and size of plasticizer molecules, ability for conformational transformations (flexibility of polymer molecules). Processes of molecular dispersion, transformations in the structure of the mixture and variations in molecular mobility occur upon contact of the polymer with the plasticizer, affecting such characteristics as glass transition temperature (T_g), flow temperature (T_f), dynamic modulus (E'), mechanical loss tangent ($\tan \delta$) and others.

From a physicochemical standpoint, the thermodynamic affinity of polymers is characterized by the amount of mutual solubility. The ability of polymers to swell or dissolve in different solvents depends on the structure of the molecules. The swelling and solubility of a polymer in a particular solvent depend on the interactions of functional groups or atoms, forming bonds producing stable complexes of polymer macromolecules with solvent molecules. As a liquid plasticizer penetrates into the polymer phase, its molecular or colloidal dispersion can occur (Fig. 1).

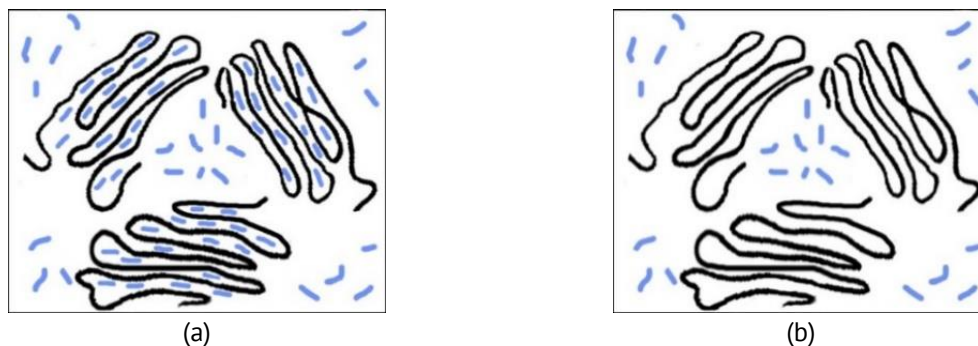


Fig. 1. Scheme of plasticizer interaction: a) molecular dispersion (intrastructural plasticization); colloidal dispersion (interstructural plasticization)

Earlier studies have accumulated knowledge on the mechanism of plasticization, when the properties of composites change depending on their polarity. Figure 1(a) shows a strong intermolecular interaction of plasticizer molecules with polymer macromolecules, plasticizer molecules penetrate into any supramolecular structures, gradually destroying them. The polymer macromolecules in the plasticizer solution are shaped like unfolded loose coils. The polymer is the dispersion medium under colloidal dispersion (Fig. 1(b)), and the plasticizer is the dispersed phase [17]. The molecules are simply embedded between individual polymer chains and destroy polymer-polymer interactions without penetrating inside. Depending on the quality of the solvent, the polymer macromolecules in the solution are shaped as more folded Gaussian coils, rather

than unfolded loose coils, since there is virtually no interaction with the solvent [18]. Such a physical interaction differs from a chemical one in that old chemical bonds do not break and new ones do not form, but forces of attraction or repulsion arise due to interactions between molecules. Intermolecular interactions (between electrically neutral molecules or atoms) were first considered by Van der Waals in 1873.

Analysis of the literature data allowed to determine the composition of the structure-forming materials used for damping composite materials and establish that there are practically no studies investigating the mechanisms behind the influence that varying the concentration of plasticizers (industrial oil (IO), chlorinated paraffin (CP) and dioctyl phthalate (DOP)) has on the elastic and relaxation properties of BR-based composite materials in a wide temperature range. For comparison, consider three different types of plasticizers, differing in their properties: non-polar, polar and weakly polar, since the properties of the compositions vary depending on the polarity of the plasticizers [19,20]. Some molecules do not have polar bonds, because the electron charge is the same on both atoms, therefore, these are non-polar molecules [21]. Polarity has a direct relationship with such quantity as compatibility, understood as the ability to 'dissolve' at the molecular level. Polymer mixtures are divided into compatible, those with limited compatibility, and incompatible. The solubility parameters of the materials (Table 1) allow to assess the compatibility of the mixture components with respect to non-polar butyl rubber.

