

## THE EFFECT OF THERMAL TREATMENT AND THE DOPINGS CONTAINING OXYGEN ON THE ESR SPECTRA OF CHLOROPRENE RUBBER (II)

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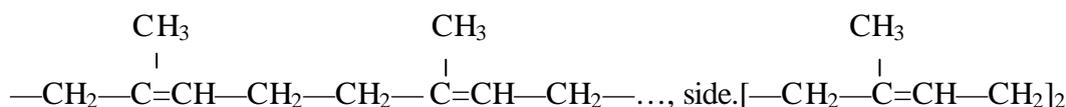
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The previous study [1] is developed to prove the concept, that is, contribution of oxygen and impurities effect the free-radical (FR) processes participating in the reactions of the side groups of macromolecules in rubbers. For this purpose, instead of the impurities which are distinguishable and which contain chloroprene rubber having a multi-component ESR (Electron Spin Resonance) spectrum and oxygen, we used the doping of diepoxy silane. It is proven that the effect of oxygen is superior to the others in reactions in which FR's take part, provided that the amount of oxygen in the polymer system is sufficient. The dopings selected help the concentration of the FR's in rubber decrease and the structure of the material be more homogeneous. It is found that there is an adverse correlation between the decrease in the concentration of the FR's and the amelioration of the strength characteristics of rubber.

### INTRODUCTION

In reference [1] it was suggested that the FR's processes which take parting the reaction of side groups of the macromolecules, in general are affected by whereas in this study the conclusions of the effects of a more special doping on the FR processes (that is, in isoprene and chloroprene rubbers) are made. For instance, the isoprene rubber is

interesting by its few characteristics. First, through the microstructure point of view, it is the most similar one to the natural polyisoprene rubber. Spectroscopically and according to the chemical structure analysis we can write for the best of polyisoprene rubber which has a stereo ordering the ordered cis-1, 4 structure.



According to chemical activity the structure of cis-1, 4 of the synthetic polyisoprenes looks like that of natural rubber, so that all the results obtained for the isoprene rubber can be used for the natural rubber as well. Secondly, the isoprene rubber is a semicrystalline polymer belonging to the class of rubbers whose crystalline phase is minimum (from 15 % up to 50 %). Due to the presence of the structures 1, 2 and 3, 4 crystallization is difficult in this rubber and in general the rubber is composed of an amorphous phase. Therefore, the processes of oxydation and degradation that signify the use parameters of the materials manufactured on the basis of this rubber occur, in general, in amorphous parts. Consequently, the investigations in the chloroprene rubber can unveil the effect of the external agents on all kinds of rubber and in oxydation and degradation processes in more detail. On the other hand, the chloroprene is different than the isoprene rubber due to the presence of the chlorine (Cl) atom having an unpaired nuclear spin and a high electronegativity and which takes place instead of the side group of CH<sub>3</sub>. Thus, since the electron freed in the polymer chain is more strongly localized on the Cl atom the results obtained for this rubber should be different than the results of ESR for other rubbers cited in reference [1] where the examinations on the chloroprene rubber with the addition of Se and Te were reported. These results are different than those of the other rubbers. Therefore, we developed these studies with a doping having a greater molecular mass and oxygen containing groups.

In the above mentioned processes it is obvious from the references that the FR's play an important part in the polymer structure due to some reasons. On the other hand, the processes of polymerization depend on the type (character) of active centre and these centres may be FR's, ions or coordination complexes [2-7]. Hence, there are two principal types of polymerization: radicals and ions. In the processes of radical polymerization, as the  $\sigma$ - bond between two carbon atoms breaks under the effect of the active centre, the electron pairs separate (homolitical breaking) and as a result of the joining of monomer molecule with the active centre a FR regenerates. In the ionic processes, the  $\sigma$ - bond breaks in such a way that each of the electrons in a pair passes on to a carbon atom and the other carbon atom is charged positively (heterolitical breaking). Hence, as a result of the interaction of the active centre and the monomer molecule, an ion forms that has a charge of the same sign as that in the active centre. Therefore, the active groups of the enlarging polymer chain either become FR's or ions. Recently a greater emphasis is given to the radical polymerization of the rubbers. Because the FR's affect both the polymerization process of rubber and its molecular and supra molecular structure (SMS) by interacting with themselves and with active centers, that is, the physico-chemical characteristics and use parameters of the materials made taking this rubber as a basis happen to vary. Indeed, the physico-mechanical characteristics of polymers depend on the degree of crystallization, the ratio of



component spectrum sits on a very wide peak. The fine structure of the  $Mn^{2+}$  ion should be composed of 6 components of equal intensity, while the HFS should be a 36-peak spectrum. However, the HFS constant is 6.8 -7.7 mT, whereas for the spectrum that we obtained this value goes up

to 9.0 – 9.5 mT as mentioned. All these data are against the idea that the multi-component spectrum that we observed in chloroprene rubber belongs to the  $Mn^{2+}$  ion, as conforming to the transition elements.

