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Influence of thermal aging on properties of EPDM peroxide vulcanizates

Aging of rubber is one of the decisive factors affecting the reliability and durability of the products. Evaluation of resistance to aging allows selecting the optimal formulation of rubber compounds and determining the warranty service and storage of rubber products. One of the most important factors determining the resistance to aging of rubber is the nature of the molecular chains of the polymer (a type of rubber). Research aimed at improving the process of sulfur vulcanization of EPDM rubber was carried out on the enterprise «Eurasian Industrial Technical Group» LLP since at present time the application of this technology is not possible due to the fact that the use of peroxide curing of rubbers is more economical.

Key words: vulcanization, vulcanizing systems, peroxide vulcanizing agent, ethylene-propylene rubber, physical and mechanical properties, curve of vulcanization, Keltan, thermal oxidizing aging.

Enterprise LLP «Eurasian Industrial Technical Group» produces a range of rubber conveyor belts possessing oil-, gasoline-, fire-, cold- and chemical resistance in addition to heat-resistant properties [1].

Most rubber products are operated in contact with oxygen, and are also exposed to temperatures raised, oils and cyclic tension loads. Reactions occurring under these conditions represent oxidative radical chain processes.

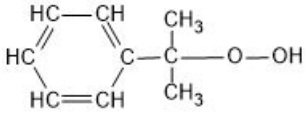
Vulcanization network structure is one of the determinants of rubber resistance to aging under the action of heat as this process is associated with degradation of the polymer and breakage of cross-linked bonds [2–5].

Varying the type vulcanizing system allows running the kinetic parameters of ethylene-propylene rubber vulcanization. Strain-strength characteristics of vulcanizates are changed simultaneously with the parameters of crosslinks network.

Thus in the manufacture of rubber products one should take into account peculiarities of the forming network of cross-linked bonds which is closely connected with the nature of the curing system. When using peroxide vulcanization systems it should be expected that the effect of covulcanization of phases leads to a sharp decrease of rheological characteristics. For rubbers with tailored properties it is advisable to carry on a preliminary assessment of the elastomeric component for Monsanto rheograms and curing mode selection based on the results foreseen.

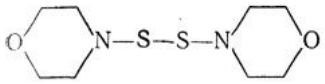
We investigated filled rubber based on three grades of rubber: Keltan 4450 (5-ethylidenebicyclo-2,2,1-heptene-2 (ENB) content of 4.3 % wt.), Keltan 2450 (ENB content of 4.1 % wt.) and rubber Keltan 3050 which is not containing ENB in the structure. Rubber manufacture was produced according to the standard recipes.

Two types of vulcanizing systems were used at compounding. Novoperox BP-40 was used as peroxide vulcanizing agent and a vulcanization initiator. Novoperox BP-40 is a white or slightly yellowish amorphous powder, 1-methyl-1-phenylethylhydroperoxyde (38–42 %) was used as the basic substance:



Acetophenone and methanol are formed at thermal decomposition of isopropylbenzene hydroperoxide (IPBHP). For the thermal decomposition of hydroperoxide by –O–O– bond therefore it is necessary to spend about 30 kcal/mol of energy. Iron ions greatly facilitate this decomposition, and the reaction proceeds with activation energy of 10–12 kcal/mol. The rapid disintegration occurs when heated up to 145 °C and above this temperature. Disintegration in acidic media leads to the formation of phenol and acetone and dimethylphenylcarbinol is obtained in alkaline media.

Sulfazan R, sulfur donor N,N'-dithiodimorpholine (DTDM) was used as a second vulcanizing system:



Reagent is a dust-free white powder with a greyish or yellowish tinge, it has a weak amine-like odour. Its application allows obtaining high temperature vulcanizates with a reduced number of polysulfide linkages having high strength and dynamic properties, high heat resistance and resistance to thermal aging and provides a significantly lower tendency to scorch the rubber compound.

Curing activator in these systems is zinc oxide, this allows obtaining rubbers with high strength and physical-mechanical parameters. Using high structural active carbon black causes an increase in modulus of rubber hardness, wear and tear resistance.

For a better dispersion of the powdered ingredients stearic acid was used. Stearin is also a secondary vulcanization activator, it reacts with zinc oxide forming zinc stearate, which is well dispersed in the rubber matrix, and in its turn activates the vulcanization accelerator.

To prevent destruction deceleration of rubber during its operation stabilizers are introduced. Derivatives of aromatic diamines such as N-phenyl-2-naphthylamine (Naphthyl-2) and N-isopropyl-N'-phenylenediamine (Diaphene PhP) provide a high resistance to aging of the rubber at its operating under different conditions, these antioxidants have a number of disadvantages associated with the release of harmful substances, their leaching from items during their lifetime. The combination of Diaphene PhP + Naphthyl-2 protects rubber from thermal aging, weathering, gives great dynamic stability. In the manufacture of rubber investigated this combination plays a role of antifatigue agents mainly and protects the rubber from oxidative aging.