Table 1. Solubility parameters of materials used [22]

Parameter	BR	IO	CP	DOP
Solubility, $\text{kJ}/(\text{cm}^3)^{0.5}$	16.6	16.1	19.5	18.2

The solubility parameter for butyl rubber was calculated in accordance with Hoy [20]. The parameters for BR and IO have similar values, therefore, they can be assumed to be compatible (*miscible, with complete mutual solubility*), interphase interactions consisting of formation of chemical bonds are absent in them [18,23]. Similarly, it can be assumed that CP is incompatible, and DOP is a weakly compatible plasticizer with BR.

Reviewing studies by Russian and foreign scholars on the processes of structure formation, development of compositions and technologies for fabricating building materials and polymer-based products, we found that experimental studies were not carried out, despite the nature of plasticiser influence, the dynamic and mechanical characteristics of various BR-based plasticizers were not considered. Our goal was thus to identify the influence of different types of plasticizers on the dynamic characteristics of a composite material based on BR in a wide temperature and frequency range, depending on the concentration of the plasticizer.

Materials and Methods

Materials

The base polymer chosen for obtaining composite materials was BR-1675N grade butyl rubber (Arsenal Kama, Russia). To reduce the viscosity of the specimens, improve machinability and damping properties of BR-based composite materials, plasticizers were introduced at a 60 / 40 % by volume: non-polar industrial oil I-40 (IO), GOST 20799-880

(Rosneft, Russia); polar chlorinated paraffin CP-470 (CP) TU 2493-379-05763441-2002 (JSC Acoustic, Russia); weakly polar dioctyl phthalate (DOP) GOST 8728-88 (BinaGroup, Russia).

Preparation of composites

The composites were prepared using a laboratory mixer with Z-shaped rotating blades at a temperature of 80 °C for 1 hour. The specimens were prepared by milling. The grades and ratios of the components are given in Table 2.

Table 2. Grades and ratios of structure-forming components

No.	Grade	Volume fraction, %		Mass fraction, g	
		BR	plasticizer	BR	plasticizer
1	BR	100	0	64.4	0
2	BM-20	80	20	51.52	12.6
3	BM-30	70	30	45.08	18.9
4	BM-40	60	40	38.64	25.2
5	BM-50	50	50	32.2	31.5
6	BX-20	80	20	51.52	17.29
7	BX-30	70	30	45.08	25.94
8	BX-40	60	40	38.64	34.58
9	BD-20	80	20	51.52	13.78
10	BD-30	70	30	45.08	20.66
11	BD-40	60	40	38.64	27.55

The mass content was calculated based on the data for the true density of plasticizers: 0.900 g/cm³ for IO; 1.235 g/cm³ for CP; 0.984 g/cm³ for DOP.

Methods

1. Dynamic mechanical analysis was carried out with a Netzsch DMA242 analyzer (Netzsch, Germany) for specimens shaped as 2 mm thick disks, which corresponds to ASTM D4065-12 *Standard Practice for Plastics: Dynamic Mechanical Properties: Determination and Report of Procedures*. The temperatures in the tests ranged from -80 to +40 °C, with a heating rate of 2 °/min. The mixtures were studied at a frequency of 1, 10, 100 Hz.
2. Spectral analysis was performed with an Infracum FT-801 FTIR spectrometer in the range of 400–4000 cm⁻¹ at ambient temperatures from 18 to 25 °C, recording the absorption spectra of the specimens.