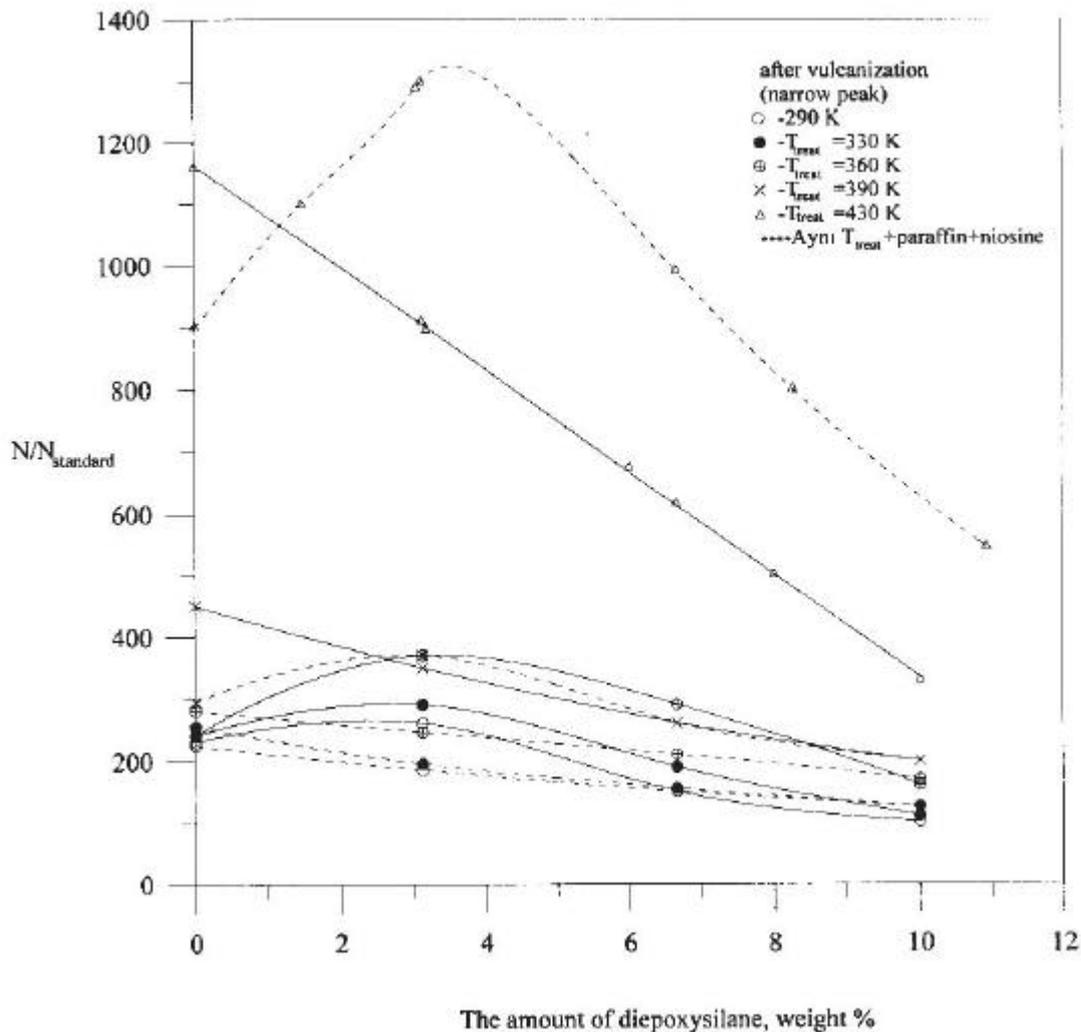


Fig.2. The dependence of the concentration of paramagnetic centers on the amount of diepoxysilane, in the rubber chloroprene and for the narrow peak, after vulcanization

The narrow central peak has  $g=2.003\pm 0.0005$  and the width  $DH_m=0.9\pm 0.05$  mT. These parameters do not depend on other things except  $T_{treat}$  and 10 weight % percentage. In only one 10 weight %  $DH_m$  increases up to 1.1 – 1.4 mT. The width is the same for all the components of the ‘isotropic’ spectrum and  $DH_m$  is (1.2 – 1.4 mT) and the HFS parameter is both the same and around 8.5 – 9.0 mT. The width of the wider peak varies greatly depending on both  $T_{treat}$  and the ratio of the dopings. Its value changes around 30 – 60 mT and increases as the amount doping gets higher, but diminishes as  $T_{treat}$  increases. This conclusion can be thought as the effect of the vulcanization. When we drop the temperature down to 77 K it decreases practically to half.

“The additional spectrum” can only be observed in the samples collected from the rolling machine and can be explained in two ways, that is, the HFS of the isotropic spectrum is practically observed at around 8 – 9 mT and the number of components depends on the conditions of manufacturing the sample. Furthermore, an asymmetric peak which is in the interval 7 – 7.5 mT is seen from the central

peak (Figure 1b). The positions and the intensities of these peaks vary in an uncontrolled way and strongly (they slide from the central peak in either direction) (Figure 1b, 1c) but the HFS constant remains fixed. The distance between the central peak and the first distinguished component is 1.8 – 2.5 mT towards the low magnetic field side, while around 8 – 9 mT towards the strong magnetic field side. This shift is sometimes so strong that these peaks slide towards the central narrow peak and unite with it (overlap) and as a result, a hardly distinguished doublet is observed (Figure 1c). The width of the above mentioned components increases depending on the percentage of the doping, from 1.2 up to 2.0 mT. The more important variations are in the intensities of the narrow and wide peaks and also proportional to the intensities of the components of both ‘isotropic’ and ‘additional spectra’.

