

PRIMARY RESEARCH

Relaxation behavior of elastomer composites: The effect of a hybrid carbon black/carbon nanotubes filler

Mansurova I. A.^{1*}, Burkov A. A.², Shilov I. B.³, Shirokova Ye.S.⁴, Dolgiy E. O.⁵, Khousainov A.B.⁶, Belozеров V. S.⁷

^{1, 2, 3, 4, 7} Vyatka State University, Kirov, Russia

⁵ PK Kirov Tire, Kirov, Russia

⁶ Kazan National Research Technological University, Kazan, Russia

Keywords

Glass transition
Elastomer
Carbon black
Carbon nanotubes
Hybrid filler

Received: 4 April 2018

Accepted: 20 May 2018

Published: 5 June 2018

Abstract

The article analyzes relaxation α -transition in elastomeric composites containing a hybrid carbon black/carbon nanotubes (CB/CNT) filler. According to the DMA data, the inclusion of hybrid particles CB/CNT in the filler leads to the expansion of the temperature dependences of the loss tangent (TanD) for all samples towards lower temperatures and the displacement of the position of the TanD maximum by a value from 4.0 up to 16 degrees in comparison with control vulcanizate. The DSC data indicate the presence of additional low-temperature α -relaxation transitions in modified vulcanizates (-123 ... -118 °C). The observed relaxation behavior of macromolecules is due to the appearance in the material of regions with less dense packing of macromolecules and, as a consequence, the expansion of their conformational set for segmental motion under low-temperature conditions. It guarantees to get material with increased fatigue resistance and frost resistance. It is shown that hybrid filler particles, in comparison with carbon black, change the final structure of vulcanizates, causing the appearance of areas with a more loose packing of macromolecules and increased segmental mobility in the low-temperature area. It gives opportunities for getting rubber with increased fatigue resistance and frost resistance.

© 2018 The Author(s). Published by TAF Publishing.

I. INTRODUCTION

Recently, the use of hybrid fillers in polymeric composites has become widespread. By a hybrid filler we mean a combination of two or more fillers consisting of particles of different shapes or particles of different chemical nature, which have a physico-chemical interaction at the nanometer level. A material, which contains a similar filler, has a complex of properties that is not achievable with the use of separate components [1, 2, 3].

Experimental results show that the simultaneous use of a combination of CB and CNT leads to a synergistic effect on the strength and fatigue endurance of vulcanizates, their electrical characteristics [4, 5, 6, 7, 8]. Taking into account the important role of molecular mobility in the formation

of a complex of mechanical properties of vulcanizates, it is interesting to consider the effect of a hybrid CB/CNT filler on the molecular mobility of rubber chains and its relationship to the viscoelastic properties of vulcanizates.

From the point of view of mobility of macromolecules, the most informative is the α -transition, caused by the main relaxation transition in polymers by glass transition. There are structural (or true) and mechanical glass transition of polymers. Structural glass transition is performed when there is no mechanical stress on the sample. Structural glass transition temperature (T_g) can be determined by the Differential Scanning Calorimetry (DSC) method to dramatically change the heat capacity when the polymer sample is heated or cooled. In this case, calorimetric measurements

*Corresponding author: Mansurova I. A

†email: I.A.Mansurova@yandex.ru



are insensitive to the motion of smaller ones than the segment of structural units of macromolecules (links, side substituents).

Mechanical glass transition occurs during cooling under the action of a cyclic load on the polymer material. The temperature of mechanical glass transition (T_{mg}) can be determined by the method of Dynamic Mechanical Testing (DMA). Here, the indicator of the mobility of the rubber chains is the position on the temperature scale of the maximum of the loss tangent ($TanD$). Additional information is given by the form and intensity of the peak of the dependence $TanD = f(T)$.

II. EXPERIMENT

The object of the study are vulcanizates containing a hybrid CB/CNT filler. The initial CNTs are single- and double-walled structures with an external diameter of ~ 1.5 nm and a length of more than $5 \mu m$ (Figure 1). The specific surface area of the CNT is $360 m^2/g$. The CNT array was preliminarily subjected to purification in $12M HNO_3$.

