

SOME PECULIARITIES OF THE PARAMAGNETIC RESONANCE FORMED IN VARIOUS INDUSTRIAL RUBBERS DUE TO TECHNOLOGICAL FACTORS (I)

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In this study some peculiarity of the paramagnetic resonance are examined in some linear and slowly branching polymers SKN-26, SKN-40M divinylnitrate, brominated, chloroprene, isoprene pure and doped rubbers. In SKN-26, SKN-40M divinylnitrate rubbers ESR spectrum is singlet, when we pass on to chloroprene rubbers, it gets more complex and becomes multicomponent, which is explained as the fortification of the mutual interaction with the side groups of the polymer chains of unpaired electrons. It is also evident that this process is more powerful when there are more electron sensitive groups on the sides. At the same in the study, the ways of weakening of the free radical process by antioxidants are given. It is also shown that the collecting kinetics of the free radicals, has an extremal character depending on the temperature and the amount of antioxidant, and that the technological parameters of the resin production prepared under extremal conditions ameliorate maximally. The result obtained indicate that in the structure of the polymer, due to various factors, ordered groups form having a certain magnitude and the speed and character of the free radicals and oxidation reactions occurring in the polymer depend on these groups.

INTRODUCTION

During the receiving of the production, treatment and exploitation, polymers subject to various processes, most prominent of which are the mechanochemical and thermal processes. It is shown at the end of long investigations that production and treatment of polymers and elastomers take part through chain-like free radical (FR) processes and the starting point of these processes is the distribution of macromolecules [1-12] during which they subject to oxidation in environment with oxygen and wearing (due to photo- and thermal effects and radiation). All these processes, along with secondary effects might change the molecular and supramolecular structure, dissolution and reaction capabilities of elastomers. It can be concluded that the wearing of elastomers proves experimentally the FR conception.

Yet the effect of the prehistory and the conditions receiving of production on the properties and the structure of the elastomers is poorly understood. The reactions with free radicals after these effects have not been obtained, nor have been compared the intensity of its formation, physical and mechanical properties and the exploitation parameters. Some results of these researches have been explained for synthetic polymers [16] such as the following, in References [16-27]:

1) Much prior to the production of the polymer materials, that is during the synthesis of the polymers, in the all cases, the first "information" is obtained about the structure. This information is taken as basis according to the influence of supramolecular formations of various sizes on the structure and properties of the polymer in later processes;

2) Mechanochemical processes and thermal treatment are chain-like free-radical processes that start on the surface of the sample and the supramolecular formation. The dynamical-mechanical properties and exploitation parameters are proportional to the intensity of these free-radical processes.

However, for elastomers, there is no systematic explanation of the electron spin resonance (ESR) of the free radicals (FR's) formed within the above mentioned limits, except a few summaries that we presented [17-19, 22-24]. Here, it can initially be asserted that rubbers, as in other polymers, possess too much "biographic" defects, doping groups and formations having low molecular weight and that rubbers are not such systems of one type. These processes become more complex if simultaneously there are mechanical, thermal,

chemical affects or radiation during treatment. With this in mind, we think that the "information" used in the polymer structure we have just mentioned, played an important part in the formation of its characteristics and the exploitation parameters of the products.

In this study, the results of the ESR investigations are given, that prove the validity of our view stated for some rubbers and resins.

EXPERIMENTAL METHODS

In this study the test substances used are pure divinylnitrate, (SKN-26, SKN-40M), chloroprene, isoprene and brominated rubbers, and also the resin mixtures on these base. The pure rubbers used are selected specially as undoped on purpose and taken from the raw materials used in factories. The brominated rubber is taken by some notable methods [14]. The reason why this type of substances are used is to specify the role of the side atoms in the chain and to explore the types of side groups and how they displace. Yet, to study the effects of the side atoms more profoundly, S (like a vulcanizing agent), Se, SeO₂ and a silicon organic compound are used in some samples, according to methods cited in literature [16-24] (0-0.8 mass fraction). The ways they are added are given below and the sizes in the doped samples are explained briefly in this paper where necessary. The silicon organic compound and the ingredients of the standard mixtures are mixed in the form of the powder in the laboratory-rolling machine at the temperature of 323±5 K during 35 to 38 minutes. The temperature and time of vulcanization are respectively 423 K and 5, 10, 20, 40 and 60 minutes, while the pressure under press during vulcanization is 1.2 MPa. The resin mixtures are taken in standard presses under neutral conditions (having no oxygen or any other gas content). Since sulphur is a vulcanizing agent samples having 3% mass of S are used as controlling samples. The thickness of the samples was 50 to 100 μm for IR spectra. For ESR measurements, samples have been cut from different parts of the film, their masses measured, and spectra examined in the R9-1306 spectrometer at 77 and 300 K. Depending on the concentration of the paramagnetic centers, the mass of the samples has been 5-100 mg, but for 0 of them, the concentration has been calculated for 1 gramme or 1 cm³. As is seen from the graphics, and stated in the text, proportions such as N/N_{5t} or