Narrow peak: a- In the absence of ingredients after the vulcanization, for 3 weight % diepoxysilane, paramagnetic centres (PC) get their greatest concentration (N). But it drops at 10 weight % and in this case N becomes less than even that

of the pure (undoped) samples (Figure 2). As  $T_{\text{treat}}$  increases  $N$  becomes higher at each value of the ratio, but the general shape of the curves does not change. Only at  $T_{\text{treat}} = 433 \text{ K}$  a drop is observed, that is, at 3 weight % a striking maximum is seen (when there are paraffin and niosine ingredients). At  $T_{\text{treat}} = 433 \text{ K}$ ,  $N$  is almost four times greater than what it is at other values of  $T_{\text{treat}}$  for all values of the doping. b- after

rolling at all values of  $T_{\text{treat}}$  a minimum is observed at 3 weight %. However, as paraffin and niosine are added the rubber becomes stabilized, that is, as the doping gets higher  $N$  drops slowly. But at  $T_{\text{treat}} = 433 \text{ K}$  and for 3 weight % a minimum is observed. As  $T_{\text{treat}}$  increases the general trend stays the same, that is,  $N$  increases as well (Figure 3).

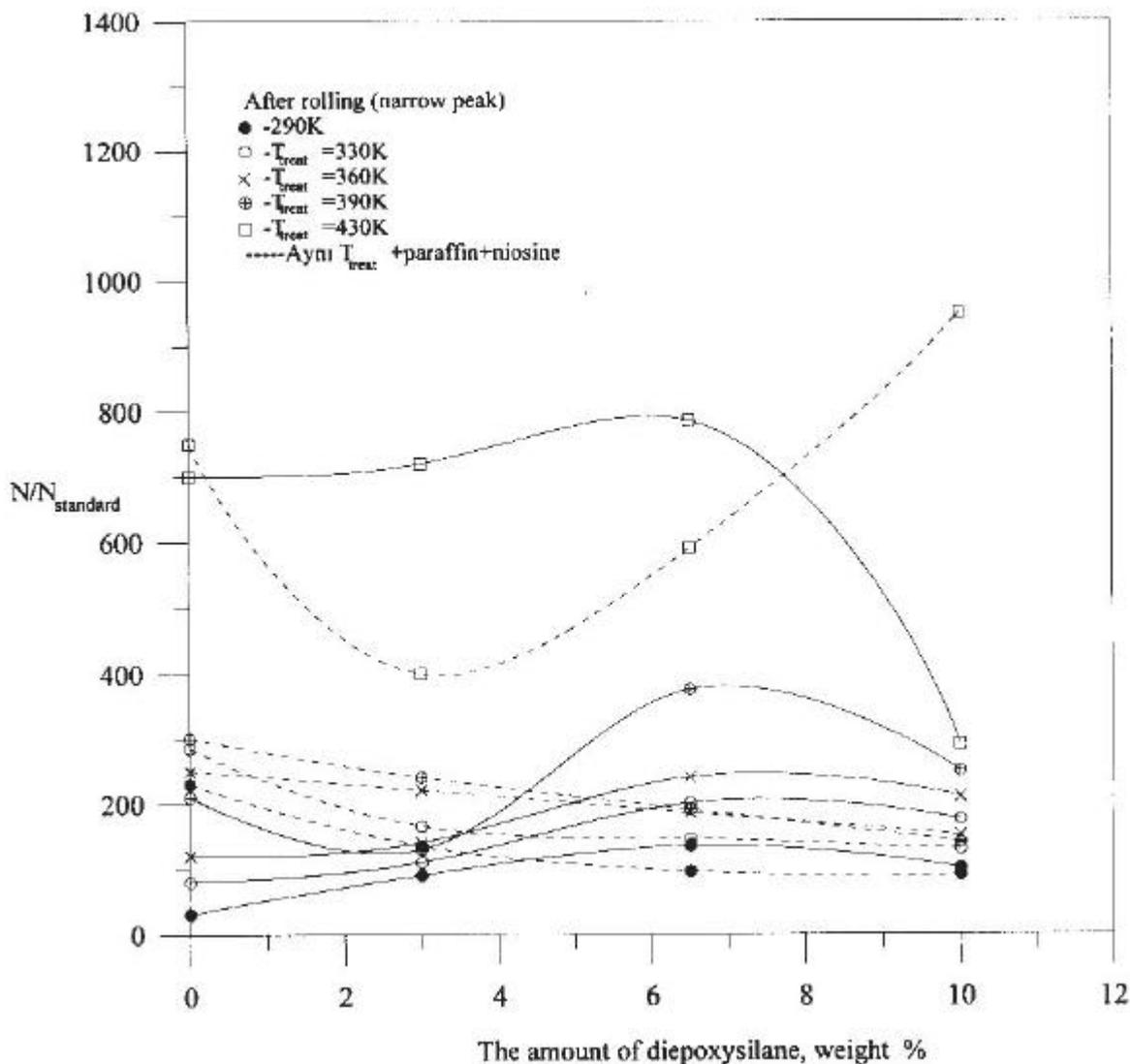


Fig.3. The dependence of the concentration of paramagnetic centers on the amount of diepoxyxilane, in the rubber chloroprene and for the narrow peak, after rolling.