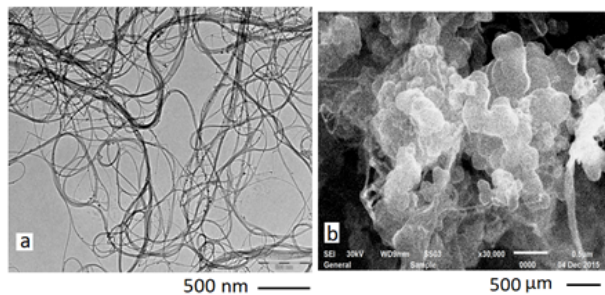


Fig. 1. TEM image of the initial CNT (a); SEM image of the masterbatch CB/CNT (sample I) (b)

Powder masterbatches consisting of CB N330 and CNT were prepared according to the procedure [9, 10]. Masterbatches (samples I - IV) differ in the content of CNT and the conditions of preparation. Samples I (0.1 phr, phr = parts by weight per hundred parts of rubber) and II (0.5 phr) were prepared in 10-fold excess of CB, samples III (0.1 phr) and IV (0.5 phr) in a 50-fold excess of CB. We introduced masterbatches into the composition of rubber mixtures together with the main filler CB N330. The total amount of filler in all vulcanizates is the same (48.5 phr), the volume fraction of filler is 0,27. The formulation of rubber compounds, phr:

IR (40.0), BR (60.0), ZnO (5.0), stearic acid (2.0), Norman oil (5.5) (2.0), IPPD (2.0), TMQ (2.0), CB N330 (48.5), sulfur (1.55), PVI (0.23). Rubber mixtures were manufactured using a laboratory twin-roll machine. Calorimetric measurements were performed using a DSC analyzer "Shimadzu", the rate of temperature rise is $2^\circ/min$. Dynamic mechanical analysis of vulcanizates was carried out using a dynamic mechanical analyzer DMA 242C ("Netzsch"), 10 Hz in oscillation mode. The mechanical properties of vulcanizates were evaluated on an AG-5kNX test machine (Shimadzu) according to GOST 270-75.

III. RESULTS

Figure 1 shows the SEM image of the CB/CNT masterbatch (sample I). It can be seen that the filamentary structures are isotropically distributed in the volume of aggregates and agglomerates of the CB. The CNT array is dispersed to beams with a diameter of 10 to 110 nm. Table 1 shows physical and mechanical properties of vulcanizates containing a hybrid CB/CNT filler, the comparison is a sample filled with CB N330. Table 1 shows that samples I and III differ in their increased fatigue resistance in comparison with the control and samples II and IV. Samples III and IV are characterized by increased voltage values with an elongation of 100, 300%, tear resistance. Figure 2 shows the temperature dependences of the dynamic elasticity modulus (the accumulation modulus) E' and $TanD$.

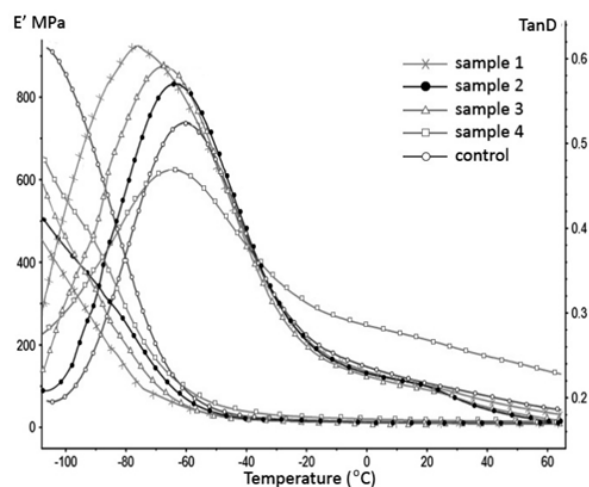


Fig. 2. The temperature dependence of the dynamic elastic modulus E' and the loss tangent $TanD$

