

FORMATION OF THE VULCANIZATION STRUCTURE OF THE ELASTOMERIC MIXTURES WITH THE PRESENCE OF ND.

Associate Prof. PhD eng. Tzolo Tzolov¹, PhD eng. Aleksandar Stoyanov¹, Mas.deg.eng.Margarita Trencheva²
 Department of Chemical Technology and Metallurgy, UCTM¹
 University of Chemical Technology and Metallurgy –Sofia²
 tzolovtz@abv.bg, anstoianov@abv.bg, margarita_trencheva@abv.bg

Abstract: In the given work the influence of detonation carbon on a complex of strain-strength parameters and supramolecular structures of standard compositions based on natural rubbers without stearin acid has been investigated.

Key words: detonation carbon, elastomer, rubber, composite material

I. Introduction

Nowadays, polymeric materials are applied practically in all areas of human activity and replace the increasingly used traditional metals and alloys from the modern fields of engineering, machine building, etc.

A particular place in the polymeric materials is elastomers. This is related to their unique mechanical properties, one of which is the presence of high values of the reversible deformation, which is based on their ability to be in their working high elastic state.

The dynamic development of nanotechnology with the processing of elastomers determines the great importance of studying the structure of the elastomeric material.

One of the important components of the composite material (CM) - the elastomeric mixture (EM) is the fillers. The importance of fillers is related to the production of materials with specified properties necessary for certain branches of the economy, research, medicine, etc.

II.Explanation

Concerning nanotechnologies and fillers for elastomeric mixtures, the influence of nanodiamonds (ND) as an element of the nanoparticles on the elastomeric mixtures before the formation of the supermolecular structure of the mixture and in the vulcanization process preceding the manufacture of the rubber article is inevitably studied.

The influence of ND on the EM should be directed to the interfacial processes and superficial phenomena of the boundary elastomer - filler, because precisely the changes occurring in them determine the emergence of a new complex of properties of CM.

As the first stage of this study, physicochemical properties of ND should be determined.

The diamond modification of carbon has the highest values of free surface energy [1], which leads to a high activity of nanoparticles in the modified material but is found in a powdery state in air, ND tends to agglomeration, leading to a reduction in excess surface energy - deactivation.

On the other hand, [2] the introduction of DB (diamond batch) in the ready-mixed mixture with a formed supermolecular structure (rubber-filler), they play the role of a solid lubricant rather than an active filler, thereby increasing the elasticity, the relative elongation at break, but a decrease in the contingent tension at 100 and 300% was observed.

It follows that it is expedient, from the point of view of the modifying effect, the introduction of ND before the formation of the supermolecular structure, i. to examine their impact on its formation.

In order to increase the ND's modifying effect on the EM, in order to preserve the values of free surface energy, the ND should be introduced together with the inert storage medium by retaining the activity of the elastomer mixture. There are two problems in the reasoning here, namely:

- Influence of fat and olefin based ingredients on surface activity of ND.

- The influence of the inert environment in which ND is stored on the characteristics of the vulcanized EM.

If an analogy between ND and diamond batch (DB) is made as the raw product of the blast, the authors [3, 4] have found that DB has a modifying effect on all types of rubber mixtures tested, regardless of type and type of rubber, the main effect of the modifying effect was the degree of filling and the means and variants for introducing the components into the mixture and, to a lesser extent, the type and activity of the filler. As proof of the claim, the following experiments can be presented:

- For example, according to [5] the cohesive strength of oil-filled blends depends to a large extent on the mode of introduction of DB, if they are introduced into a composition with the oil, the cohesive strength falls, and if introduced together with the soot and then the oil increases.

- It is also found [2] that the modifying activity of DB depends on the presence of plasticizers (oil) in the composition of the EM and on the mode of incorporation of DB into the mixture.

In addition, the introduction of ND along with the stearic acid [6], besides wetting the filler particles, in this case ND, the polar acid residue is oriented towards the particles of the filler by covering them with a monomolecular layer, thus deactivated.

So far, we can conclude that if we want to preserve free surface energy values of ND in the EM (formulations), fat and olein-based ingredients should be excluded from the composition, irrespective of their importance in the formation of the necessary physical-mechanical and vulcanization characteristics.

On the question of the inert environment in which NDs are stored.

In general, the inert environment falling into the mixture would have to evaporate, react with the components of the mixture, or remain in the mixture without adversely affecting the formation of the actual vulcanisation agent (AAV).

When introducing ND along with accelerators, more than one accelerator can be used to model the properties of vulcanisates in the process of forming the AAB.

According to [4], dual accelerator systems, the impact they exert on the properties of vulcanisates can be divided into:

- Systems with mutual activation of accelerators (dibenzthiazolyl disulfide (Altax) and diphenylguanidine (DPG)).

- Systems with activation of one accelerator (cyclohexylbenzothiazole sulfenamide (CZ) and DPG).

- Systems with additive action of accelerators (sulfenamide and tetramethyl thuram monosulfide (TMTM)).