Wide peak: a- after the vulcanization, it is generally observed that it obeys the stability rule. 3 weight % and 6.5 weight % (at low and high values of  $T_{\text{treat}}$ , respectively) but for higher than 6.5 weight %  $N$  increases absolutely (7 – 8 fold). When paraffin and niosine are added the shapes of the curves do not change, but  $N$  increases a bit all the time (Figure 4). This trend is observed to be weaker for narrow peak. As  $T_{\text{treat}}$  gets bigger so does  $N$ , but at 433 K a sudden drop is seen ( $N$  becomes less than even that of the pure sample). All these phenomena are observed in more detail when the ingredients are added. b- Following the process at the rolling machine as the amount of diepoxyxilane gets greater, so does the value of  $N$  for the PC. However, at 293 K at 3 weight % a minimum is observed. For all the ratios of

doping, as  $T_{\text{treat}}$  increases so does  $N$  and when the ingredients are added  $N$  becomes even greater (2 – 3 fold) (Figure 5). But at 10 weight % it is different. At  $T_{\text{treat}} = 433 \text{ K}$  the PC's appropriate for the peak are not practically observed, but at 10 weight % another narrow peak is seen.

That the HFS is not observed in the rubber divinyl nitrile [1] shows that the unpaired electrons (UE) arise from the breaking of the chemical bonds as a result of the mechanical processes, are strongly localized on the C atoms and do not interact with the side protons. The observation of the 7-component spectrum in pure rubber of chloroprene shows that these UE's are drawn from the C atom toward the Cl atom (due to the high electronegativity of the Cl atom) and in mutual interaction with the nucleus of the Cl atom (spin of

the nucleus  $I = 3/2$ ). It is known that the number of peaks in the HFS must be  $(2nI + 1)$  (where  $n$  is the number of nuclei that are in mutual interaction). Consequently, the 7-component spectrum in the rubber of chloroprene can be explained by the interaction with the nuclei of the two Cl atoms ( $n = 2$ ). The isotropy of HFS proves the equivalence of these two chlorine nuclei. The above explanation is supported by the rule that gives the ratio of the intensities for the interaction of the HFS components with the two equivalent nuclei [19], that is, 1: 2: 3: 4: 3: 2: 1. There may sometimes be small deviations from these ratios that originate from the weak interaction between the Cl atom and side protons, because the UE has moved to the side atom. These variations are more pronounced when silicon organic compounds are added. That is, dopings play a filling role rather than a cross

role. Indeed, the concentration of the FR's increases as a result of the breaking bonds on the one hand (narrow peak, in Figure 6a) and the  $N$  value of the PC's that are appropriate for the wide peak increases on the other (Figure 6b, 6c). It may be thought that the wide peak originates from the formation of the peroxide radicals, the mutual reinforcement of the UE's with the UE's of the oxygen molecule and the formation of the anion radicals as a result of the joining of the oxygen containing groups of diepoxysilane. This thought is supported by the fact that the narrow central component of the spectrum widens (as a result of the spin-orbital interaction) and the exchange is cancelled. The narrowing of the peak as the measurement temperature of the wide peak drops supports also the explanation we have given for the formation of this peak.