TABLE 1
PHYSICAL AND MECHANICAL CHARACTERISTICS OF VULCANIZATES CONTAINING A HYBRID FILLER

Indicator	Control	Vulcanizates Containing Samples of Masterbatch CB/CNT			
		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 ($\epsilon = \text{const}$)	670	2120	170	1450	510
Resistance to tear , kN/m	68	72	66	76	79
Number of cross-links per unit volume of vulcanizate , nc-10 ¹⁹ , sm ⁻³	7,5	6,8	8,2	6,9	10,6
Density, g/sm ³	2,03	1,75	1,88	1,83	2,04

Figure 2 shows that vulcanizates containing hybrid particles are characterized by a decrease in the value of E' in the glass transition area. In this case, the position of the maximum TanD and the shape of the peak change significantly. Thus, the position of the TanD maximum on the temperature scale shifts toward lower temperatures by a value from 4 (sample II) to 16 (sample I) degrees. In the case of samples I, II, III, the TanD increases, with the loss tangent peak widening on the glass side of the glass-to-rubber transition. In the case of sample IV, TanD decreases, expanding both in the region of lower and higher temperatures relative to the maximum transition of glass-to-rubber.

Table 2 shows the DSC data for vulcanizates containing a hybrid filler (samples I and IV) in comparison with an unfilled rubber mixture based on a combination of IR and BR rubbers and control vulcanizate. Table 2 shows that with the introduction of CB N330 into the rubber mixture the temperature of structural glass transition of T_g composites is shifted towards higher temperatures by 5 degrees for the BR component and 2 degrees for the IR component. With the introduction of the hybrid particles (sample I), the temperature of the structural glass transition of the BR component is reduced to the value of the unfilled rubber mixture and, in addition, a low-temperature peak of -118°C appears.

With the introduction of sample IV, on the contrary, the temperature of structural glass transition of the BR component shifts towards higher temperatures, but a low-temperature peak of -123°C also appears (Figure 3).

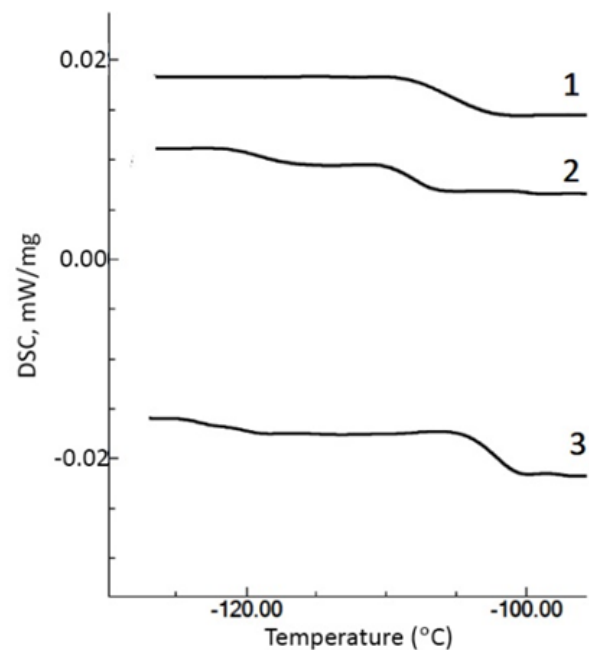


Fig. 3. DSC curves of control vulcanizate (1), vulcanizates containing samples I (2) and IV (3)

TABLE 2
DSC DATA FOR RESEARCH OBJECTS

α -Transition Temperatures, °C	Unfilled Rubber Compound	Vulcanizates		
		control	Sample I	Sample IV
BR	-	-	- 118	- 123
	- 109	- 104	- 108	- 101
IR	- 65	- 63	- 63	62

IV. DISCUSSION

According to the current understanding of the glass transition of polymers, the mobility of macromolecules depends

on the intensity of intra- and intermolecular interactions, the conformational capabilities of macromolecules, and the presence of free volume in the polymer [11]. In filled poly-

mers, the segmental mobility of macromolecules located near solid particles can be limited by physico-chemical interactions with the filler surface [12].

Detailed studies of the segmental mobility of a nonpolar rubber by the DMA method have shown [13] that it is practically independent of the particle size, the specific surface area and the structural structure of the CB (the scope of the study included CB from N990 to N110, the volume fraction of the filler in the vulcanizates was 0.18). It was shown in [14] that the temperature of the structural glass transition of the filled elastomer (DSC method) depends little on the specific surface area of the CB.

