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ВЛИЯНИЕ ГИБРИДНОГО НАПОЛНИТЕЛЯ ТЕХНИЧЕСКИЙ УГЛЕРОД/УГЛЕРОДНЫЕ НАНОТРУБКИ НА РЕЛАКСАЦИОННОЕ ПОВЕДЕНИЕ ВУЛКАНИЗАТОВ

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Методами динамического механического анализа и дифференциальной сканирующей калориметрии исследован процесс стеклования в эластомерных композитах, содержащих гибридный наполнитель на основе технического углерода и углеродных нанотрубок. Модуль накопления E' и тангенс угла механических потерь TanD регистрировали в интервале температур от –100 до 100 °C и частоте 10 Гц. Термический анализ проводили со скоростью подъема температуры 2 °C/мин. Вулканизаты изготовливали по традиционной технологии. Углеродные нанотрубки вводили в состав резиновых смесей в виде порошкообразных мастербатчей технический углерод/углеродные нанотрубки, полученных в условиях совместной ультразвуковой обработки. Содержание углеродных нанотрубок в резиновых смесях варьировали от 0,1 до 0,5 мас. ч. на 100 мас.ч. каучука. По данным динамического механического анализа установлено, что включение гибридных частиц наполнителя приводит к расширению пиков температурных зависимостей TanD для всех образцов в сторону более низких температур и смещению положения максимума TanD на величину от 4,0 до 15,6 градусов. Данные дифференциальной сканирующей калориметрии указывают на наличие дополнительных низкотемпературных α-релаксационных переходов в модифицированных вулканизатах (-123…-118 °C). Наблюдаемое релаксационное поведение обусловлено увеличением доли свободного объема в вулканизатах, повышением сегментальной подвижности части макромолекул в сравнении с контрольным образцом. В вулканизате с наибольшим содержанием частиц гибридного наполнителя снижение TanD в переходной зоне от стеклообразного к высокоэластическому состоянию и увеличение в высокоэластическом состоянии указывает на формирование дополнительных взаимодействий «наполнитель-наполнитель». Таким обра-

зом, обработка углеродных нанотрубок техуглеродом приводит к синергетическому эффекту во влиянии на динамические характеристики вулканизатов и может быть использована для снижения нижнего температурного предела эксплуатации резин.

Ключевые слова: стеклование, эластомер, технический углерод, углеродные нанотрубки

EFFECT OF HYBRID CARBON BLACK/CARBON NANOTUBES FILLER ON VULCANIZATES RELAXATION BEHAVIOR

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The glass transition in hybrid carbon black/carbon nano-tube (CB/CNT) filled elastomer composites has been studied through dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The storage modulus E' and loss tangent (TanD) are recorded from -100 to 100 ° C and a frequency of 10 Hz. The thermal analysis was carried out at 2° C/min temperature increment. The vulcanizates were made as per conventional technology. The CNT were introduced into rubber compounds as CB/CNT masterbatches resulting from joint ultrasound processing. The CNT content in the rubber compounds varied from 0.1 to 0.5 phr. The DMA data proved that introduction of CB/CNT hybrid particles resulted in the spread of TanD temperature peaks for all the samples towards lower temperatures and the subsequent shift of the maximum TanD position by 4.0 to 15.6 degrees. The DSC data demonstrated the existence of additional low-temperature α-relaxation transitions in the modified vulcanizates (-123…-118 °C). The observed relaxation behavior could be explained by the increase in vacant volume in the vulcanizates along with the rise in segmental mobility of some macromolecules when compared against the reference sample. The highest hybrid filler content vulcanizate demonstrated certain TanD drop in the glass-to-rubber transition zone and the TanD rise in the high-elasticity state, which fact indicated formation of additional filler-filler interactions. Thus, the CNT treatment with carbon black resulted in a synergy effect upon the rubbers' dynamic characteristics; hence, it can be applied to the task of raising the material frost resistance point.