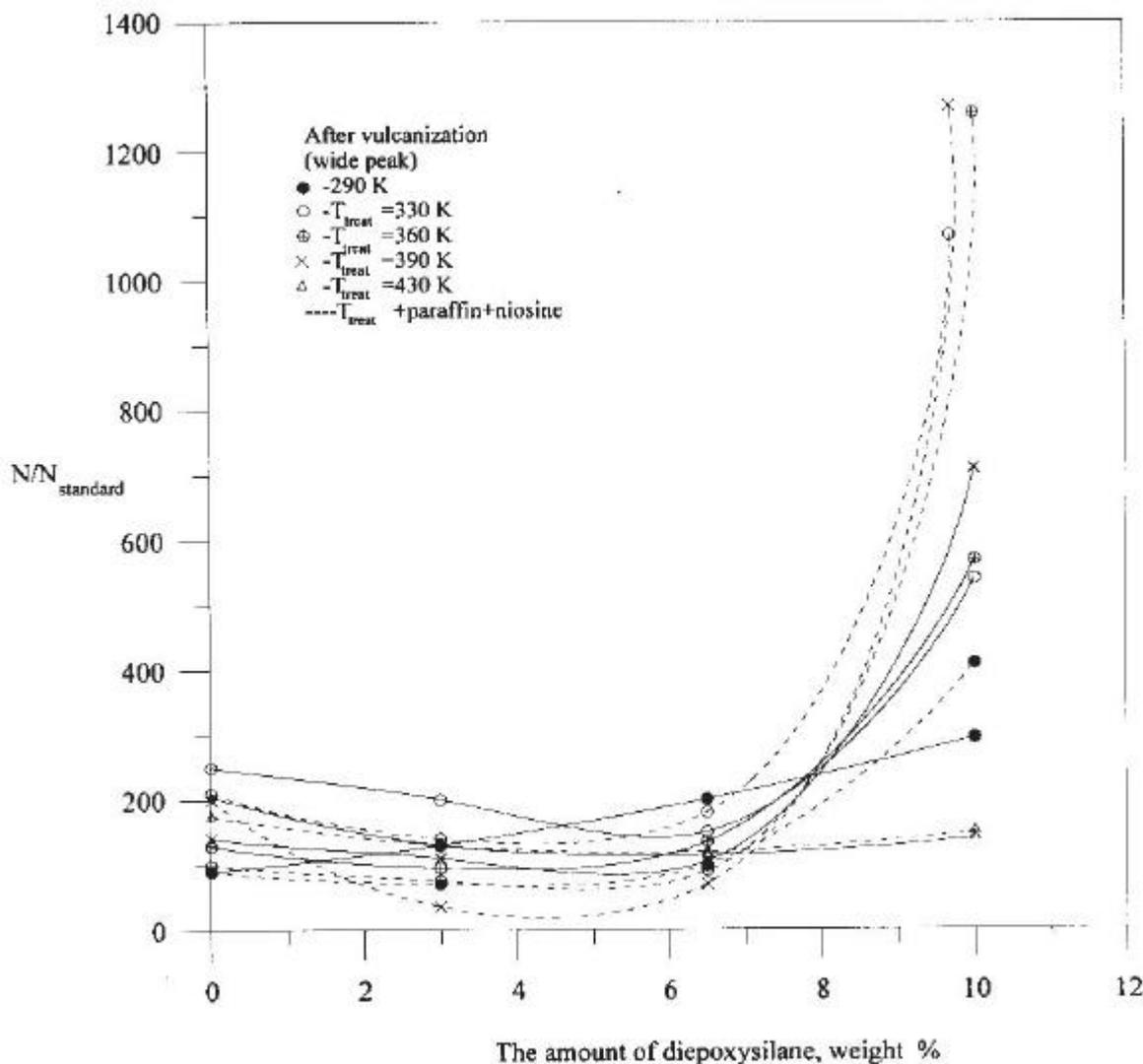


Fig.4. The dependence of the concentration of paramagnetic centers on the amount of diepoxysilane, in the rubber chloroprene and for the wide peak, after vulcanization

If we take into account the formation of FR's above the narrow central peak that has a HFS, the formation mechanism of the wide peak and the dependence of  $N / N_{st}$  (where  $N_{st} = 5.4 \times 10^{15}$  is the amount of spin in a spin-standard sample) on various factors (Figures 6a-c) then we can explain the obtained results as follows. The silicon organic compound causes a great deal of bond breakings by playing a filling role. Indeed, the increase in the value of  $N$  for the PC's

belonging to the narrow peak as the dopings and  $T_{treat}$  get higher, supports this idea. This phenomenon becomes more emphasized by the presence of the diepoxysilane bigger molecular volume. Consequently, the supra molecular structure (SMS) of the rubber equalizes according to its dimensions, that is, the rubber becomes more homogeneous structurally. Therefore, the successive steps of polymerization and vulcanization become easier.