I/I_{St} are used, which imply that the amount of sample has no meaning. Measurements of both bulk samples and thin films have been performed and same correlations taken. As we state below and the literature indicates, the destruction and wearing processes start always from the surface. In both mechanochemical reactions and thermal processes, as a result of the breaking of the polymer chains or side branches, free radicals form. To explain the effect of temperature during the vulcanization, pure samples obtained from factories have been evacuated down to a pressure of about 10^{-5} - 10^{-6} mmHg and sealed, then heat treated in stages of quartz ampoules at temperatures around 293 to 433 K and after every stage (each one lasting 1 hour) ESR values have been measured. We think that during the 1-hour heat treatment, the processes of destruction and of structuring of rubber terminate and it is thought that the rubber wears completely at temperatures greater than 443 K. In industry, the direct vulcanization of resins takes place in this way. The samples and standards have been measured together. The mechanical strength and proportional elongation (that is deformation, ϵ) have been measured in a device that keeps the value of the tension constant, at fixed temperature from the loading of the sample until the breaking (method of lever mechanism) [15]. IR spectra are measured in a spectrometer UR-20 (Karl-Zits, Germany). The simultaneous distribution of the doping substances has been controlled by a polarization microscope.

EXPERIMENTAL RESULTS AND INTERPRETATION

In all the divinyl nitrate rubber samples, roughly a symmetric singlet with $\Delta H_m \approx 0.4$ - 0.5 mT and $g = 2.003$ is observed (Fig.1a). The concentration (N) of the paramagnetic centers (PC) varies between 10^{16} - 10^{17} spin/gm. Depending on the time of vulcanization, the intensity of ESR signal attenuates and the signal disappears, a phenomenon which occurs at a faster rate in case that there are ingredients such as ZnO, stearin, coptax in the contents of the rubber. In the brominated rubber, a five-component spectrum is observed to take place superimposed on a wide central component with $\Delta H_m \approx 29.0$ mT and $g = 2.07$ (Fig.1b). The distances between the centers of the lines (components of superfine structure of spectra-SFS) are 18.1: 4.3: 4.3: 18.1 mT. As one passes on to brominated and chloroprene rubbers that is the side atoms of the chain replace with the bromine (Br), chlorine (Cl) respectively, the spectrum gets more complex and as a result, it turns into a multi-component spectrum, at the centre of which a component of less intensity exists (Fig.1c; $g = 2.014$; $\Delta H_m \approx 1.1$ mT). According to the decay of the outermost part of the spectrum, some parts are observed and a seven-component pure spectrum is appeared (Fig.1c). The constant SFS, not being isotropic for all lines, takes the values of 4.0: 4.0: 4.0: 4.0: 6.0: 4.0 mT. At room temperature, all the components except the central line are asymmetric all both asymmetry and anisotropy are well observed in high magnetic field region. At liquid nitrogen temperatures the side components of the spectrum become approximately symmetric, and more discernible, the SFS anisotropy decreases in the low magnetic field region but increases where magnetic-field is high (Fig.1d). In addition to the seven-components, two more are observed and for them, the SFS constant is significantly high. The intensity of the central line



Fig.1. The ESR spectra for different rubber: a) The untreated divinyl nitrate SKN-26 and SKN-40M rubbers at room temperature (T_{room}); b) Brominated rubber at T_{room} ; c) Chloroprene rubber at T_{room} ; d) Chloroprene rubber at liquid nitrogen temperature; e) Isoprene rubber after being treated in the rolling machine.