Key words: glass transition, elastomer, carbon black, carbon nanotubes

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INTRODUCTION

Currently, the composite-materials science is greatly interested in the use of hybrid fillers. The term hybrid filler refers to a combination of two or more fillers, composed of particles of different shapes or those of different chemical nature, while there is a physical-and-chemical interaction among the particles on the nanometer scale [1]. The material containing the hybrid filler exhibits properties (mechanical, tribological, electrical, and thermal), otherwise unachievable, in case the components are used individually [2, 3]. The researchers pay special attention to hybrid fillers based on allotropic sp^2 carbon forms: CB, CNT, graphene or graphite nano-filler consisting of several graphene layers [4-6]. The experiments demonstrated that the simultaneous use of a CB/CNT combination results in a synergistic effect upon the strength and fatigue endurance of vulcanizates, as well as on their electrical characteristics [7-13]. The authors believe that this effect is due to high similarity of thread-like and spherical particles, composed of graphene planes; the ability of the particles to form a filler hybrid network within the vulcanizate structure [7]; vulcanizates' increased resistance to fatigue cracks formation [9, 10]; natural rubber like behavior of CNT [13]; and a better CNT spread within rubber in the CB presence [12].

Given the importance of molecular mobility in the formation of the vulcanizates' mechanical properties, the authors are especially interested in studying the effect of CB/CNT hybrid filler upon molecular mobility of rubber chains, as well as the chain mobility's connection with the vulcanizates' viscoelastic properties.

The most informative from the point of view of the macromolecules' mobility is the α-transition, due to the main relaxation transition in polymers –i.e. glass transition. One can distinguish structural and mechanical glass transitions in polymers. Structural vitrification occurs in the absence of mechanical load upon the sample. The structural vitrification temperature (T_g) can be determined by differential scanning calorimetry (DSC) through a sharp change in the polymer sample's heat capacity when cooled or heated [14]. At which point the calorimetric measurements can hardly register movements of such structural units as chains, side chain substituents, in other words, units, smaller than a macromolecule's segment [15].

Mechanical glass transition occurs when the polymer material is cooled under cyclic load. The mechanical vitrification temperature (T_{mg}) can be determined by dynamic mechanical tests (DMA) [16]. In this case the indicator of the rubber chains mobility is the temperature point of the maximum mechanical loss tangent (TanD). Both the shape and the steepness the TanD = f (T) dependence peak provide additional data.

PROCEDURE

Vulcanizates containing hybrid CB/CNT filler are this study's object. The original CNT's were manufactured by means of the CVD technology (OCSiAl, Novosibirsk, Russia). According to the manufacturer the CNT's are two-wall structures (1-2 walls) measuring ~1.5 nm in diameter and over 5 μm in length. The CNT specific surface area is 360 m^2/g (specific surface area was determined by the Brunauer-Emmett-Teller method). The impurities of carbon and metal were removed from the CNT batch by exposing it to 12M HNO_3 (48 h, room temperature). The cleaning of CNT was performed through annealing in a muffle furnace at 400 °C for 1 h. According to the TGA curve, the content of metallic impurities in the CNT as a result of the purification process was reduced from 23 to 9 wt.%.

The content of the filler in all vulcanizates is the same - 48.5 phr (phr = parts per hundred parts of rubber), the volume fraction of the filler is 0.27. In the modified vulcanizates, some of the original CB N330 was replaced with CB/CNT masterbatches. Masterbatches consisting of CB N330 and CNT were jointly prepared by ultrasonic treatment of the components in a volatile solvent medium [17]. Samples I - IV differ in the CNT content and preparation conditions. Sample I (0.1 phr) and II (0.5 phr) was prepared in 10-fold excess of CB, sample III (0.1 phr) and IV (0.5 phr) - in 50-fold excess of CB. The masterbatches were introduced into the rubber mixes along with the CB N330 main filler.

The formulation of research mixtures complies with the sidewall formulation of a pneumatic tire (phr): synthetic rubber cis-isoprene IR-3 (40.0), neodymium cis-1,4-polybutadiene BR-Nd (60.0), ZnO (5.0), stearic acid (2.0), Norman oil (5.5), paraffin wax (2.0), IPPD (2.0), TMQ (2.0), CB N330 (48.5), sulfur (1.55), PVI (0.23). Rubber stocks were mixed in a laboratory two-roll mill.