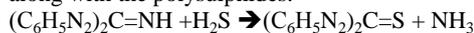
If a system with activation of one accelerator is considered (CZ and DPG), the DPG substitution lowers the tear resistance and reduces the modulus to mixtures with CZ only [7]. In the present case, according to [6] there is activation of DPG with CZ.

An explanation of the process can be given in the following way:

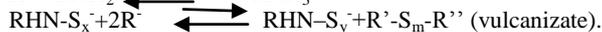
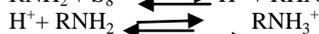
- in the initial stage, the accelerators interact with one another to form a less active complex with respect to the addition of sulfur to the elastomer mixture;

- in the next stages of the process, the complex decomposes to radicals initiating the interaction of sulfur with rubber and other structuring processes.

Historical data were obtained [6] in studying the mechanism of action of DPG in sulfur vulcanization. DPG heated in an inert environment disintegrates with the formation of ammonia, aniline, tetraphenylamines, triphenyldiuramide. With the method of infrared and ultraviolet spectroscopy in the products of interaction of DPG and sulfur, linear polysulfides containing from two to five atoms of sulfur are found. Also, thioketones and ammonia have been found along with the polysulphides.



Sulfur vulcanization in the presence of amines may be described by an ionic mechanism:



According to [6] with the DTMA method the influence of DPG on the vulcanization process was investigated. It has been found that DPG is not only an accelerator, but also acts as a water regulator on the vulcanization process. In turn, the released water is a catalyst for the oxidation reaction of the SH groups.

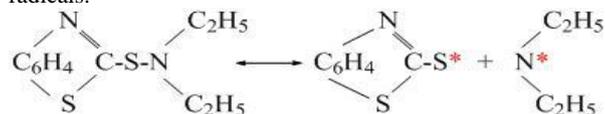
The basis of the mechanism of action of accelerators containing no sulfur is the following factors [8]:

Sulfur-containing amine-containing accelerators participate in oxidation-reduction processes and produce the formation of free radicals causing rubber to be structured;

Mixture code Ingredients / mass. p.	C-1	C-2
Natural Rubber (SVR10)	100	100
ZnO	5.0	5.0
S	1.5	1.5
CZ	1,5	1,5
DPG	0.5	0.5
Nanodiamonds	1,5	0

- Amino-accelerators, promote faster exchange reactions, activate the sulfur by the formation of intermediate amine polysulphides, upon decomposition of which the active sulfur fragments structuring the elastomer mixture are separated.

In the presence of sulphenamid accelerators, vulcanization takes place under the action of the bezthiazol nucleus and the amine radicals.



The addition of the amine radical to the sulfur molecules results in the formation of polysulphides of the amines.



In case of elemental sulfur deficiency, the number of sulfur atoms in polysulfide bonds decreases.

In addition, complex compounds are formed using vulcanizing systems involving metal compounds, and complexes are formed using thiazoles, such as activators and zinc compounds.

If water is the inert environment in which ND is stored in the mixture, it may:

- to act as a catalyst for the oxidation reaction of SH groups;
- part of it evaporates when the roller mixture is processed and in the vulcanization process;
- and one part may remain in the mixture in the form of a capillary physically associated with ND water.

Confirmation of the claim is the finding by [9] of the presence in the ND of connected and sorbed water. It is not even released when drying at 393 K.

If we come back to the question of ND's modifying action, it should be noted whether or not they are purified.

Ideally, we assume that purified NDs do not chemically react with the individual components of the mixture, and the amplification effect [10] is associated with the formation of a

physical network of supramolecular structures that are formed by the surface activity of the nanoparticles.

According to [11] the high degree of segmental movement in rubber, the presence of ordered structures in the amorphous polymers structure suggests that modifying the structure of polymers at low nanoparticle concentrations can lead to a purposeful change in the structure and properties of the rubber and vulcanizates on this basis.

On the other hand, the dimensions of ND and their surface stiffness will contribute to the formation of their own hierarchy of supramolecular structures, averaging the density of packings of macromolecule chains over the polymer matrix volume [12]. For which will also aid the dispersion effect of the intermolecular interaction (London component).

Therefore, the introduction of ND in the mixture together with the accelerators will inevitably increase the ND modifying effect.

A natural rubber (NR) was used to carry out the experiment as an elastomeric matrix.

The rubber mixture was made in an open laboratory rubber mixer (rollers) of the dimensions: L / D 400x150 and friction 1: 1.17, for 25 minutes, after plastification were introduced into the ND mixture and the accelerators. The sample vulcanization was carried out on a vulcanization press at 150 ° C for 6 minutes.

A study has been carried out on the influence of the mode of introduction is the EM and the modifying activity of ND, as well as the influence of the EM on ND modifying activity.

The finished mixture, taken off the rolls in the form of a thicker sheet, is left to stand for 24 hours before being subjected to analysis, testing and / or vulcanization.