increases as expected from Curie's law, which exhibits that the FR is at ground level. The stage by stage heat-treatment of the chloroprene rubber causes the intensity of the low field components to drop, of some to disappear at the heat treatment temperatures $T_{treat.}$ of around 383 to 393 K and of high field components to increase somewhat. Then in the high-field region, a new ESR line is observed where $g = 2.003$ and whose intensity rapidly increases as $T_{treat.}$ gets higher. In addition to this, a weak line is observed at low $T_{treat.}$ temperature and low magnetic fields. The typical ESR spectra following the heat-treatment of chloroprene rubber at temperatures of 383 K (a) and 393 K (b) are given in Fig.2. When the chloroprene rubber is vulcanized with soot at 77 K and 300 K a six-component isotropic spectrum (SFS=8.2 mT) superimposed on a symmetric line of high intensity and linewidth ($\Delta H_m \approx 24.8$ mT, $g = 2.003$) is observed (Fig.2c). Hence from the experimental data the following situation is observed: as one passes from doping the rubbers with oxygen to the replacement of the bromine (Br) with chlorine (Cl), first a widening in the signal (provided that the narrow component is detected) then formation of the spectra of initially a wide and unnoticeable and later a relatively narrow but noticeable components (such as Br) and finally the disappearance of the wide signal and a completely discernible multi-component spectrum are observed (such as chloroprene rubber).

It is known that, upon the appearance of FR's and ions, the mechanical strength causes the destruction of the molecular chains, and they in turn enter the reaction that is a mechano-chemical process starts [1,2,6]. Since the sizes of the elastomer molecules are large and linear, the binding en-

ergy within macromolecules might be very much greater than

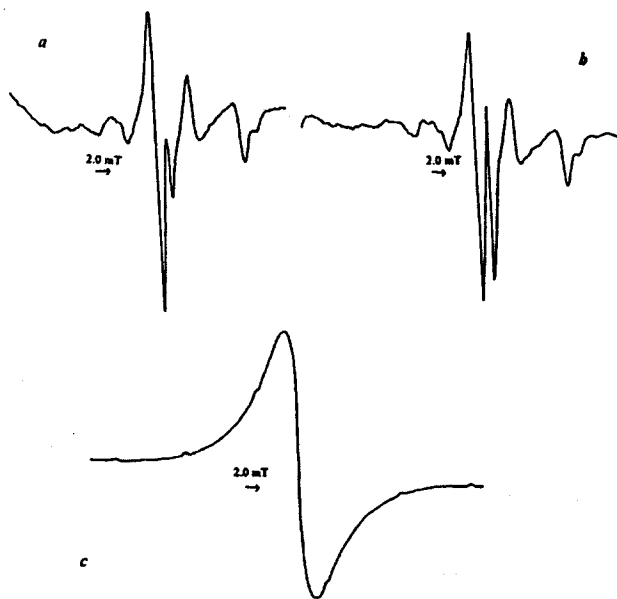


Fig. 2. The ESR spectra for chloroprene rubber at T_{room} :
 a) $T_{treat} = 383$ K; b) $T_{treat} = 393$ K;
 c) after the vulcanization.

of the chemical bonds in the chain. According to this such a high tension forms in the molecular chains that, the valence energy between these atoms becomes smaller than the binding energy [1,2,4,6], a chemical breaking occurs, polymer FR's form which in turn participate in the chemical reactions belonging to the alkyl or alkenyl radicals. With the addition of the oxygen and elongation of the heating time, these reactions become more intense.

According to the above mentioned and we presented equation some thirty years ago [27], the formation of the free radicals depends on the surface area of the sample, the amount of oxygen and also on the surface of the supramolecular formation in the sample and also depends exponentially or the ratio of the surface area to the volume ($N \sim S/V$).

As reported above, while producing the resin and later in the laboratory rolling-machines and passing to the pressing processes, the rubbers are subject to the effects of temperature, high pressure, and mechanical forces and with varying degrees of displacement forces, high local tensions and through them molecular destruction (mechanochemical reaction) occurs. According to this, the formation at the ESR signals is explained by the breaking of the chemical bonds under these conditions. Besides, the existence of the singlet in SKN-26 and SKN-40M rubbers can possibly be explained by the breaking of C=C bonds in the monomer unit of the rubber. This view is proven by both our previous investigations [16] on the effects of the ESR and IR absorption of Se and Te doping in SKN-40M rubber and by the present experimental results.