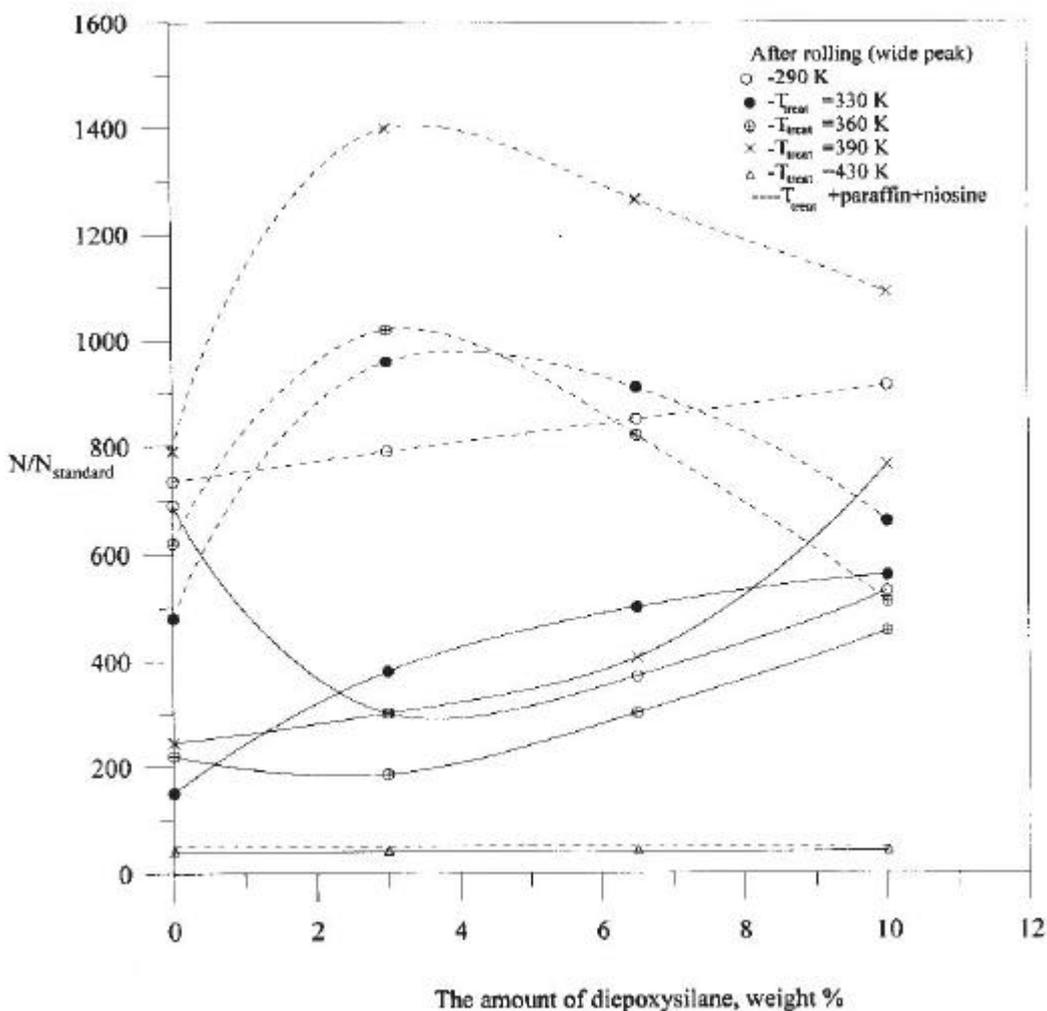


Fig.5. The dependence of the concentration of paramagnetic centers on the amount of diepoxysilane, in the rubber chloroprene and for the wide peak, after vulcanization

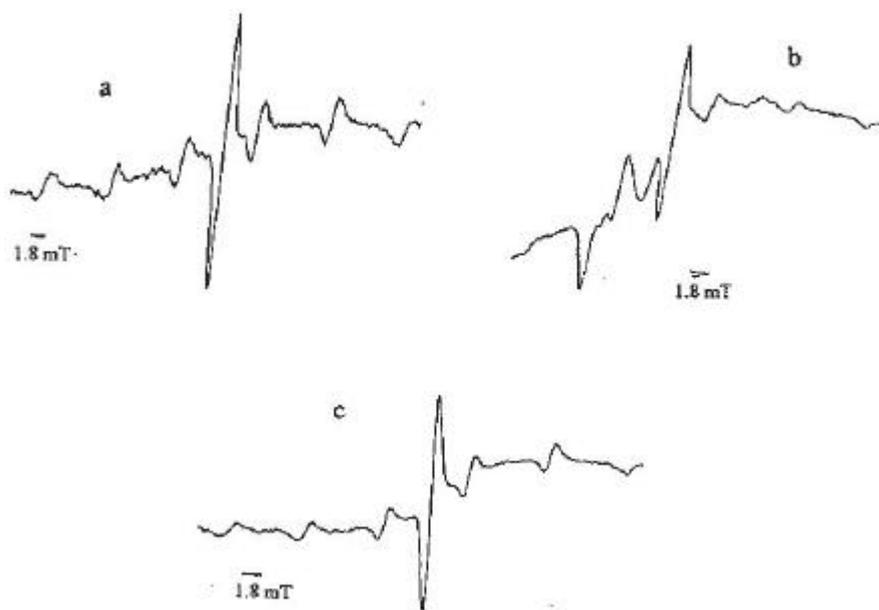


Fig.6. a) ESR spectrum with the narrow peak, in the rubber chloroprene with the amount of diepoxysilane after the vulcanization; b) the ESR spectrum with the wide peak, in the rubber chloroprene with the amount of diepoxysilane after the vulcanization; c) the isotropic ESR spectrum in the rubber chloroprene after vulcanization.