Results and Discussion

Figure 2 shows the variation in the dynamic elastic modulus (E') and the mechanical loss tangent ($\tan \delta$) of composites with three different types of plasticizers (CP, IO, DOP) at a concentration of 20 %. It can be observed from the DMA curves in this temperature range that the elastic modulus for all three plasticizers decreases monotonically with increasing temperature, becoming the most pronounced at 1000 MPa for BR modified with chloroparaffin, exhibiting an average value of 800 MPa for the composite with dioctyl phthalate, and reaching the lowest value at 100 MPa for the composite with industrial oil (comparison of all three composites was performed in the temperature range from -80 to

+40 °C). The value of $\tan \delta$ has an extreme character, with the the peak on the graph corresponding to the transition of the material from a glassy to a highly elastic state. The peaks of $\tan \delta$ have the following values: 1.6 at a temperature of -60 °C for CP; 1.6 at -57 °C for IO, 1.39 at -55 °C for DOP. The maximum value of the loss tangent (the main characteristic of vibration damping) is found in mixtures with CP and IO. Increasing the vibrational frequency by an order of magnitude leads to a shift in all curves towards an increase in temperature by approximately the same values, 16–17 degrees.

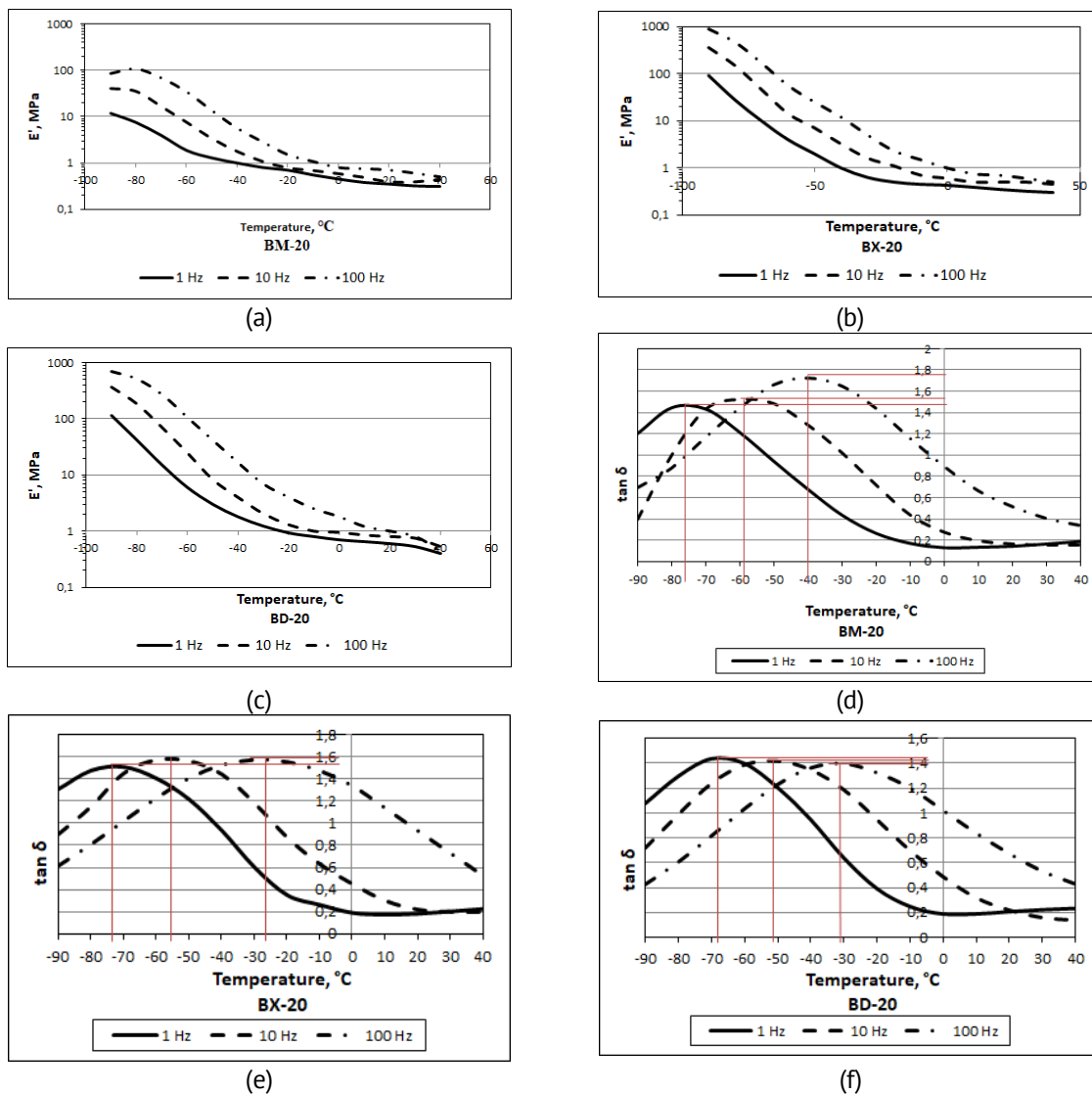


Fig. 2. Dependences of E' and $\tan \delta$ on temperature for: BM-20 (a,b), BX-20 (c,d), BD-20 (e,f) (with a volume fraction of BR/plasticizer 80/20 at frequencies of 1 Hz, 10 Hz, 100 Hz)

