

# Morphological and Dynamic Mechanical Analysis of Vibration Damping Composite Material Based on Different Elastomers

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*This work deals with the problem of developing vibration damping polymeric materials which are effective at low temperatures (from minus 40 to 0°C). Due to the fact that the vibration damping efficiency in the composite is mainly determined by the properties of the polymer matrix, it is necessary to study its properties depending on the type and amount of structure-forming parameters. The purpose of the work is to determine the changes in the dynamic properties of the polymer composition based on butyl rubber, EPDM, ethylene-vinyl acetate copolymer (EVA) filled with increasing amount of calcium carbonate. The leading methods of studying this problem were the method of scanning electron microscopy and the method of dynamic mechanical analysis. It has been stated that the selected polymers can be considered as competent candidates for damping materials at low temperatures, and the calcium carbonate filler allows more fully to realize the vibration damping properties of the polymer. The obtained dependences can be used as initial data for analytical predicting of damping properties of polymer composites.*

**Keywords:** *Vibration damping material, loss factor, DMA, temperature dependence, butyl rubber, EPDM, EVA.*

Damping materials are used to reduce vibration, noise, shock loads in structures and devices of various purposes. As a rule, they are based on polymers that have a relatively low modulus of elasticity and viscoelastic properties [1, 2]. Damping in either free or constrained layer configurations is reflected by the dynamic mechanical properties, the temperature dependence of the storage modulus  $E'$ , the loss modulus  $E''$ , and the ratio  $E''/E'$  as the loss factor  $\tan D$  [3, 4]. Vibration damping materials generally have the following requirements: high values of  $\tan D$  or  $E''$  over wide temperature and frequency ranges. For example, for vibration damping materials used in the automotive industry, the value of  $\tan D$  is often required to be above 0.3 in the temperature range up to plus 60-80°C at a frequency of 200 Hz [5]. The main disadvantage of vibration damping materials existing on the market for cars is their low efficiency at negative temperatures [6-10]. This is unacceptable for the climatic conditions of some countries such as Canada, Norway, Russia, Sweden, etc. For example, Russia is located in three climatic zones (Arctic, subarctic and temperate), and it is characterized by a very wide range of operating damping temperatures. Even within the temperate zone, the average temperatures in January range from -40 to 0°C. Thus, the development of vibration damping materials, which are effective in the temperature range from -40 to 0°C and suitable for operation in climatic conditions of Russia, is an actual task.

As it is known, the most effective damping properties of a polymer material are realized in the field of the main relaxation transition in polymers due to the thawing of the segmental mobility of macromolecules ( $\alpha$ -transition) [11]. Its position on the temperature scale is determined by the glass transition temperature  $T_g$ . The strain of the material at temperatures close to the glass transition temperature is accompanied by the greatest mechanical losses, the transfer of part of the mechanical energy into heat. Therefore, to develop vibration damping materials which are effective at negative temperatures, it is preferable to use nonpolar polymers with flexible macromolecules having low glass transition temperatures and high  $\tan D$ .

Such polymers can be butyl rubber [12-14], EPDM [15-17], EVA [18-19].

Addition of ingredients, such as a plasticizer or filler, to the polymer affects the dynamic characteristics of the polymer [20]. The main effect of the filler addition to the polymer is that part of the polymer passes to the boundary layers directly interacting with the surface of the filler particles due to the high degree of adhesion with the polymer [21]. It leads to a quasi-solid phase with a film matrix which properties differ from the properties of the polymer matrix in general [21]. In most cases, an increase of the filler amount in the polymer, as a result of loss of mobility and restriction of conformational transitions of macromolecules under the influence of a solid filler surface, results in a natural increase in the glass transition temperature of the polymer, a change in the relaxation-time, and a decrease in the composite loss coefficient [20, 22]. Therefore, it is desirable to use filler that has weak adhesion interactions with the polymer, which facilitates relaxation processes and enables more fully to realize vibration damping properties of the polymer. These requirements are met by calcium carbonate, which refers to inert fillers and has one more important characteristic - the lowest price [23]. There is a large number of vibration damping materials containing calcium carbonate, for example [13, 14, 19].

Using scanning electron microscope and dynamic mechanical analysis the authors of the article study polymer compositions based on butyl rubber, EPDM, ethylene-vinyl acetate copolymer (EVA), which are filled with a different amount of calcium carbonate in order to optimize the damping performance at the chosen temperature ranges.