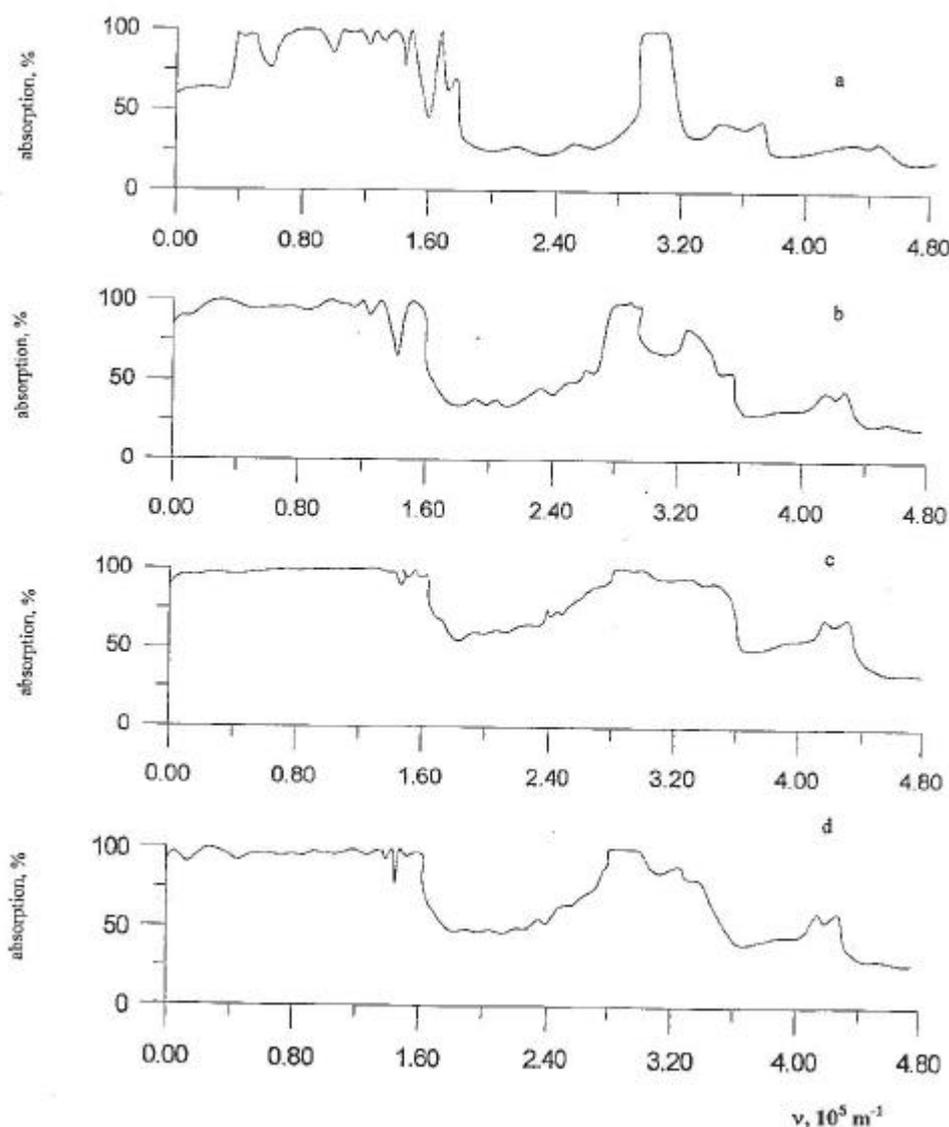


Fig. 7. The characteristic IR absorption spectra in the rubber chloroprene with the amount of diepoxysilane: a) pure rubber; b) 3 weight %, c) 6.5 weight %, d) 10 weight%.

Since an ordered vulcanization network results during vulcanization the nuclei of Cl become completely equivalent and thus an absolutely isotropic spectrum occurs (Figure 1a, 6a, 6c). If the samples undergo only the process of rolling the above mentioned homogeneity is not observed, the isotropy of the spectrum is deteriorated (Figure 1b, 1c, 6b) and also both the intensities of the HFS components and the distances between them change considerably. On the other hand, an additional spectrum with the HFS, which is a bit different than the HFS constants of the isotropic spectrum is observed and this spectrum is placed with the peaks of the isotropic spectrum in pairs. The intensity, number and the placement of the 'additional spectrum' vary according to the prehistory of the sample. All the above said can be explained by the results of the mechano-chemical processes of the rubber. In fact, the multi chemical bonds that are uncontrolled during rolling break and these breakings are random. Simultaneously with it form various associates which are quite different from each other. Therefore, the UE's interact with the nonequivalent nuclei of Cl and protons. Furthermore, the UE's that are localized in different structural units form different ESR spectra [19, 20], that is, the shape, parameters and the

gathering kinetics of the PC's vary strongly, since they depend on the local environment of these centres. The possibility of observing the additional spectrum in the ESR spectrum shows that the SMS's in the rubber are not homogeneous.

The contribution of the silicon organic compounds causes with the addition of oxygen containing groups (that exist in the structure of diepoxysilane), the chemical complexes and unifications. Consequently, due to the above said, as a result of the addition of diepoxysilane to the structure of rubber chloroprene, a binary situation arises. The structure of rubber is homogeneous according to the SMS's on the one hand and the FR processes vary greatly on the other. If we consider the stimulating role of the FR's in the radical polymerization processes of the elastomers, then they take part in two "competing" processes [2], that is, radical polymerization and oxidation reaction. In the later stages of the vulcanization of the rubber whose prehistory was given above (the one that has SMS and PC's with FR's) some part of the FR's continue the oxidation chain and worsen the characteristics of the rubber (that is, material) and some other part make the characteristics better by starting the radical polymerization

(that is, stimulating). The resulting effect, whether positive or negative, depends on the superposition of these factors. The disappearance of the FR's that occurred by the addition of oxygen after the vulcanization proves that they pass on to the oxidized form. The greater the concentration of FR's of this type, the more oxidized becomes the rubber. Its properties worsen and this is observed better at higher values of the ratio of the doping and on the contrary, the observation of the multi-component isotropic spectrum shows that the UE's become stable in the homogeneous structure of the rubber. In other words, the better the network of vulcanization, the better will be the degree of isotropy of HFS. This is observed better at 3 weight % of diepoxysilane. Under these circumstances, it can be said that ordered SMS's that have optimum dimensions form beforehand and help the process of vulcanization. Therefore, the final structure of the rubber based resins is more homogeneous and the physico-mechanical and use characteristics of this resin should be ameliorated.