Rubbers manufactured had to meet the standard for physical and mechanical characteristics for the coating rubber necessary for rubberized-fabric strips. The actual values of physical and mechanical properties of rubber exceed the norm by 10–20 %.

To study the properties of the peroxide vulcanizates of ethylene propylene rubbers, including their heat resistance, two groups of samples were examined. In the first group comparing rubbers on the basis of saturated rubber (Keltan 3050) and unsaturated (Keltan 4450) ethylene-propylene rubber vulcanized by IPBHP was carried on. In the second group properties of EPDM Keltan 4450, Keltan 2450 were studied. According to the curve of vulcanization (Fig. 1) induction period for curing rubber on the basis of Keltan 4450, is equal to 2.5 minutes, and the curing optimum is equal to 33 minutes. Scorch curve shows that duration of the scorch process is more than 40 minutes. The viscosity is equal to 63 Mooney units.

The reason for changing the properties of the elastomeric compositions under heat action is oxidation and formation of radicals. This process can be characterized by the degree of change in the physical and mechanical properties.

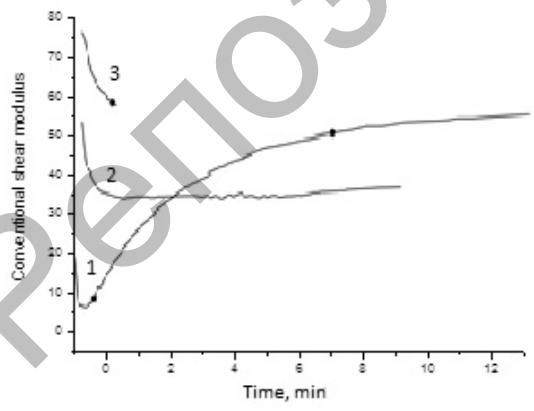


Figure 1. Kinetic curves of vulcanization (1), scorch (2) and viscosity (3) of rubbers based on rubber Keltan 4450 (recipe № 1)

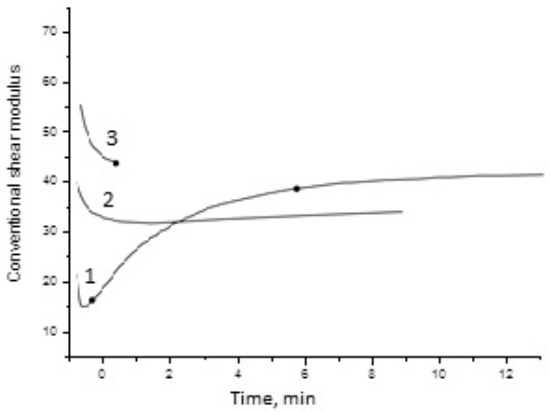


Figure 2. Kinetic curves of vulcanization (1), scorch (2) and viscosity (3) of rubbers based on rubber Keltan 3050

When comparing the physical and mechanical properties before and after aging we'll see an increase in conditional tensile strength up to 17.21 % and hardness up to 13 Shore units, a decrease in the value of elongation at break up to 31.65 %.

According to the curve of vulcanization (Fig. 2) induction period for curing rubber based on Keltan 3050 is 2.5 minutes, and the vulcanization optimum was 29 minutes. Based on the scorch curve the scorch process time is over 40 minutes, and a viscosity is equal to 48 Mooney units.

Change of characteristic exponents for these rubbers was negligible: increasing conditional tensile strength up to 4.8 %, elongation at break up to 2.86 % and hardness up to 13 Shore units.

Change of plasto-elastic and physical & mechanical properties at thermal oxidizing aging is caused by degradation processes, or structuring often occurring at the same time, due to the formation of free radicals as a result of covalent bonds breakage after thermal exposure. At aging saturated rubbers were oxidized slower than unsaturated and their mechanical properties are changed correspondingly. Consequently, unsaturated rubbers having a degree of unsaturation of more than 1 % are more prone to oxidation and changing in the mechanical properties of thermal oxidizing aging rather than saturated ones due to the presence of double bonds in the side chain.

According to the curve of vulcanization the induction period for curing rubber based on Keltan 2450 is 3.5 minutes and the vulcanization optimum is 32 minutes and based on the curve scorching time of scorch process is more than 40 minutes, and the viscosity is 44 Mooney units (Fig. 3).