In the present study, vulcanizates containing sample I (0.1 phr of CNT, a ratio of CB/CNT in a masterbatch of 10:1) are characterized by an increase in fatigue resistance (Table 1), expansion of the TanD peak on the glassy side of the extreme dependence $\text{TanD} = f(T)$, a significant shift of T_{mg} to lower temperatures in comparison with the control (Figure 2). It indicates a change in the structure of the material with the introduction of hybrid particles. Taking into account the decrease in the number of cross-links, the density of the material (Table 1), it can be assumed that regions with more loose packing of macromolecules appear in the bulk of the material. It means that macromolecules have a wider set of conformational possibilities for segmental motion in low-temperature conditions. This is confirmed by the DSC data: the appearance of a new relaxation α -transition with an average glass transition temperature -118°C .

The nature of the temperature dependence of the TanD material containing sample IV (0.5 phr of CNTs, 50:1) indicates the appearance of additional filler-filler and filler-polymer interactions in the volume of vulcanizate. To overcome them, mechanical energy is also used in the area of the developed highly elastic state (Figure 2). The material is characterized by a higher degree of crosslinking, which is reflected in the growth of stiffness and tear resistance (Table 1). Taking into account the data on the effect of CNT

on the vulcanization process [15], it can be assumed that in this case, nanotubes in the hybrid filler contribute to an increase in the degree of crosslinking of macromolecules. In addition, they influence the process of flocculation of the particles of the hybrid filler and the formation of the final structure of the material during the vulcanization process. This structure does not exclude the presence of regions with both denser and less dense packing of macromolecules in the material. In particular, areas with denser packaging, i.e., less mobile macromolecules correspond to rubber, which is inside the aggregates of the filler, the so-called "trapped rubber", "dead rubber" [16]. According to the data in Table 2, a part of the BR component may correspond to such a rubber in the material, the temperature of its structural glass transition shifts by 3 degrees towards higher temperatures. In addition, there are regions with a more loose packing of macromolecules, which corresponds to α -transition with an average glass transition temperature of -123°C (DSC data), and an expansion of the TanD peak on the glassy side of the $\text{TanD} = f(T)$ curve (DMA data).

The mechanical behavior of vulcanizates containing samples II (0.5 phr, 10:1) and III (0.1 phr, 50:1) as a whole corresponds to the behavior of samples IV and I, respectively, indicating that the number of CNTs plays the predominant role in the formation of a complex of properties of vulcanizates, rather than the ratio of the components in the preparation of CB/CNT masterbatches.

V. CONCLUSION

The paper analyzes the effect of a hybrid CB/CNT filler on the molecular mobility of rubber chains and its relationship to the viscoelastic properties of vulcanizates. It is shown that hybrid filler particles, in comparison with carbon black, change the final structure of vulcanizates, causing the appearance of areas with a more loose packing of macromolecules and increased segmental mobility in the low temperature area. It gives opportunities for getting rubber with increased fatigue resistance and frost resistance.

REFERENCES

- [1] U. Szeluga, B. Kumanek, and B. Trzebicka, "Synergy in hybrid polymer/nanocarbon composites. a review," *Composites Part A: Applied Science and Manufacturing*, vol. 73, no. 5, pp. 204-231, 2015. doi: <https://doi.org/10.1016/j.compositesa.2015.02.021>
- [2] L. T. D. Ha and K. M. T. Tsai, "Numerical study on optimization of wooden-steel hybrid beams base on shape factor of steel component," *International Journal of Technology and Engineering Studies*, vol. 1, no. 2, pp. 53-62, 2015. doi: <https://doi.org/10.20469/ijtes.40004-2>
- [3] I. Sugiyatno, A. Djunaedi, and N. A. Mahardiono, "Modelling and simulation of hybrid control system in solar cell-battery-super capacitor," *International Journal of Technology and Engineering Studies*, vol. 1, no. 3, pp. 74-80, 2015. doi: <https://doi.org/10.20469/ijtes.40002-3>