## Experimental part

### *Materials and methods*

The authors use butyl rubber BK-1675N (SIBUR Holding, Russia), the amount of isoprene units is 1.4-1.8 % mol.; EPDM Mitsui EPT 3092PM (Mitsui Chemicals, Japan), the amount of ethylene units is 65 %, diene is 4.6 %; EVA LG EVA ES 28005 (LG Chem, South Korea), the amount of

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vinyl acetate units is 28 %. Calcium carbonate is used as a filler.

#### Formula and Preparation of Polymer Compositions

Composites were made in two stages. In the first stage, masterbatch was prepared by mixing polymer and industrial oil I-40 in a ratio of 60/40 vol.% in Laboratory Intermesh Kneader SKI-3L at 120°C at 44 rpm for 4 min. In the second stage, a filler was added to the master batches using a roll mill machine with a diameter and a roll length of 160 and 320 mm, respectively. The mixing temperature was  $30 \pm 5^\circ\text{N}$  for butyl rubber and  $50 \pm 5^\circ\text{N}$  for EPDM & EVA. The amount of the filler in the composites was 15, 30, 40 and 50 vol.%.

#### Morphological Study

The composite images were obtained by scanning electron microscope (SEM) using JEOL GSM 6510 LV (SEI mode). To visualize the surface, the samples were covered with platinum in a vacuum.

#### Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was performed on a dynamic mechanical analyzer Netzsch DMA 242 (Netzsch, Germany) using samples in the form of a disk 2 mm thick with a diameter of 2 mm. The temperature range of the test was from -100 to 60 °C and fixed frequencies of 1, 10 and 100 Hz in oscillation mode. The storage modulus  $E'$

and loss factor  $\tan D$  were recorded for all samples under identical conditions.

## Results and discussions

#### Morphological Analysis

SEM images of composites based on EPDM, filled with calcium carbonate in the amount of 15, 30, 40 and 50 vol. % are shown in figure 1.

In the EPDM matrix, the filler is evenly distributed in the form of clearly defined particles of irregular shape and their agglomerates. An increase in the filler amount up to 50 vol. % leads to increase of the average size of its inclusions due to an increase in the proportion of agglomerated particles (fig. 1d).

Composites based on butyl rubber are more homogeneous in comparison with EPDM, single filler agglomerates are visualized on the surface of a poorly filled sample (15 vol%) (fig. 2a). In a butyl rubber composite with a filler amount of 50 vol. % the main part of the filler is *immersed* in the polymer mass in comparison with EPDM (fig. 3).

The morphology of EVA-based composites changes with an increasing filler amount from cellular (15 vol%) to fibrillized (50 vol%). Unlike EPDM, the filler particles are well wetted by the polymer (fig. 5). EVA macromolecules of the polar vinyl acetate units are probably the reason for this affinity.

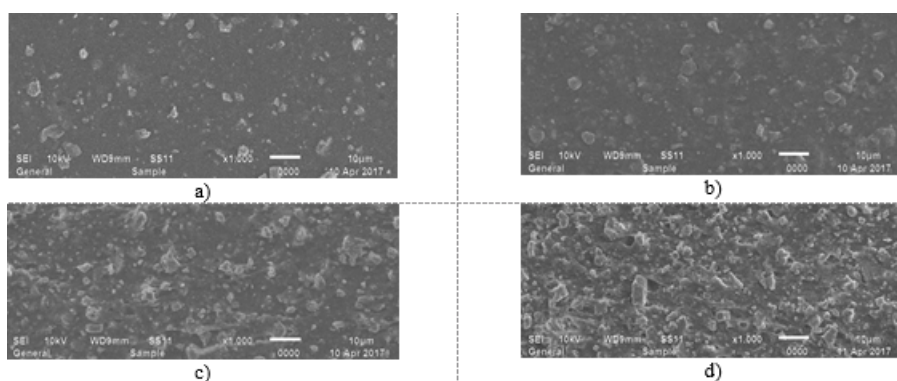


Fig. 1. SEM images (scale 10µm) for EPDM filled with increasing amounts of calcium carbonate [vol. %]: a) 15; b) 30; c) 40; d) 50.