The EM has been developed in options:
- not filled without stearin with ND - 1,5 mass parts per 100 mass parts NK (C-1);

- unfilled without stearin without ND NK (C-2);
The composition of the tested mixtures is shown in Table

1.

The results of the physico-mechanical tests of the above-mentioned elastomeric mixtures are shown in Table 2:

Table 2 Strengths of pre-aging vulcanisates.

Characteristics	C-1	C-2
Tension at 100% deformation M_{100}, MPa	1,8	0,88
Tension at 300% deformation M_{300}, MPa	5,7	2,65
σ, MPa	20	3,5
$\epsilon_{OTH}, \%$	590	310
$\epsilon_{OCT}, \%$	<6	15
Hardness Shore A, ref. a.	50

The results of the physical-mechanical tests of the above-mentioned elastomeric mixtures are shown in Table 3:

Physical Mechanical characteristics of vulcanizates after 24 hours

Characteristics	C-1	C-2
Tension at 100% deformation M_{100}, MPa	1,4	0,8
Tension at 300% deformation M_{300}, MPa	4,8	-
σ, MPa	18,8	-
$\epsilon_{OTH}, \%$	550	-
$\epsilon_{OCT}, \%$	<6	-
Hardness Shore A, ref. a.	50	52

The C-1 mixture retains its strength and mechanical performance while decreasing slightly, while C-2 (without ND) does

not withstand 300% deformation by stretching and does not retain its strength-mechanical performance.

In the study of the degree of swelling of the investigated vulcanizates, the following results are shown in Table 4.

Table 4 Degree of swelling in toluol

Characteristics	C-1	C-2
Degree of swelling in toluol for 24 hours in%	308	310

In the case study it is evident that the equilibrium degree of swelling of the individual vulcanizates is commensurate. This shows that the density of the vulcanization network in the studied composites is almost the same.

III. Conclusion

By using the above-mentioned composition and method of introducing ND into the elastomer mixture, the formation of its own hierarchy of supramolecular structures is achieved by:

- averaging the packing density of the macromolecule chains over the entire polymer matrix volume;
- uniform distribution of ND in the polymer mixture;
- enhancing the modifying effect of ND with a significant increase in the strength, mechanical and vulcanization characteristics of the elastomer mixture.

The amplification of the ND modifying effect is achieved by:

- exclusion of fat and olein-based ingredients from the composition of the mixture, maintenance of ND in active state allowing the use of the dispersion effect of the intermolecular interaction (London composition);
- the use of water as a catalyst for the oxidation reaction of the SH groups;
- the use of suitable accelerators for the vulcanization process.

IV. References:

1. Мокоучина Т.В., диссертация Упрочняющее модифицирование продуктов нефтепереработки углеродными наночастицами, "Российский государственный университет нефти и газа имени И. М. Губкина", 2015г.

2. Композиционные материалы на основе эластомерных и полимерных матриц, наполненных наноалмазами детонационного синтеза, http://sktb-technolog.ru/composite_materials_based_on_elastomeric_and_polymeric_matrices, 12, 2009г.

3. Сакович Г.В., Комаров В.Ф., Петров Е.А., Брыляков П.М., Потапов М.Г., Идрисов И.Г., в кн. Докл. V Всесоюз. совещ. по детонации. Т.2., Красноярск. 1991г.

4. Петров Е.А., Зеленков В.М. В кн. Докл. V Всесоюз. совещ. по детонации. Т.2, Красноярск, 1991г.

5. Долматов В.Ю., Возняковский А.П., Шевцова К.А., Кутянина В.С., Веретенникова М.В. в кн. Породоразрушающий и металлообрабатывающий инструмент – техника и технология его изготовления и применения. Вып.8. (Научн. труды ИСМ им. В.Н.Бакуля НАН Украины), Киев. 2005.

6. Г.А.Блох, Органические ускорители вулканизации каучуков, Химия, Ленинград, 1964г.

7. Долматов В.Ю., Сверхтвердые материалы. 2005г., №1.

8. Дж.Марк, Б. Эрман, Ф. Эйрич, Каучук и резина, Наука и технология. Монография, Перевод с английского. Научное издание, Долгопрудный, Издательский дом „Интеллект”, 2011г., ISBN 987-5-91559-018-1.

9. Сверхтвердые материалы 3, Г.В.Сахович, В.Ф.Комаров, Е.А.Петров, 3-2002г.

10. Л.Ю.Матвеева, Ю.Ю.Брацыхин, В.В.Солодкий, Разработка методов получения наномодифицированных каучуковых композитов и наноструктурированных резин для эксплуатации в условиях низких температур, УДК 621.762

11. Тугорский, И.А. Межфазные явления в полимерных композитах / И.А. Тугорский, М.Д. Скловский - М.: ЦНИИТЭнефтехим, 1994г.

12. И.М.Цыпкина, А.П.Вознаковский, Л.Ю.Матвеева, Влияние наноглерода детонационного синтеза на эксплуатационные свойства, резин на основе каучуков общего назначения, УДК:678.044:678 063