The calorimetry analysis was performed with Schimadzu DSC analyzer, heating rate was 2 °/min. The dynamic mechanical analysis was done with *Netzsch* DMA 242C dynamic mechanical analyzer, in 10 hz oscillation mode in -100 to +60 °C temperature range. Based on the obtained data we calculated the compounds' dynamic elasticity modulus (the so-called storage modulus E′), the maximum value of the mechanical loss tangent ($TanD_{max}$), the $TanD_{max}$ temperature. The vulcanizates' mechanical properties were tested with *Shimadzy* AG-5kNX tensile tester per *GOST* (State Standard) 270–75 requirements.

The TEM images of the hybrid filler particles were made through *JEOL* JEM2100 microscope (at 200 kV accelerating voltage).

RESULTS AND DISCUSSION

Fig. 1 shows TEM image CB/CNT masterbatch (sample I). The primary CB aggregates are seen to be aligned along the CNT bundles. Table 1 lists physical and mechanical properties of the vulcanizates containing hybrid CB/CNT filler, the control is the vulcanizate filled with N330 CB only. Unfortunately, it was not possible to produce a rubber mixture containing 48.5 phr CNT. According to the SEM images, quite large CNT agglomerates were present in the volume of the rubber mixture. This did not allow parallel testing of the vulcanizates. According to [7], it is possible to distribute satisfactorily in the polyisoprene matrix not more than 11.3 phr CNT using a Brabender type mixer.

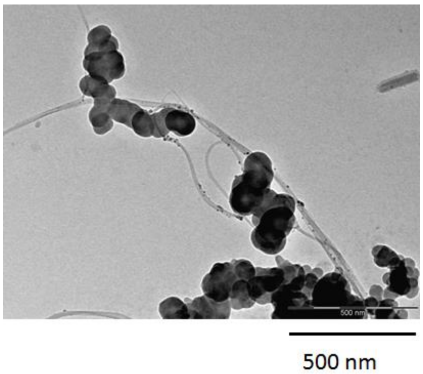

Fig. 1. CB/CNT masterbatch TEM image

Рис. 1. ТЕМ изображение исходного CB / CNT

Table 1

Physicomechanical characteristics of vulcanizates containing hybrid filler

***Таблица 1*. Физико-химические характеристики вулканизатов, содержащих гибридный наполнитель**

Indicator	Control	Vulcanizates containing samples of CB/CNT masterbatch			
		I	II	III	IV
Tensile stress at 100 %, MPa	1.8	2.0	2.5	2.0	2.9
Tensile stress at 300 %, MPa	6.8	6.6	7.3	11.0	11.5
Tensile strength at break, MPa	18.0	18.0	15.2	17.0	17.5
Elongation at break, %	530	580	510	550	430
Fatigue resistance, number of cycles (ε = const)	670	2120	170	1450	510
Resistance to tear, kN/m	68	72	66	76	79
Density, g/sm^3	2.03	1.75	1.88	1.83	2.04

Table 1 demonstrates that samples I and III exhibit longer fatigue life as compared to the control and samples II and IV. Samples III and IV are characterized by increased stress values at 100% elongation, and 300% increase in tear resistance.

Fig. 2 presents temperature dependence of the dynamic elasticity modulus (storage modulus) E′ and TanD. Fig. 2 demonstrates, that vulcanizates, containing hybrid filler, display a decrease of the E′ value in the vitrified state. At which point the TanD$_{max}$ position and the dependencies change greatly. Thus, the TanD$_{max}$ position moves along the temperature axis towards lower temperatures by 4 (sample II) to 16 (sample I) degrees Celsius. In the case of samples I, II, III the TanD$_{max}$ value rises broadening the TanD peak on the glass side of the glass-to-rubber transition. In the case of sample IV theTanD$_{max}$ value goes down against the control vulcanizate, however the peak broadens on both the glass side and highly elastic side of the glass-to-rubber transition.