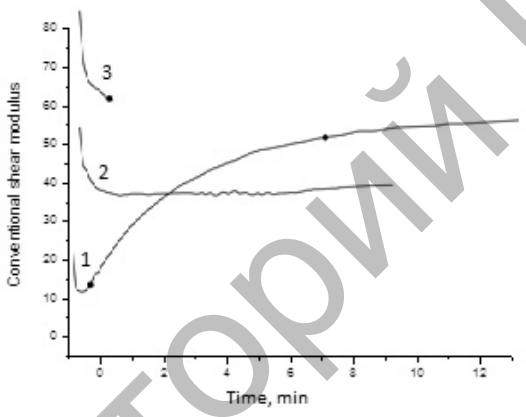


Figure 3. Kinetic curves of vulcanization (1), scorch (2), and viscosity (3) of rubbers based on rubber Keltan 2450 (recipe № 2)

From the foregoing it can be concluded that Keltan 2450 has greater heat resistance than Keltan 4450. This is due to higher viscosity which is caused by both growth of molar mass and increasing the intermolecular interaction due to the greater degree of unsaturation of Keltan 4450 and, consequently, an increase of the relaxation time and strain at which the chain coils are untangled under the same processing conditions. Because of this the tendency to degradation is higher for high viscous systems.

Experimental part

The experimental part means the testing of samples of rubber finished in three stages. To begin with there was a necessity to determine the physical & mechanical properties of the samples under standard conditions according to State Standard 263–75 «Rubber. Method for determination of hardness according Shore A» and State Standard 270–75 «Rubber. Method for determination of elastic and strength properties under tension». Then the samples were subjected to thermal action (125 °C) in atmospheric oxygen for 168 hours according to State Standard 9.024–74 «Rubbers. Methods of testing for resistance to thermal aging». After aging physical and mechanical properties of rubber samples were determined repeatedly.

Different durometers are applied for determination of rubber hardness. In our case TM-2 Durometer (Shore type) was used the rubber hardness. This hardness gage has a blunted needle connected with a spring placed inside the device. Hardness is determined by the depth of impression of the needle into the sample under action of compressed spring in contact of device basis plane with the sample surface (State Standard 263–75). Impression of needle is proportional to the movement of the arrow on the scale of the instrument. Maximum hardness is corresponding to the hardness of glass or metal, and is equal to 100 conventional

units. Rubber has a hardness ranging from 40 to 90 conventional units depending on the composition and degree of curing. With increasing fillers content and increasing duration of vulcanization hardness increases; emollients (oils) reduce the hardness of the rubber. Tests are carried out at room temperature (23,2 °C) and raised (up to 100 °C) temperatures. Test temperature was 23,2 °C.

After aging the samples are removed from the thermostat and conditioned at least for 16 hours and no more than 6 days at 23,2 °C in room protected from direct sunlight and substances harmfully influenced on rubber, and then determine the value of the specific indicator according to the standard of method for determining it.

As a result of testing it can be accepted the change of characteristic indicator after aging (S) calculated (except for the hardness) as a percentage by the formula:

$$S = \frac{A_1 - A_0}{A_0} \times 100\ \%,$$

where A_0 — value of characteristic indicator before aging; A_1 — value of characteristic indicator after aging.

The change of hardness (ΔH) is calculated by the formula:

$$\Delta H = H_1 - H_0,$$

where H_0 — hardness value before aging; H_1 — hardness value after aging.

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Этиленпропиленді каучуктердің пероксидті вулканизаттарының қасиеттеріне термиялық ескірудің әсері

Резеңкелердің ескіруі бұйымдардың ұзақ қызмет етуіне және сенімділігіне әсер ететін шешуші факторлардың бірі болып табылады. Ескіруге қарсы тұруды бағалау резеңкелі қоспалардың тиімді қатынастарын таңдап алуға және резеңкелі бұйымдарды сақтаудың және пайдаланудың кепілдік мерзімдерін анықтауға мүмкіндік береді. Резеңкелердің ескіруге қарсы тұруын анықтайтын маңызды факторлардың біріне полимердің молекулалық тізбектерінің табиғаты (каучук типі) жатады. «Eurasian Industrial Technical Group» ЖШС өнеркәсіп орындарында каучуктерді күкірт арқылы вулканизациялау үрдісін жақсартуға бағытталған зерттеу жұмыстары жүргізілген, себебі қазіргі кезде каучуктерді пероксидті вулканизациялау экономикалық жағынан тиімдірек болып саналады.

Л.К.Салькеева, Г.М.Каколина, Е.К.Тайшибекова, Л.М.Сугралина, Г.Т.Хасенова, С.Ю.Паншина, Д.Ю.Горбач, А.А.Муратбекова, А.К.Салькеева

Влияние термического старения на свойства пероксидных вулканизатов этиленпропиленовых каучуков

Старение резин является одним из решающих факторов, влияющих на надежность и долговечность изделий. Оценка стойкости к старению позволяет подбирать оптимальные рецептуры резиновых смесей и определять гарантийные сроки эксплуатации и хранения резиновых изделий. Одним из важнейших факторов, определяющих стойкость резин к старению, является природа молекулярных цепей

полимера (тип каучука). На предприятии ТОО «Eurasian Industrial Technical Group» проведены исследования, направленные на усовершенствование процесса вулканизации серой каучуков СКЭПТ, так как в настоящее время применение данной технологии не является возможным вследствие того, что использование пероксидной вулканизации каучуков экономически более выгодно.

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