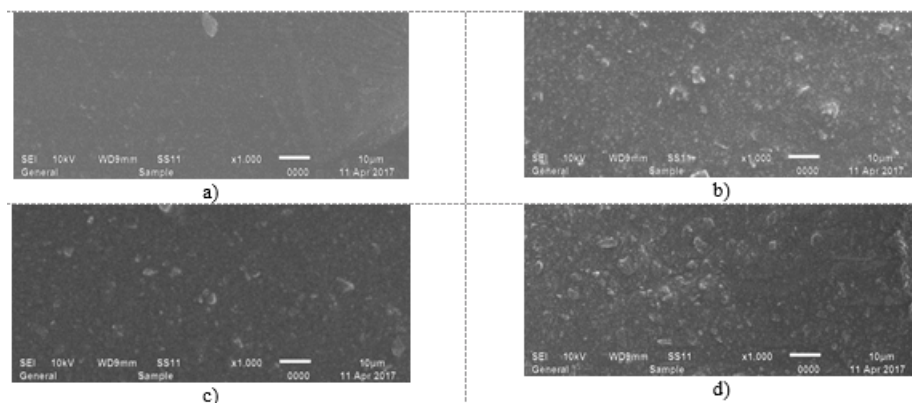


Fig. 2. SEM images (scale 10 µm) for a butyl rubber filled with increasing amounts of calcium carbonate [vol. %]: a) 15; b) 30; c) 40; d) 50.

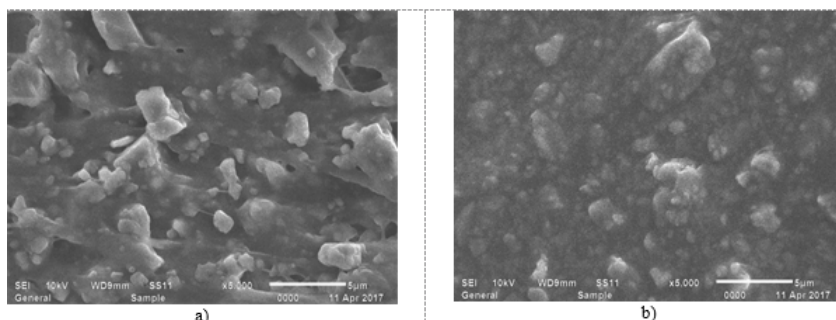


Fig. 3. SEM images (scale 5 µm) for a polymer filled with 50 vol. % of calcium carbonate: a) EPDM; b) butyl rubber.

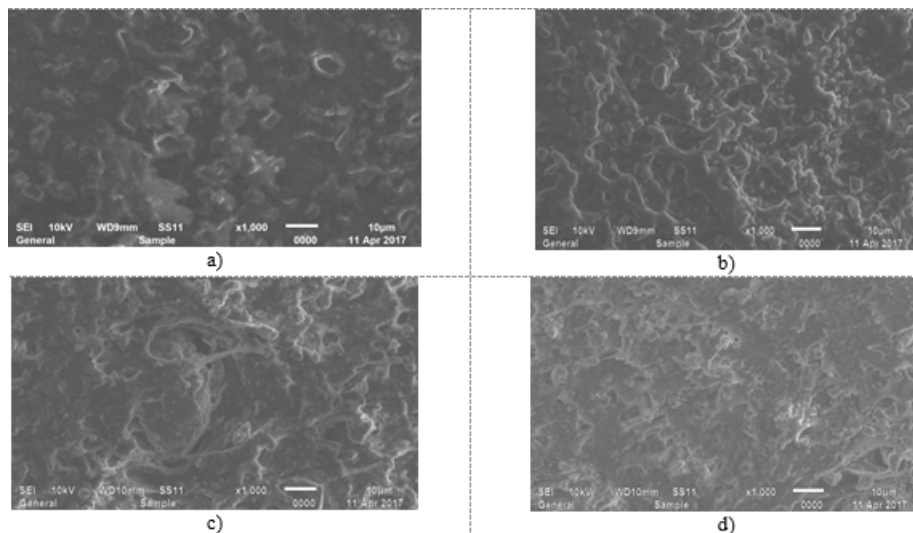


Fig. 4. SEM images (scale 10  $\mu\text{m}$ ) for EVA filled with increasing amounts of calcium carbonate [vol. %]: a) 15; b) 30; c) 40; d) 50.