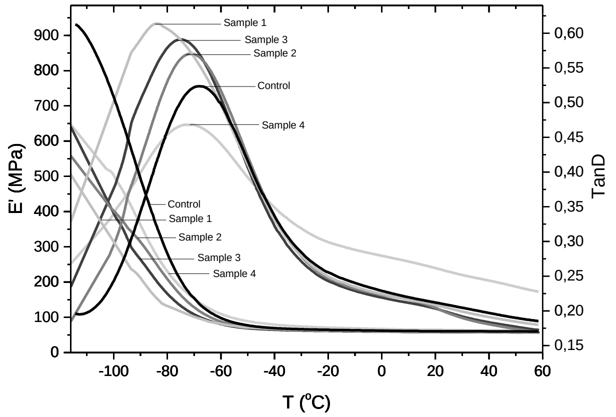

Fig. 2. The temperature dependence of the storage modulus E' and the loss tangent TanD

Рис. 2. Температурная зависимость модуля хранения E' и тангенса угла потерь TanD

Table 2 presents DSC data for vulcanizates containing the hybrid filler (samples I and IV), as compared against unfilled IR-3/BR-Nd-based rubber stock and the control vulcanizate.

Table 2

DSC data for objects under study

***Таблица 2.* ДСК данные исследуемого объекта**

α-transition temperatures, °C	Unfilled rubber compound	Vulcanizates		
		control	Sample I	Sample IV
BR-Nd	- – 109	- – 104	– 118 – 108	– 123 – 101
IR-3	– 65	– 63	– 63	– 62

Table 2 demonstrates that introduction of N330 CB-filler into the rubber compound, the T$_g$ structural transition temperature shifts towards higher temperature by 5 degrees for the BR-Nd component, and by 2 degrees for the IR component. Introduction of the hybrid particles (sample I) resulted in the reduction of the structural transition temperature of the BR-Nd component up to that of the unfilled rubber compound, moreover, there occurred the −118 °C low-temperature peak. When sample IV was introduced, the structural transition temperature of the BR-Nd component, to the contrary, shifted towards higher temperatures, while the −123 °C low-temperature peak still occurs (Fig. 3).

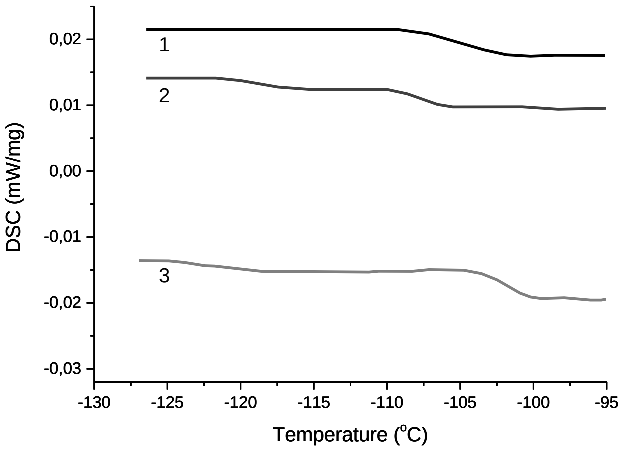

Fig. 3. DSC curves of control vulcanizate (1), vulcanizates containing samples I (2) and IV (3)
Рис. 3. Кривые ДСК контрольного вулканизата (1) и вулканизатов, содержащих образцы I (2) и IV (3)

As to the commonly accepted knowledge of the polymers glass transition process, the macromolecules' mobility depends on the degree of the intra- and inter-molecular interactions, macromolecules' conformational abilities, and the availability of some free volume/space within the polymer [18]. Within filled polymers segmental mobility of the macromolecules in the vicinity of solid particles can be restricted by the physical and chemical interactions with the surface of the filler [19, 20].

Detailed DMA studies of the unfilled non-polar rubber's segmental mobility demonstrated [21], that the mobility didn't depend on the particles size, specific surface area, and the CB structure (the samples ranged from N990 CB to N110 CB, the in-vulcanizates filler volume fraction was 0.18). In publications [22, 23] it was demonstrated that the structural glass transition temperature for filled polymers (DSC technique) practically didn't depend on the fillers' specific surface area and particle size.