Increasing the concentration of the plasticizer (for example, industrial oil, Fig. 3) leads to a decrease in the glass transition temperature of the composite, manifesting as a shift of the $\tan \delta$ peak towards a decrease in temperature with a simultaneous increase in the maximum $\tan \delta$ value.

Graphs for the variation in the glass transition temperature (T_c) and the maximum $\tan \delta$ depending on the type and volume fraction of the plasticizer are shown in Fig. 4.

Analyzing the results obtained for the values of T_c and $\tan \delta$, we found that an increase in $\tan \delta$ and an expected decrease in T_c occur for all studied plasticizers with an increase in the proportion of plasticizer in all mixtures with a filling from 0 to 20 %. However, further increasing the fraction of plasticizer to 40 % produces a slight increase in the T_c of mixtures with weakly polar DOP and polar CP, while the glass transition temperature of the mixture with non-polar IO continues to decrease to -70 °C. Mixtures with DOP and CP have a slight increase in $\tan \delta$, and the mixture with non-polar IO exhibits a large increase in $\tan \delta$ to 1.6 arbitrary units.

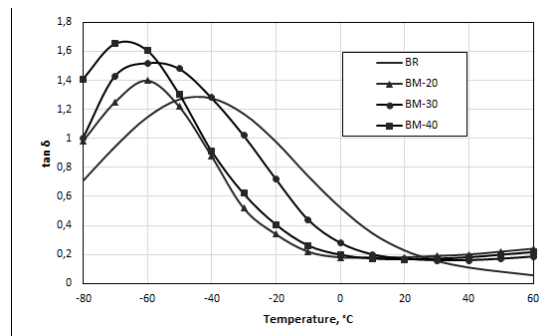


Fig. 3. Dependence of $\tan \delta$ in a BR/oil mixture with different volume fractions: 100/0, 80/20, 70/30, 60/40 (vol. %) at a frequency of 10 Hz

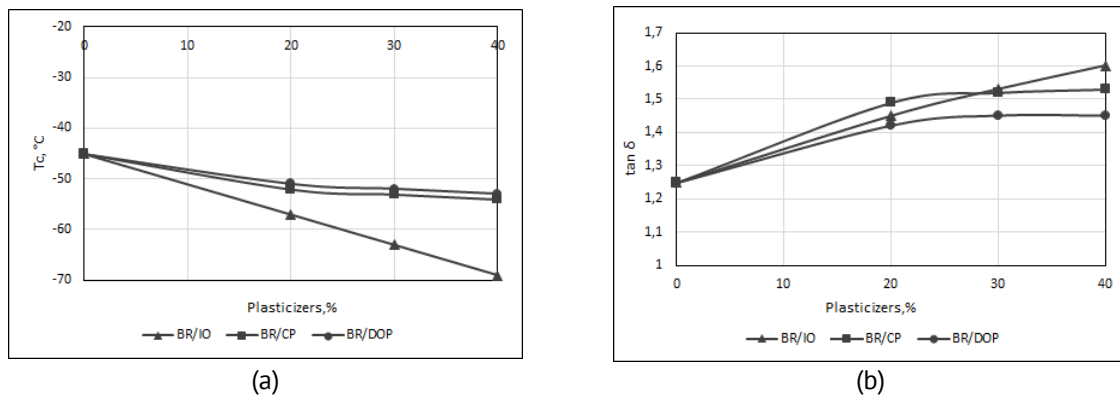


Fig. 4. Variation in T_c (a) and maximum $\tan \delta$ (b) for all three types of plasticizers with the concentration varied from 0 to 40 vol. %