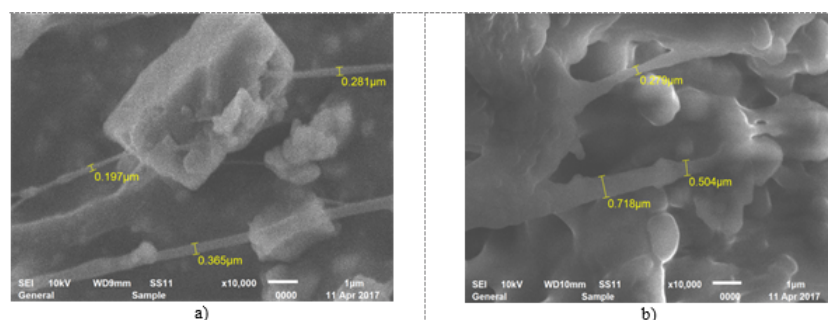


Fig. 5. SEM images (scale 5  $\mu\text{m}$ ) for a polymer filled with 50 vol. % of calcium carbonate: a) EPDM; b) EVA

### Dynamic Mechanical Analysis

The temperature dependences of the storage modulus  $E'$  and loss factor  $\tan D$  of EPDM composites have a classical form (fig. 6). The accumulation modulus sharply decreases with the transition of macromolecules from the glassy state to the highly elastic (rubberlike) state, with the loss factor changing along the curve with the maximum. An increase in the frequency of the action from 1 to 100 Hz, as well as an increase in the filler amount in the composite, is accompanied by an increase in the glass transition temperature  $T_g$  (table 1). The loss factor of composites decreases with increasing filler amount due to an increase in the proportion of macromolecules bound to the surface of the filler particles.

The temperature dependences of the loss factor  $\tan D$  of composites based on butyl rubber at filler amounts of 15 and 30 vol. % are characterized by the presence of two distinct peaks at a frequency of 100 Hz (fig. 7). Taking into account the nature of the temperature dependences of the accumulation modulus, which have a classical form, and also the electron microscopy data, the presence of additional peaks can be associated with the thawing of the segmental mobility of macromolecules located in the field of action of the polymer-filler interaction forces. Strengthening the process of agglomeration of particles in composites containing 40 and 50 vol. % of filler, probably reduces the proportion of macromolecules that are located directly near the surface of the filler.

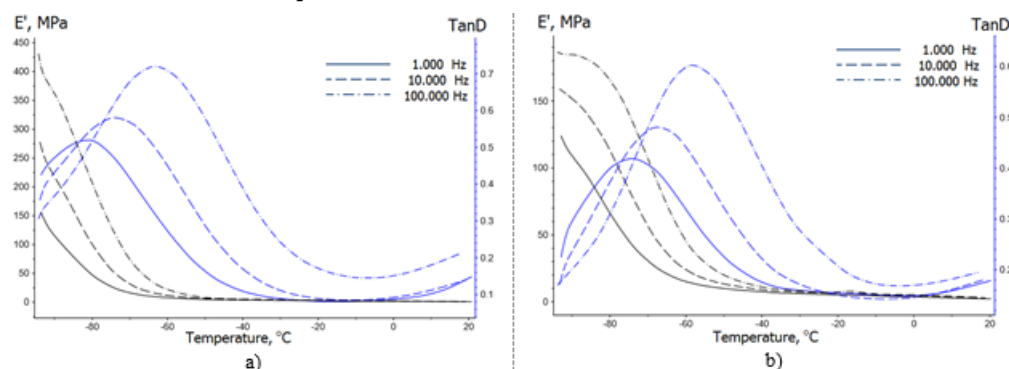


Fig. 6. Storage modulus  $E'$  and loss factor  $\tan D$  at different frequencies versus temperature for EPDM filled with increasing amounts of calcium carbonate [vol. %]: a) 15; b) 50

Sample	$T_g$ [°C]	Storage modulus at -80 °C $\log E'$ [MPa]	$\tan D$ at $T_g$
EPDM / calcium carbonate 15 vol. %			
1 Hz	-80.0	1.69	0.52
10 Hz	-72.2	1.99	0.58
100 Hz	-62.8	2.31	0.72
EPDM / calcium carbonate 50 vol. %			
1 Hz	-74.1	1.83	0.42
10 Hz	-66.2	2.05	0.48
100 Hz	-58.3	2.26	0.60