In this study the compound containing sample I (0.1 CNT phr, 10:1 CB/CNT ratio in the masterbatch) featured enhanced fatigue endurance (Table 1), broadening of the TanD peak on the vitrification side of the TanD = f(T) extreme dependency, a significant T_{mg} shift towards lower temperatures as compared against the control vulcanizate (Fig. 2). This indicated a change in the structure of the material with the introduction of the hybrid particles. Given the decrease in the density of the vulcanizate (Table 1) it can be assumed that in its volume there appeared some areas with less densely packed macromolecules. This means that the macromolecules have more conformational capabilities in segmental movement at lower temperatures. This fact is backed by the DSC data: there is a new α-relaxation transition point having a meant glass-transition point temperature of −118 °C.

The nature of the TanD temperature dependence of the compound containing sample IV (CNT 0.5 phr, 50:1) indicates the appearance of intensive inter-component interactions within the vulcanizate. To overcome such interactions additional mechanical energy is spent in the highly elastic state, i.e. in the -30 to +60 °C temperature range (Fig. 2). It can be assumed this phenomenon is due to the formation of a filler network composed of hybrid CB/CNT particles (the ones formed in preparation of masterbatch IV) and CB particles. The obtained data are consistent with the study [7], in which through electron microscopy the hybrid filler networks were proved to form in vulcanizates filled with the two CB and CNT fillers. The fillers network is nothing else but the CB aggregates linked by nanotubes. Moreover, the formation of a continuous unbroken network depends on the CB and CNT content in the vulcanizates.

The filler network formation is known to occur during the vulcanization process, while the compound still retains its plasticity and the filler aggregates flocculate, thus forming the material's final structure, its mecanical properties and, specifically, energy dissipation at cyclic deformations [24]. This structure includes areas with low-mobility macromolecules inside the filler nodes (shaded area, Fig. 4), the so called «dead rubber» [25].

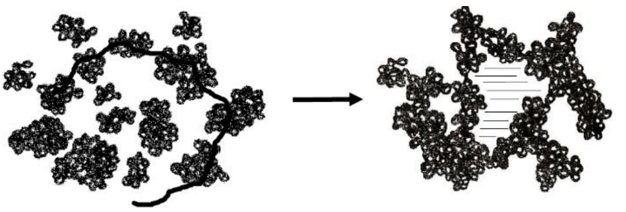

Fig. 4. Filler aggregates flocculation during vulcanization
Рис. 4. Флокуляция агрегатов наполнителя при вулканизации

It can be assumed that, on the one hand, the long curved CNT's (Fig. 1) threading the CB aggregates facilitate the low-mobility rubber areas. The existence of such areas results in the increase of the material's rigidity and tear strength (sample IV, table 1). On the other hand, CNT presence reduces the number of filler-polymer interactions, which leads to more unoccupied volume in the vulcanizate, thus increasing the rubber macromolecules' mobility. This mobility can be the reason for the detected low-temperature α-transitions (the DSC data), as well as the TanD peak broadening on the vitrification side of the TanD = f (T) dependency (the DMA data).

In general, mechanical behavior of the vulcanizates containing sample II (0.5 phr, 10:1) and sample III (0.1 phr, 50:1) correlates with the behavior of sample IV and I correspondingly. This fact demonstrates that the CNT amount is paramount in the formation of uninterrupted filler network, and as such, in the formation the vulcanizates' properties, rather than the CB/CNT ratio in the masterbatch formula.

CONCLUSION

The study has looked into the effect of CB/CNT hybrid filler upon molecular mobility of rubber chains, as well as the chain mobility's connection with the vulcanizates' viscoelastic properties. It has been demonstrated that filler particles in combination with CB change the vulcanizates' final structure by creating areas with less densely packed macromolecules, exhibiting increased segmental mobility at lower temperatures. This opens up possibilities for manufacturing rubber with higher fatigue endurance and frost resistance properties.

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