Such an increase in $\tan \delta$ can be associated with an increase in the flexibility of molecules. A true solution is spontaneously formed during the intrastructural plasticization of non-polar BC with non-polar industrial oil (Fig. 1(a)). A simplified explanation for the effect of plasticizers is that relatively small IO molecules penetrating between polymer molecules weaken intermolecular bonds and thus increase the mobility of polymer molecules. To achieve this, plasticizers must combine well with the polymer and form a stable mixture with it [24].

The main factors influencing the plasticizing efficiency are the chemical structure of the polymer and plasticizer, their thermodynamic compatibility, the volume and shape of plasticizer molecules, their capability for conformational transformations (their flexibility).

We compared the structure of butyl rubber and IO plasticizer at the molecular level for further analysis. By chemical composition, petroleum oils are a mixture of hydrocarbons with a molecular weight of 300–750, containing 20–60 carbon atoms in the molecule. Base oils consist of groups of isoparaffin, naphthenoparaffin, naphthenoaromatic and aromatic hydrocarbons with varying degrees of cyclicity. Paraffin oil is an industrial-grade oil [15]. The general chemical formula is C_nH_{2n+2} . The BR molecule is characterized by an almost complete lack of structuring, it contains a small amount of carbon–carbon double bonds and has tightly packed linear chains. The plasticization process proves the empirical like-dissolves-like rule, i.e., non-polar BR is easily dissolved in non-polar IO, which is explained by the absence of intermolecular chemical interactions between BR and IO. The dissolution of butyl rubber happens with a swelling stage, which is characterized by an increase in the mass and volume of the polymer as a result of absorption of a low-molecular-weight liquid. The molecules of the low-molecular-weight plasticizer IO in the BR chain increase the free volume and mobility of not only the main chain, but also its individual segments. As a result, the polymer swells. The plasticizer spreads the segments apart, replacing the polymer–polymer interactions with the plasticizer–polymer interaction, which means that intermolecular interactions are weakened, resulting in a decrease in T_c . Since energy is consumed for these interactions, $\tan \delta$ increases, and vibration-damping properties increase accordingly.

Under colloidal dispersion, due to the presence of oxygen and chlorine in the structural formulas, DOP and CP have a higher polarity compared with IO, and, accordingly, have less compatibility with non-polar BR. Plasticization of non-polar BC with a polar plasticizer CP and a less polar DOP also proves the like-dissolves-like rule. A plasticizer with no affinity for the polymer does not spontaneously penetrate it, so there is no swelling of BR. Plasticizer molecules are located on the surface of supramolecular formations, between non-polar groups of BR macromolecules (Fig. 1(b)). The emulsion formed in the colloidal system is thermodynamically and aggregatively unstable, and therefore can become stratified. Due to high viscosity of the system, stratification occurs slowly, sometimes during storage or operation of the product. This is manifested, for example, as plasticizer droplets appearing on the surface of the product. Plasticizer molecules are located on the surface of supramolecular formations, between non-polar groups of BR macromolecules (Fig. 1(b)). The plasticizers CP and DOP act as a sort of lubricant between the BR segments. An insignificant amount of plasticizer is combined with the polymer during such plasticization; the plasticizer molecules are adsorbed (*process of spontaneous redistribution of matter*) on the surface of the interface between the structures, forming the thinnest monomolecular layers of the so-called boundary lubricant, facilitating the mobility of supramolecular structures under external mechanical action. Mixtures with DOP and CP do not increase the mobility of polymer molecules, accordingly, a small amount of energy is consumed for these interactions and a slight increase in $\tan \delta$ occurs.