**Table 1**  
DATA OF DMA AT DIFFERENT FREQUENCIES FOR EPDM FILLED WITH CALCIUM CARBONATE



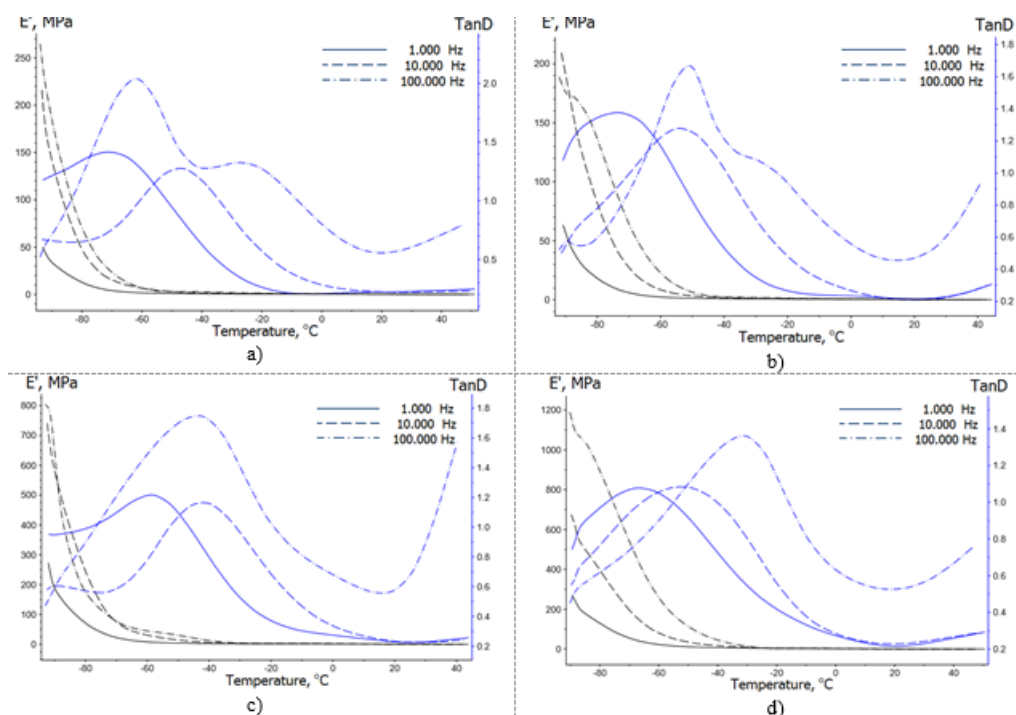


Fig. 7. Storage modulus  $E'$  and loss factor  $\tan D$  at different frequencies versus temperature for a butyl rubber filled with increasing amounts of calcium carbonate [vol. %]: a) 15; b) 30; c) 40; d) 50

**Table 2**  
DATA OF DMA AT DIFFERENT FREQUENCIES FOR A BUTYL RUBBER FILLED WITH CALCIUM CARBONATE

Sample	$T_g$ [°C]	Storage modulus at -80 °C $\log E'$ [MPa]	Tan D at $T_g$
butyl rubber / calcium carbonate 15 vol. %			
1 Hz	- 69.8	1.25	1.41
10 Hz	- 45.6	1.69	1.30
100 Hz	- 61.3	1.86	2.04
	- 24.3		1.33
butyl rubber / calcium carbonate 30 vol. %			
1 Hz	- 73.6	1.32	1.35
10 Hz	- 53.4	1.94	1.28
100 Hz	- 49.8	2.15	1.69
	- 25.0		1.15
butyl rubber / calcium carbonate 50 vol. %			
1 Hz	- 65.2	2.15	1.00
10 Hz	- 50.4	2.60	1.11
100 Hz	- 30.1	2.96	1.38

**Table 3**  
DATA OF DMA AT DIFFERENT FREQUENCIES FOR EVA FILLED WITH CALCIUM CARBONATE

Sample	$T_g$ [°C]	Storage modulus at -80 °C $\log E'$ [MPa]	Tan D at $T_g$
EVA / calcium carbonate 15 vol. %			
1 Hz	- 80.0	2.08	0.34
	- 42.3		0.34
10 Hz	- 78.3	2.25	0.37
	- 36.2		0.36
100 Hz	- 64.8	2.45	0.40
	- 26.4		0.51
EVA / calcium carbonate 30 vol. %			
1 Hz	- 39.9	1.80	0.40
10 Hz	- 34.7	1.91	0.40
100 Hz	- 24.8	2.01	0.51
EVA / calcium carbonate 50 vol. %			
1 Hz	- 30.3	1.81	0.31
10 Hz	- 17.2	1.91	0.33
100 Hz	- 14.3	1.98	0.42

