ВЛИЯНИЕ ХИМИИ ПОВЕРХНОСТИ НАПОЛНИТЕЛЯ И ТЕРМИЧЕСКОЙ МОДИФИКАЦИИ КОМПОЗИЦИЙ БНКС-40/ПВХ НА ВИБРОПОГЛОЩАЮЩИЕ СВОЙСТВА МАТЕРИАЛА

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В работе исследовано влияние химии поверхности кремнекислотного наполнителя Newsil 1165MP и термической модификации композиций на основе бутадиен-нитрильного каучука и поливинилхлорида (80:20) на вибропоглощающие свойства материала. По данным термического анализа (термогравиметрия и дифференциально-термический анализ, анализатор “Shimadzu”, скорость подъема температуры 10 °С/мин), ИК спектроскопии («Инфрафот ФТ-08», техника многократного нарушенного полного внутреннего отражения) установлено, что адсорбция органосилана бис(триэтоксисилилпропил)дисульфида и последующая силанизация Newsil 1165MP (145 °С, 5 мин) более эффективно протекают на поверхности кремнекислотного наполнителя, подвергнутого предварительному высушиванию в мягких условиях (70 °С). Дегидратация поверхности кремнекислотного наполнителя способствует увеличению доли органосилана, физически связанного с его поверхностью (в 2,4 раза), нежели химически (1,1 раза). Силанизация кремнекислотного наполнителя приводит к снижению вязкости по Мунни композиций (МБ 1+4, 100 °С, усл. ед) и тем в большей степени, чем выше содержание свободного органосилана. По данным динамического механического анализа (“Netzsch DMA 242”, при температурах от -60 до +60 °С и частотах от 0,1 до 10 Гц) установлено, что свободный органосилан пластифицирует полимерную матрицу, увеличивая тангенс угла механических потерь TanD и смещая положение максимума в область более низких температур. При этом эффективный температурный интервал вибропоглощения (где TanD ≥ 0,3) несколько сужается в сравнении с композицией, содержащей исходный кремнекислотный наполнитель. Термическая модификация композиций на основе бутадиен-нитрильного каучука и поливинилхлорида (120 °С, 4 ч) сопровождается расширением эффективного температурного интервала вибропоглощения как в области температуры стеклования эластомера, так и температуры стеклования переходной зоны эластомер-термо-пласт. Это обусловлено диффузией полимеров в межфазных зонах наполнитель-эластомер/термопласт и эластомер-термопласт. Термическая модификация эффективна в случае композиций, содержащих силанизированный наполнитель с наименьшим количеством свободного органосилана.

Ключевые слова: вибропоглощение, кремнекислотный наполнитель, силанизация, бутадиен-нитрильный каучук, поливинилхлорид
INFLUENCE OF SURFACE CHEMISTRY OF THE FILLER AND THERMAL MODIFICATION OF BNKS-40/PVC COMPOSITIONS ON THE VIBRO-ABSORBING PROPERTIES OF THE MATERIAL

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The study looks into the effect of a silicic acid filler’s (SAF) surface chemistry and thermal modification of BNKS-40/PVC-based (80:20) compounds upon material's vibration-absorbing properties. The thermal analysis (TGA and DTA, Shimadzu analyzer, the temperature rise rate -10 °C/min), IR spectroscopy (Infralume FT-08, MFTIR) demonstrated, that adsorption of organosilane bis(3triethoxysilylpropyl)disulfide (TESPD) and the following silanization of Newsil 1165MP (145 °C, 5 min) occur more readily on the surface of the SAF, dried in mild conditions (70 °C) in advance. Dehydration of the SAF surface contributes to an increase in the proportion of organosilane physically associated with its surface (2.4 times), rather than chemically (1.1 times). SAF silanization results in the decrease in the compounds' Mooney viscosity (MB 1+4, 100 °C, CU) and the higher content of free TESPD, the more pronounced the decrease is. The dynamic mechanical analysis (Netzsch DMA 242, in the temperature range from -60 to +60 °C and the frequency range from 0.1 to 10 Hz) demonstrated that, free TESPD plasticized the polymer matrix, increasing TanD as well as shifting the peak of mechanical losses into the lower temperature range. In this case, the effective temperature range of vibration absorption (ETRVA, where TanD ≥ 0.3) is somewhat narrowed in comparison with the compound containing the initial SAF. Thermal modification of BNKS-40/PVC compounds (120 °C, 4 h) is accompanied by ETRVA expansion in the elastomer glass transition range, as well as in the glass transition temperature of the elastomer-thermoplast transition range. This fact is due to the diffusion of polymers in the filler-elastomer/thermoplast- and the elastomer-thermoplast inter-phase zones. Thermal modification is effective with compounds containing silanized filler with the least amount of free TESPD.