- [4] B. Dong, C. Liu, Y. Lu, and Y. Wu, "Synergistic effects of carbon nanotubes and carbon black on the fracture and fatigue resistance of natural rubber composites," *Journal of Applied Polymer Science*, vol. 132, no. 26, pp. 45-50, 2015. doi: <https://doi.org/10.1002/app.42075>
- [5] H. Ismail, A. F. Ramly, and N. Othman, "The effect of carbon black/multiwall carbon nanotube hybrid fillers on the properties of natural rubber nanocomposites," *Polymer-Plastics Technology and Engineering*, vol. 50, no. 7, pp. 660-666, 2011. doi: <https://doi.org/10.1080/03602559.2010.551380>
- [6] L. Bokobza, M. Rahmani, C. Belin, J. L. Bruneel, and N. E. El Bounia, "Blends of carbon blacks and multiwall carbon nanotubes as reinforcing fillers for hydrocarbon rubbers," *Journal of Polymer Science Part B: Polymer Physics*, vol. 46, no. 18, pp. 1939-1951, 2008. doi: <https://doi.org/10.1002/polb.21529>
- [7] F. Umer and N. Cetinkaya, "Transient analysis due to short circuit faults in wind hybrid systems," *Journal of Advances in Technology and Engineering Research*, vol. 3, no. 3, pp. 89-100, 2017. doi: <https://doi.org/10.20474/jater-3.3.4>
- [8] K. Rassiah, M. M. H. Megat Ahmad, and A. Ali, "Effect on mechanical properties of rice husk/e-glass polypropylene hybrid composites using Sodium Hydroxide (NaOH)," *Journal of Advances in Technology and Engineering Research*, vol. 2, no. 4, pp. 105-112, 2016. doi: <https://doi.org/10.20474/jater-2.4.1>
- [9] C. G. Robertson and C. M. Roland, "Glass transition and interfacial segmental dynamics in polymer-particle composites," *Rubber Chemistry and Technology*, vol. 81, no. 3, pp. 506-522, 2008. doi: <https://doi.org/10.5254/1.3548217>
- [10] I. Mansurova, A. Burkov, O. Isupova, I. Zagrai, A. Khlebov, E. Durnev, and K. Gavrilov, "Functionalization of carbon nanotubes by carbon black or polymers to modify the dynamic mechanical properties of rubber," *Inorganic Materials: Applied Research*, vol. 8, no. 9, pp. 69-80, 2017. doi: <https://doi.org/10.1134/s2075113317020149>
- [11] V. G. Rostiashvili, V. I. Irzhak, and B. A. Rosenberg, *Glass Transition of Polymers*. Sofia, Bulgaria: Khimiya, Leningrad., 1987.
- [12] Y. S. Lipatov, *Physico-Chemical Basis of Polymer Filling*. Moscow, Russia: Himiya, 1991.
- [13] C. G. Robertson, C. J. Lin, M. Rackaitis, and C. M. Roland, "Influence of particle size and polymer-filler coupling on viscoelastic glass transition of particle-reinforced polymers," *Macromolecules*, vol. 41, no. 7, pp. 2727-2731, 2008. doi: <https://doi.org/10.1021/ma7022364>
- [14] M. Huang, L. B. Tunnicliffe, A. G. Thomas, and J. J. Busfield, "The glass transition, segmental relaxations and viscoelastic behaviour of particulate-reinforced natural rubber," *European Polymer Journal*, vol. 67, no. 5, pp. 232-241, 2015. doi: <https://doi.org/10.1016/j.eurpolymj.2015.03.024>
- [15] S. Musto, V. Barbera, V. Cipolletti, A. Citterio, and M. Galimberti, "Master curves for the sulphur assisted crosslinking reaction of natural rubber in the presence of nano- and nano-structured sp² carbon allotropes," *Express Polymer Letters*, vol. 11, no. 6, pp. 435 - 448, 2017. doi: <https://doi.org/10.3144/expresspolymlett.2017.42>
- [16] M. J. Wang, "The role of filler networking in dynamic properties of filled rubber," *Rubber Chemistry and Technology*, vol. 72, no. 2, pp. 430-448, 1999. doi: <https://doi.org/10.5254/1.3538812>