After the direct treatment, in the 2550cm^{-1} , $2900\text{-}3600\text{cm}^{-1}$ regions of the IR spectra of rubber, lines occur which in turn are related to the C=N, NH and OH groups. At the same time, an intense neutral scattering is observed that indicates changes of supramolecular formation -and molecular origin in the structure of rubbers [25, 26]. If these are assumed to be true, our results also verify the results of the examinations on

the dynamical-mechanical and electric strength of the same rubbers performed previously [16-24]. If we take into consideration the influence of doping through the side chain atoms in rubbers, then we can explain the effect of the dopings to the ESR Spectrum by the mutual interaction of the unpaired electrons (UE) and UE's of O_2 by way of the spin-orbital bond and by the formation of the second peroxide radicals. Here, unlike the divinylnitrate rubber, the breaking of the oxide compound and the delocalisation of the UE away from the carbon atoms towards the side atoms occur. This delocalisation increases as the affinity of the side atoms towards the electron increases. It is obvious that electron affinity increases from left to right in the Periodic Table, but in small groups from top to bottom. Then, since the electron affinity increases in the order O, Br, Cl, the localization in the side atoms of the UE gets higher, the mutual interaction between the atoms at the sides of the chain becomes stronger, which in turn causes the ESR spectra to pass gradually from the wide line to the completely discerned form.

The form of the spectra shows that they are composed of the two multi-component spectra occurring due to the mutual interactions of UE's with both some equivalent protons and the nuclei of Br and Cl having unpaired nuclear spins ($I=3/2$). When the electron affinity is less (such as Br, O_2) the UE's participate in other mutual interactions that cause a wide spectrum to form. In fact, at liquid nitrogen temperatures since the system of the UE's is frozen, due to the weakening of mutual interaction, thermal motion and with the feeble effects of the near protons, and bromine and chlorine nuclei, the asymmetry and the anisotropy disappear.

In the isoprene rubber, the doublet structure of the ESR spectrum is observed (Fig. 1e) ($\Delta H_{m1} = 0.4 \pm 0.05$ mT, $\Delta H_{m2} = 0.4 \pm 0.05$ mT and $g_1 = 2.003 \pm 0.005$, $g_2 = 2.004 \pm 0.0005$). The N of the PC's decreases rapidly, depending on the processing temperature (Fig. 3a). When the antioxidant is added, N varies extremely (Fig. 3b), passes from the doublet on to the singlet with $\Delta H_m \approx 0.8$ mT and $g = 0.003$, and where N , the concentration is always less than that of pure rubber. The width of the line (ΔH_m) first decreases at $T_{treat} = 333\text{-}353$ K then rises abruptly to 1.2 mT but later drops again (Fig. 3b). The factor g and the form of the ESR spectrum do not change related with T_{treat} , that is the formation mechanism of the PC's is the same.

The ESR spectrum in the isoprene rubber probably forms differently at different proportions of the structure of the rubber and composed of several lines belonging to some stabilized FR's. From the observation of the doublet in the non-heat treated rubber, one can conclude a very heterogeneous structure, whereas from the presence of the singlet in the doped rubber, a homogeneous structure is observed to predominate. Upon the addition of the dopings, a more ordered supramolecular formation consisting of macromolecules of almost the same size comes up. The breaking of bonds and the formation of FR's take place in the amorphous part of the polymer, that is at the border of the supramolecular formation, therefore, a difference in structure possibly causes a difference in the ESR spectrum. This situation also verifies completely the measurements of the mechanical properties of the same resin mixtures similarly, the same kind of measurements confirm our ideas for the resin mixture basically of chloroprene rubber [23]. For example, we observe the following: 15 % extremal increase in the mechanical and electrical stability; 30 % increase in the glass formation tem-

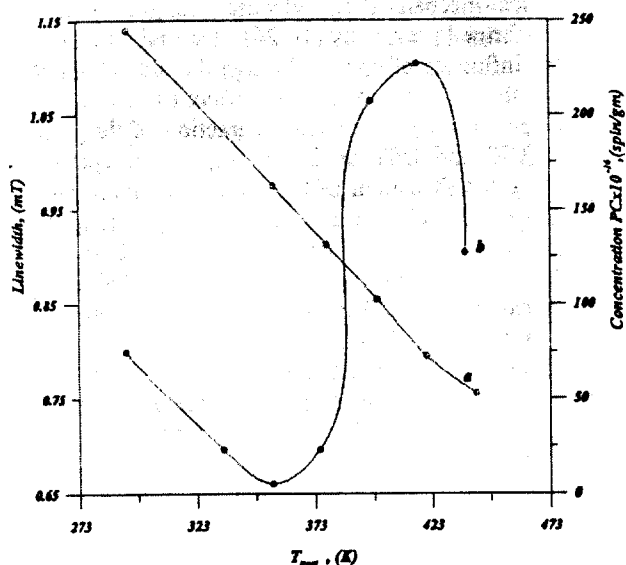


Fig.3. In the isoprene rubber, the N (a) and line-width (b) are plotted versus T_{treat} .

perature, and 60 % decrease in the elongation at a temperature above the glass formation temperature.