Key words: vibration absorption, silicic acid filler, silanization, butadiene-nitrite rubber, poly(vinylchloride)

INTRODUCTION

The use of vibration-absorbing materials (VAM) in Russian climates requires development of such compound formulas as to guarantee effective vibration absorption in a wide temperature range. One of the main polymer formula factors is the segmental mobility of macromolecules, which, when deformed, dissipate vibrational energy. The greatest mechanical losses in the material are observed at the glass transition temperature of the polymer matrix [1]. At which point the segmental mobility of the macromolecules
significantly drops, hence, due to the relaxation character of the deformation process, the mechanical energy transforms into heat most fully. To ensure vibration absorption temperature range, the VAM polymer base is preferable to be the polymer compounds, such as elastomer/thermoplastic block-copolymers as well as various mixtures of polymers having different glass transition temperature and forming either semi-interpenetrating or interpenetrating networks inside the material's structure [2-5].

It is possible to further widen the VAM relaxation range by adding a filler. Along with the polymer, the filler is capable of absorbing a certain amount of vibrational energy, thus, contributing to the vibration absorption process [6, 7]. However, in this case it is necessary to take into account the fact, that the level of physical-and-chemical interactions among the components of the compound should be optimal. On the one hand it should ensure the formation the compound's required strength properties (rigidity, framework), while on the other hand – is should ensure adequate mobility of macromolecules for them to dampen the vibrational energy while being deformed.

In this work, the object of the study are compositions based on a mixture of BNKS-40 / PVC and silica filler. Polymers contain polar functional groups and links (–C= N, –HC=Cl), capable of physical interaction both among themselves and with the functional groups of the filler e.g. formation of hydrogen bonds ≡Si–OH…Si≡– [8-10]. The role of hydrogen bonds in damping vibrational energy is especially noticeable when designing VAM [11-13]. In spite of the polar nature of macromolecules, the dispersion and distribution of the filler in the polymer is rather complicated. By modifying the silicic acid filler (SAF) with organosilane it is possible to reduce its polarity, to improve its distribution within the polymer matrix, and provide additional donor-acceptor interactions, capable of increasing the internal friction within the volume of the material.

SAF modifying is a multi-stage physical-and-chemical process. It includes initial organosilane adsorption onto the surface of the particles, sequential reaction of hydrolysis/condensation involving the filler's silanic groups as well as organosilane's alkoxyl groups in the presence of water. In the case the high degree of modification of the particle's surface is achieved through the participation of the greatest possible number of available reaction centers. However, due to easy adsorption of hydroscopic moisture, the hydrated SAF demonstrates some hydroxyl-hydrate film on the surface. Its presence reduces the number of possible rubber-filler interactions [7], inhibits organosilane adsorption, and reduces the filler's silanization [14]. It is possible to remove the adsorbed moisture by preliminary drying the filler at the temperature not affecting the silanol groups ≡Si–OH proper. According to the printed sources [15] the dehydration temperature range for the silica surface lies within 25 to 150 °C range. Given the surface moisture catalyzes interactions of the organosilane alkoxyl groups with the filler’s silanol groups [16], it is imperative to run dehydration in rather mild conditions. In the printed sources there are practically no descriptions of the effect the SAF silanization conditions have upon the BNKS-40/PVC-based compounds' vibration-absorbing properties in order to improve them.

Thermal treatment can become another tool to control the relaxation range of VAMs, based on the thermodynamically compatible polymers. Such treatment affects the supramolecular structure, the size of the intra-bond areas, and as such, the material's macroscopic properties [17]. It has been demonstrated [18], that thermal modification of the PVC/SKN-40 binary compound at the temperature exceeding the glass transition point, results in the increase of the average loss tangent's maximum temperature dependency. Thus, the objectives of this study are the evaluation of the effect of the SAF silanization, and that of the heat treatment of polymeric compounds upon the technological and vibration-absorbing properties of the BNKS-40/PVC-based material.