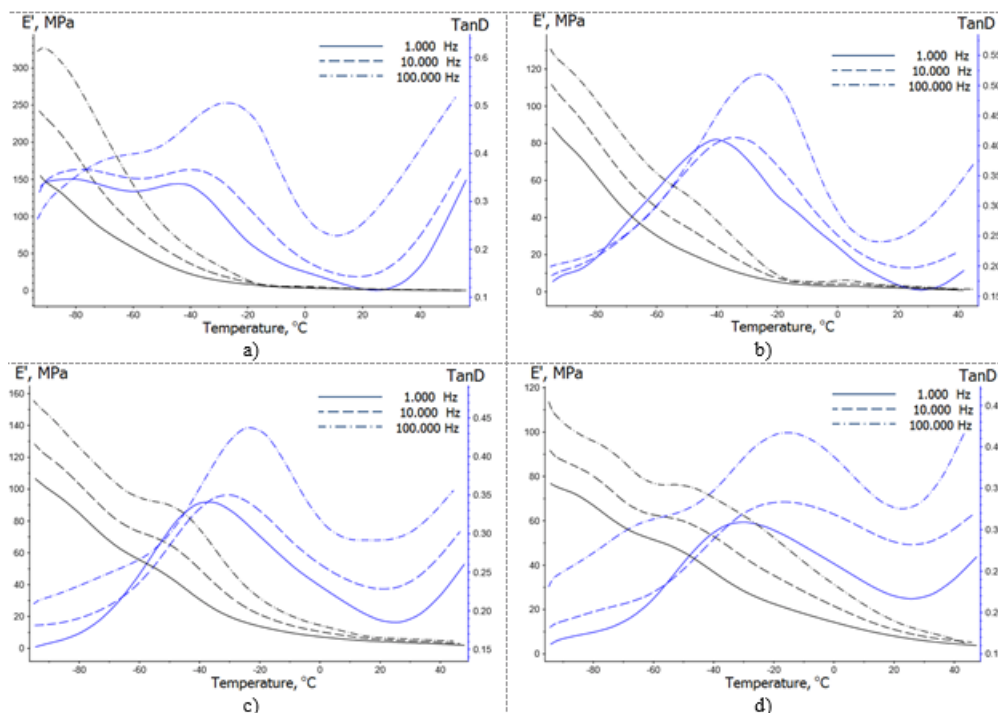


Fig. 8. Storage modulus  $E'$  and loss factor  $\tan D$  at different frequencies versus temperature for EVA filled with increasing amounts of calcium carbonate [vol. %]: a) 15; b) 30; c) 40; d) 50

The nature of the temperature dependences of the storage modulus  $E'$  of composites based on EVA significantly changes with increasing filler amount. It indicates a change in the phase morphology of the composites when the filler is added, in particular in an amount of 50 vol. %, when the temperature interval for the variation of  $E'$  is substantially broadened. Judging by the temperature dependences of the loss factor  $\tan D$ , an increase in filler amount above 15 vol. % sharply reduces energy loss in composites in the low-temperature field, the dependences are unimodal in nature with a shift in the peak values of the loss factor to higher temperatures (table 3).

### Summary

Investigated polymers such as butyl rubber, EPDM and EVA can be considered candidates for damping materials at low temperatures. Maximum of  $\tan D$  for composites based on a masterbatch consisting of polymer and industrial oil I-40 in a ratio of 60/40 vol.%, filled with calcium carbonate 50 vol.% at a frequency of 100 Hz were found at temperatures for butyl rubber:  $-30.1^\circ\text{C}$ ; for EPDM:  $-58.3^\circ\text{C}$ ; for EVA:  $-14.3^\circ\text{C}$  and made up respectively 1.38; 0.6 and 0.42.

The filler calcium carbonate has weak adhesion interactions with the polymer, which facilitates relaxation processes and makes it possible to more fully realize the vibration damping properties of the polymer. In three polymers a decrease in the maximum values of  $\tan D$  at a frequency of 10 Hz with an increase in the volume fraction of the filler from 15 to 50% was 15-18%. The least effect of calcium carbonate was on EPDM and butyl rubber, the largest one on EVA. Morphological analysis revealed that the filler particles are well wetted with EVA polymer unlike EPDM and butyl rubber. The reason for this is the presence of polar vinyl acetate units in EVA macromolecules. The interaction effect can be estimated by the displacement and expansion of the loss peak: if for butyl rubber and EPDM an increase in the volume fraction of the filler from 15 to 50%, the displacement and expansion of the peak is minimal, then EVA is characterized by an appreciable temperature shift and a change in the character of the curve.

An increase in the frequency from 1 to 100 Hz, as well as an increase in the amount of the filler in the composite, is accompanied by an increase in the glass transition temperature.

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