As is reported above, the comparison of the spectroscopic data with dynamical-mechanical and electrical strength characteristics is of high importance technologically. The vulcanization causes the UE's to be localized in the network of the rubber, the dipole-dipole interactions to be stronger and lets a wide symmetric central line be observed.

Consequently the experimental data given in the paper prove the following conclusions: 1 - The dopings added to the polymer come into mutual interaction with the side bonds of the monomer unit, 2 - Upon the addition of highly electro-negative atoms to the side atoms of the rubber, the localization of the UE's the newly added atoms takes place and according to this, a certain amount of oxidation and destruction processes are impeded.

In the second part of the article, the effect of the large scale and oxygen containing dopants on the paramagnetic resonance mechanism in rubbers will be held.

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ТЕХНОЛОЈІ ФАКТОРЛАРИН ТӘ'СИРИ АЛТИНДА ТӘКРАР İSTEHSAL VƏ İSTİSMAR OLUNAN MÜXTƏLİF SƏNAYE REZİNLƏRİNİN ПАРАМАҚНІТ РЕЗОНАНСИНİN ХУСУСИYYƏTLƏRİ

Bu məqalədə, bə'zi saf və əlavələrlə xətti və az şaxələnmiş polimerlərdə məsələn, SKN-26, SKN-40M divinilnitrilli, bromlu və xloroprenli kauçuklarda paramaqnit rezonansın bə'zi xüsusiyyətləri tədqiq olunmuşdur. SKN-26, SKN-40M divinilnitrilli kauçuklarda EPR-in singlet spektri müşahidə olunur, həmçinin xloroprenli kauçuka keçid də mürəkkəb və çox komponentli olur ki, bu da polimer zəncirində buxarlanmayan elektronların yan qruplarla qarşılıqlı təsirinin güclənməsi ilə izah olunur. Bu proses, yan qrupların polyarlıqlı və elektromənfiliyi güclənərsə, daha çox nəzərə çarpır. Eyni zamanda məqalədə sərbəstradikalı proseslərin antioksidantlarla gecikməsinin bə'zi misalları göstərilir. Digər tərəfdən göstərilir ki, sərbəst radikalın artım sayının kinetikasi temperaturdan və əlavələrin miqdarından asılı olaraq ekstremal xarakter daşıyır və optimal şəraitdə hazırlanan texnoloji parametrlərin miqdarı maksimaldır. Alınan eksperimental nəticələr göstərir ki, sərbəst radikalın müxtəlif faktorların təsiri ilə olan təkrar istehsalda müəyyən struktur və miqdarı formalaşır ki, bu da polimerdə oksidləşmə reaksiyalarına güclü təsir edir.

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ОСОБЕННОСТИ ПАРАМАГНИТНОГО РЕЗОНАНСА, НАБЛЮДАЕМОГО ПРИ ПЕРЕРАБОТКЕ И ЭКСПЛУАТАЦИИ РАЗЛИЧНЫХ ИНДУСТРИАЛЬНЫХ РЕЗИН ПОД ДЕЙСТВИЕМ ТЕХНОЛОГИЧЕСКИХ ФАКТОРОВ

В этой статье изучены некоторые особенности парамагнитного резонанса в некоторых чистых и с добавками линейных и слабоветвленных полимерах, таких, как SKN-26, SKN-40M дивинилнитрильных, бромированных и хлоропреновом каучуках. В дивинилнитрильных каучуках SKN-26, SKN-40M наблюдается синглетный спектр ЭПР, однако, при переходе к хлоропреновому каучуку он становится сложным многокомпонентным, что объясняется усилением взаимодействия неспаренных электронов с боковыми группами полимерных цепей. Этот процесс еще более заметен, если полярность электроотрицательных боковых групп усиливается. Одновременно в статье приводятся некоторые сведения о замедлении свободнорадикальных процессов антиоксидантами. С другой стороны, показано, что в зависимости от температуры и содержания добавок кинетика возрастания концентрации свободных радикалов носит экстремальный характер, и величина технологических параметров, изготовленных при оптимальных условиях максимальна. Полученные экспериментальные результаты показывают, что под действием различных факторов переработки формируются определенная структура и количество свободных радикалов, которые сильно влияют на окислительные реакции в полимере.