EXPERIMENTAL

The bis(3-triethoxysilylpropyl)disulfide adsorption onto the surface of Newsil 1165MP filler was done from CCl₄ solution (the filler to organosilane ratio was 2:1, adsorption time – 7 days). The filler was used both in its original state and after preliminary drying in a thermostat to its equilibrium state at 70 °C. The filler silanization was performed in the thermostat at 145 °C for 5 min. The filler modification process was monitored through IR spectroscopy (InfraLume FT-08, MFTIR), TGA and DTA (Shimadzu, temperature rise rate – 10 °C/min). The Mooney viscosity was taken as per GOST (State standard) 10722-76 (Prescott viscometer).

The polymer compounds were prepared in a Brabender laboratory mixer at 130-140 °C and rotors rate of 40-50 rpm. The polymers ratio in BNKS-40:PVC was 80:20, SAF content was 11 % vol. The vibration-absorbing properties of the compounds, including the ones subjected to thermal treatment (120 °C, 4 h) were evaluated by Netzsch DMA 242 analyzer using disc-shaped samples of 2 mm both in diameter and thickness. Based on the obtained data we calculated the
compounds' dynamic elasticity modulus (storage modulus, $E'$), maximum loss tangent ($\tan \delta_{\text{max}}$), $\tan \delta_{\text{max}}$ position on the temperature scale (Max peak/$^\circ$C), value of effective vibration dampening temperature range, i.e. the temperature range, where $\tan \delta \geq 0.3$.

RESULTS AND DISCUSSION

Fig. 1 demonstrates both the TGA and DTA curves for the initial and silanized SAF samples (preliminary drying and no drying). The TGA curve of the initial SAF demonstrates a drop in the sample's mass in the 16-600 °C temperature range, the loss is 8.8%, of which 5.6% are recorded at temperatures from 30 to 97 °C. The endothermic peak with its maximum at 61.7 °C on the DTA curve matches the process. It is evident, that the sample's mass loss is due to evaporation of the physically adsorbed molecular moisture. On the TGA curves of the silanized SAF samples such losses are virtually non-existent. However, there are observed stepwise losses of the sample mass in the intervals from 182 to 233 °C and from 330 to 350 °C. High-temperature sample weight loss on the DTA curve matches the exothermal peak with the maximum at 336.6 °C. Decomposition of the original TESPDM in similar conditions shows that the bulk sample burns up in the 242-302 °C range, which corresponds to the DTA curve's exothermal peak with its maximum at 300.6 °C. The obtained data prove that the mass loss in the silanized SAF samples in the 182-233 °C temperature range is due to the removal of organosilane, physically bonded to the surface of the particles. The organosilane chemically bonded to the particles decomposes in the 330-350 °C temperature range. It is possible to estimate the TESPDM amount physically bonded to the SAF by analyzing the samples mass loss $\Delta W$ (%) in the 150-250 °C temperature range,

$$\Delta W (%) = \frac{M_{150} - M_{250}}{M_{150}} \cdot 100\%$$

where $M_{150}$ and $M_{250}$ are the sample's residual weight at 150 and 250 °C respectively, as per the TGA data.

Similarly, it is possible to determine the TESPDM amount chemically bonded to the SAF surface, taking into account the loss of the sample mass in the 300-400 °C temperature range. Calculations demonstrate that the greater part of organosilane is physically bonded to the SAF surface, which corresponds to 16.1 and 6.6% for dried and undried filler respectively. At the same time, 4.4 and 3.9% of organosilane are chemically bonded to the SAF surface, respectively.

Additional data on the surface chemistry of the modified SAF can be obtained using the IR spectroscopy. It is known that upon the silica surface there are isolated silanol groups $\equiv \text{Si-OH}$, vicinal and geminal silanols, and siloxane groups $\equiv \text{Si-O-Si}$. The molecular moisture adsorption centers are closely spaced silanols, coordinately unsaturated silicon atoms and, to a lesser extent, isolated silanols [15]. Dehydration of the closely-spaced silanols is accompanied by the formation of stressed $\equiv \text{Si-O-Si}$ bonds=, According to [15], the IR spectrum of the original there were registered the following absorption bands: 3726 cm$^{-1}$ ($\nu_\text{OH}$ single silanol groups), 3660-3632 cm$^{-1}$ and 954 cm$^{-1}$ ($\nu_\text{OH}$ and $\delta_\text{SiOH}$ silanol groups tied with hydrogen bonds), 3550 cm$^{-1}$ ($\nu_\text{OH}$ water molecules, tied to the silanol groups with the hydrogen bonds), 3372 and 1645 cm$^{-1}$ ($\nu_\text{OH}$ and $\delta_\text{OH}$ adsorbed water), 1090 cm$^{-1}$ and 789 cm$^{-1}$ (siloxane groups oscillations). The IR spectrum of the undried silanized filler differs in the significantly reduced intensity of the siloxane groups adsorption bands (maxima 1086 and 789 cm$^{-1}$), at the same time there are no valency and deformation oscillations bands for the adsorbed moisture. The IR spectrum of the preliminarily dried silanized SAF differs in showing no 3726 cm$^{-1}$ absorption band, while demonstrating an intensive 3698 cm$^{-1}$ absorption band along with the increase in the intensity of the 954 cm$^{-1}$ absorption band. In addition, there appears a 1436-1403 cm$^{-1}$ absorption band, which can be correlated to the deformation oscillations of the C-H bond in the CH$_2$ groups. The IR spectra data indicate that the silanization is more effective in the silicas preliminarily dried in mild conditions, at which point the greater part of TESPDM is physically bonded to the filler (~80%).