As can be seen, the ESR results of the rubber chloroprene that was produced by the contribution of the diepoxysilane plays a vital role in both manufacturing and using processes of the FR's that we suggested in reference [1]. The ideas that we gave above are also supported by the results of the IR absorption spectra in the same type of rubber samples that we used for ESR. A typical example of these spectra is given in Figure 7. When we added the contribution two types of phenomena are observed: the optical densities of the peaks that belong to the C=C and C=O bonds vary and a scattering occurs at the limit of SMS of the IR rays. Furthermore, the optical densities of the peaks become respectively minimum and maximum for the C=O and C=C bonds at 3 weight % of the silicon organic compounds. Also at certain values of  $I$  the  $I$ -dependent scattering is observed to have a maximum value. If we take into account the mechanisms that we suggested in this study and in reference [1] and explain the formation of the background by the dispersion of the IR rays at the limits of the SMS's, then at the 3 weight % of the contribution, the SMS's occur spontaneously, dispersion diminishes and thus, the vulcanization network that has formed as a result of the vulcanization becomes more ordered. Therefore, the load that affects the rubber externally is distributed homogeneously in its volume and consequently increases the strength of the rubber against degradation and breaking. The interpretation for the ESR and IR spectra of the rubber chloroprene given above supports both the results of the dynamic-mechanical and electrical measurements of the diepoxysilane used in these rubbers and also the results of the use parameters of the appropriate mixtures of resin. Indeed, as the amount of the diepoxysilane increases, so does, the breaking tension- $S$  and at 10 weight % it becomes maximum (the strength gets 35 % greater). The electrical strength varies in the same manner. The glass transition temperature drops gradually and becomes saturated, relative deformation increases first, at 6.5 weight % it becomes maximum, then decreases a little. The resin materials made of such mixtures have good technological and use parameters.

## CONCLUSIONS

We can summarize the results for the characteristics of the ESR in linear rubbers that we presented as follows.

Although in references the ESR is observed in these rubbers, all of these PC's arise under various strong external factors. But, in spite of some thoughts in favour of the addition of the FR's in the degradation and breaking processes of these rubbers, no PC is observed in them after the processes. Our results prove that such centres play an important role in the oxidation and breaking processes with FR's and this determines the degradation and breaking properties of the materials made of these rubbers in later stages. Consequently, FR's result after breaking the chemical bonds, in the processes of synthesis of the rubbers. Since the FR's have a great chemical activity, they develop the oxidation reactions similar to the chain following degradation. The chemical bonds with the neighbouring macromolecules in the region where FR's settle become excited and brittle, also the breaking activation energy diminishes. The breaking in chains can continue through the thermal fluctuations. These radicals which have a long lifetime are secondary type of FR materials and are generally localized in amorphous regions and where the structure is defective. As one passes from the rubber devinyl nitrile to rubber chloroprene, the ESR spectrum becomes more like the component form instead of singlet. We can explain this, in case that there are atoms or groups of atoms in the side chains, whose electronegativity is greater, by its stronger interaction with these groups. As can be seen from the observed ESR spectra, as the amount of oxygen increases in the rubber system, the concentration of FR's becomes higher. When different structures are added to the structure of the rubber, both the concentration of FR's, the SMS and the molecular structure of the rubber change. The structure of the rubber becomes more homogeneous, that is, the following network of vulcanization becomes better. On the other hand, a correlation is observed between both the concentration of the FR's and structural variations and also the physico-mechanical and electrical strengths of the rubbers and other use parameters. For all that we said we can conclude the following. The rubber materials have a certain structural information, the so called 'prehistory' before they are manufactured and this factor determines later the degradation and breaking phenomena of these materials.

The concentration of FR's shows an extremal variation in both the amount of the oxygen containing groups and the physico-mechanical and electrical strength of the rubbers, depending on the ratio of  $T_{treat}$  and the dopings. This extremal situation which depends on the molecular and SMS of the rubbers can be explained with the mechanism that we presented in our previous paper [1], that is, the presence of the supra molecular compounds which are special for each of the rubbers. As we thought, the overall effect of the dopings goes up to the point that the dopings cover the surface of the above said structure with a mono atomic or mono molecular layer [21, 22, 23]. For the optimum amounts of dopings and  $T_{treat}$ , some optimum ratio of the amorphous and crystalline phases occurs and this brings about the best physico-mechanical and technological properties of the materials. Therefore, the results of these two papers allow to arrange the use parameters of the rubbers and resins we investigated and to choose the composites and mixtures of resins that have the best parameters.

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Received: 13.06.02