The spectral analysis method was used to confirm the impossibility of chemical reactions in these composite mixtures (Fig. 5). Tests of specimens by infrared spectroscopy revealed that absorption lines for superimposed curves practically coincide, the characteristic vibrations of physical groups of the BR polymer are very pronounced, and its alternating bonds appearing as its free functional groups at wavelengths of 2900 and 1400 cm^{-1} can be seen from the position of the peaks.

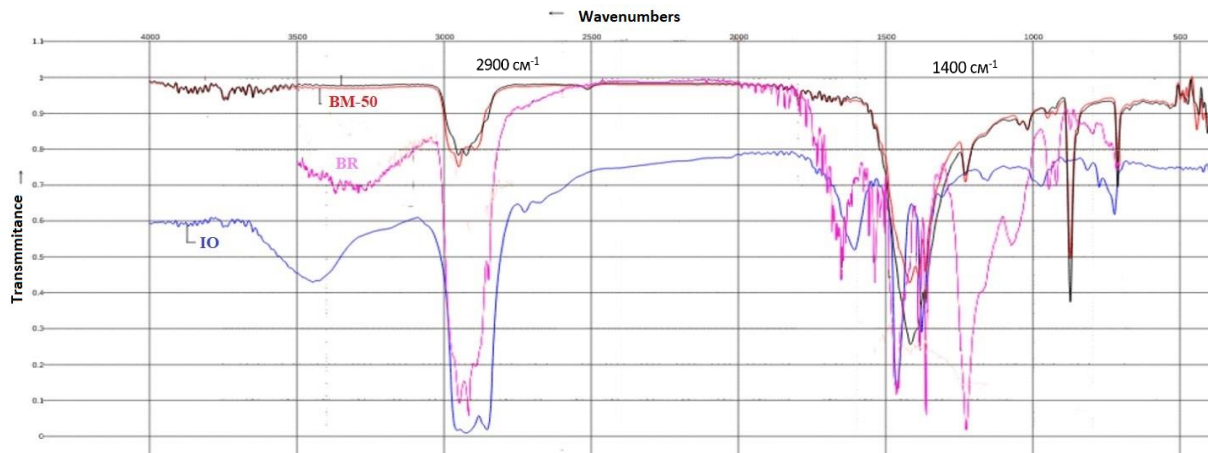


Fig. 5. Infrared spectrum of modified mixtures: pink curve corresponds to 100% BR, blue curve to 100% IO plasticizer, red curve to BM-50 (50% IO + 50% BR)

This means that the device records only the polymer matrix, no new peaks were detected, the influence of the components on the intensity or magnitude of the peak was not traced, which means that chemical interaction does not occur in the polymer matrix of butyl rubber.

Conclusion

1. We considered mixtures containing butyl rubber plasticized with either industrial oil, chlorinated paraffin, or dioctyl phthalate in different volume ratios as a polymer binder to study the effect of structure-forming components on the dynamic mechanical characteristics. Our findings indicate that all three types of plasticizers can be used to obtain a composite material with high damping properties, with an increase in the plasticizer content from 0 to 20 vol. %, while industrial oil should be used to obtain materials that are also self-adhesive, as it has the highest values of $\tan \delta$ as the main measure of vibration damping, with the minimum volume content of industrial oil within 40 %. Due to limited compatibility of DOP with BR and incompatibility of CP with BR, migration can be observed in these mixtures, starting with specimens with a plasticizer content of 20–30 % and above, making them unsuitable as plasticizers for vibration-damping composite materials.

2. We confirmed that introducing plasticizers of different types and polarities into butyl rubber leads to the transformation of the structure and properties of the compositions depending on the concentration of the plasticizer, the molecular structure and the forces of intermolecular interaction. Infrared spectroscopy revealed that chemical interaction in the polymer matrix of butyl rubber does not occur, since the influence of the components on the intensity or magnitude of the peak was not traced (the appearance of new peaks was also not detected).

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