Original filler (compound A), undried modified filler (compound B), preliminarily dried modified...
filler (compound C) were introduced into BNKS-40/PVC mixes. It was found that the Mooney viscosity of the obtained compounds (MB 1+4, 100 °C) was: A 149, B 108, C 99 CU.

Fig. 2 shows how the compounds’ storage modulus E’ and TanD of compounds B and C change as compared to the reference compound (compound A).

Fig. 2. E’ (1, 2, 3) and TanD (4, 5, 6) temperature dependencies of the studied compounds (10 Hz): compound A (1 and 4), compound B (2 and 5), compound C (3 and 6)

It is obvious, that in the -19 +22 °C temperature range the E’ value is somewhat lower than that of the reference sample and substantially higher at lower temperatures. The dynamic mechanical analysis data (DMA) (Table 1) demonstrate that the TanDmax maximum value belongs with compound C, at which point the TanDmax position along the temperature scale shifts towards lower temperatures.

Table 1. Данные ДМА полимерных композиций на основе смеси BNKS-40/ПВХ

<table>
<thead>
<tr>
<th>Sample</th>
<th>TanDmax (0.1/1.0/10.0 Hz)</th>
<th>Max peak/°C (0.1/1.0/10.0 Hz)</th>
<th>ETRVA (10 Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.44/0.46/0.52</td>
<td>-21.8/-12.5/-5.3</td>
<td>from -23 to +38</td>
</tr>
<tr>
<td>B</td>
<td>0.52/0.52/0.56</td>
<td>-21.1/-15.4/-6.4</td>
<td>from -24 to +33</td>
</tr>
<tr>
<td>C</td>
<td>0.58/0.59/0.61</td>
<td>-25.8/-19.6/-11.5</td>
<td>from -28 to +28</td>
</tr>
</tbody>
</table>

With the appearance of TESPD on the filler's surface the viscosity of compounds B and C (100 °C) drops as expected. This is primarily due to the decrease in the number of donor-acceptor interactions among the SAF particles [5]. Moreover, given lower viscosity of compound C, one can assume that while being mixed in, the physically adsorbed TESPD will diffuse into the polymer matrix (mostly consisting of the elastomer) adjacent to the particles' surface, thus reducing the intermolecular interaction and plasticizing the interphase layer. This causes the increase in the mobility of a part of the elastomer's macromolecules, TanDmax rise, and the shift of the TanDmax maximum into the area of lower temperatures. A significant increase in E’ of B and C compounds in the elastomer’s highly-elastic-to-glass transition area is explained by the fact that the physically adsorbed TESPD plays the role of a structuring agent, when the thermal mobility of macromolecules drops. Organosilane, having active centers in its molecules, ensures cross-linking through the formation of hydrogen bonds (–C=H–…5-H–C≡N) the more so, the higher the free TESPD content (compound C). Additionally, it cannot be ruled out that at higher temperatures and shear stresses when mixing, the free TESPD is capable of cross-linking some of the elastomer's macromolecules by free-radical reactions.

Fig. 3 (0.1 Hz) and table 2 (10 Hz) show data on the effect of thermal treatment upon dynamic characteristics of polymeric compositions. Analysis of the obtained data demonstrates the fact that thermal treatment is inefficient in case of the original compound (compound A’), however, it contributes to the growth of mechanical losses in the vibration-absorbing temperature range in case of compounds containing silanized SAF. As such, the TanDmax of compound B’ rises by 14%, the effective temperature range of vibration adsorption extends by ~10 degrees. Fig. 3 shows that mechanical losses in compound B’ increase throughout the entire temperature range of vibration adsorption.

Table 2. Данные ДМА композиций (10 Гц), подвергнутых термобработке (120 °C, 4 ч)

<table>
<thead>
<tr>
<th>Sample</th>
<th>TanDmax</th>
<th>Max peak/°C</th>
<th>ETRVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A’</td>
<td>0.57</td>
<td>-7.3</td>
<td>from -28 to +27</td>
</tr>
<tr>
<td>B’</td>
<td>0.65</td>
<td>-6.7</td>
<td>from -28 to +37</td>
</tr>
<tr>
<td>C’</td>
<td>0.59</td>
<td>-11.3</td>
<td>from -28 to +30</td>
</tr>
</tbody>
</table>

Fig. 3. TanD (1, 2, 3) and E’ (4, 5, 6) temperature dependencies of the tested compounds (0.1 Hz): compound A’ (1 and 4), compound B’ (2 and 5), compound C’ (3 and 6)

Рис. 3. Температурная зависимость TanD (1, 2, 3) и Е’ (4, 5, 6) исследуемых композиций (0.1 Гц): композиция A’ (1 и 4), композиция B’ (2 и 5), композиция C’ (3 и 6)
Although, BNKS-40 and PVC are considered to be thermodynamically compatible polymers (parameter of solubility is 19.6 and 19.4 (MJ/m²)²/³ respectively [19]), on the microscopic level the binary mixture’s structure is heterogeneous due to phase separation of the polymers and the co-existence of the transitional zones. It was established [20], that the diffusion coefficients of PVC in SKN-40 and SKN-40 in PVC (100 °C) were close at 11.3·10⁻¹² and 11.7·10⁻¹² cm²/s respectively. In which case one can assume that in the thermal treatment process of the compounds at the temperature exceeding of PVC glass transition temperature, the macromolecules’ segments are involved in the mutual diffusion, including the filler-polymer matrix interphase zones. Data analysis shows that in the presence of the filler the diffusion process is determined by the balance of physical interactions among filler-BNKS-40/PVC and SKN-40/PVC in the volume of the material. Thus, in case of the silanized SAF with lower free TESPD content (compound B’) after thermal treatment the effective temperature range of vibration adsorption grows both in the BNKS-40 glass transition range and in the area of positive temperatures, matching those of the BNKS-40/PVC transition zone (Table 2). On the one hand, this phenomenon is due to the reduction of the filler-elastomer interactions owing to the diffusion of some polar rubber macromolecules into the transition zone, and on the other hand, due to the reduction of the macromolecule packing density in the thermostplast zone, as the PVC density is higher than that of BNKS-40 (~1.38 and ~0.99 g/cm³ respectively [21]). The reduction of the storage modulus Е’ in compound B’ in the highly-elastic-to-glass-state transition zone reflects such reduction in the number of interactions (Fig. 3).

Thermal treatment of the compound containing the original filler (A’) results in the ETRVA reduction in the positive temperature range by 11°C (Tables 1 and 2). It can be assumed that in case of BNKS-40 the polar surface of the SAF is preferable for the formation of physical bonds, rather than active centers of the PVC macromolecules. It is the diffusion of BNKS-40 from the BNKS-40/PVC transitional polymer layer into the filler/BNKS-40 interphase layer during the thermal modification that causes the Е’ increase from 91 MPa to 189 MPa. And, finally, the excess of free TESPD in the filler/BNKS-40 interphase layer (compound C’) inhibits the diffusion of rubber macromolecules into the transitional polymer layer during thermal treatment.

CONCLUSION

The study has looked into the effect of the surface moisture upon silanization of Newsil 1165MP with the TESPD bi-functional organosilane, the effect of the filler’s surface chemistry upon the BNKS-40/PVC-based (80:20) material’s vibration-absorbing properties. It has been demonstrated that once compared to the original Newsil 1165MP the preliminary mild drying of the filler results in the increase of the physically bonded organosilane, rather than the chemically bonded one. The free organosilane plasticizes the polymer matrix, thus increasing TanD and shifting the TanD maximum into the lower temperature range. It has been established that thermal modification of BNKS-40/PVC-based compounds (at the temperature exceeding of the PVC glass transition) can be successfully applied to the improvement of the material’s vibration-absorbing properties. Due to inter-diffusion of thermodynamically compatible polymers the effective temperature range of vibration adsorption grows both in the elastomer’s vitrification temperature range and in the area of elastomer/thermostplast glass transition temperature. Silanization of the filler without its prior drying lends assistance to the process.

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