Binary mixtures and adhesive compounds of chlorine-containing polymers with unsaturated elastomers

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KINETICS OF COVULCANISATION OF POLYCHLOROPRENES WITH UNSATURATED ELASTOMERS

Dogadkin et al. have described in [1] the anomalous unrestricted covulcanisation of chlorine-containing polymers (CP) with elastomers greatly differing from them in degree of unsaturation. For example, halogenated butyl rubber, polyethylene, chlorosulphonated polyethylene (CSPE) and ethylene-propylene-diene copolymers (EPDC) can be covulcanised with natural rubber, polydienes or copolymers of vinyl monomers. Halogenated or hydrohalogenated natural rubber, polychloroprene, chlorinated polychloroprene, 1,4-poly-1,1,2-trichlorobutadiene are successfully used in adhesives for “hot” bonding of rubbers based on low-unsaturation butyl rubber and ethylene-propylene-diene copolymers, saturated ethylene-propylene rubbers (EPR) and polyisobutylene to various substrates. In these cases the determining role of the chemical component of adhesion, i.e. covulcanisation, is beyond doubt. It may be supposed that the anomalous behaviour of the chlorine-containing polymers is due to the presence in their macromolecules of reactive chlorine atoms and the participation of these atoms in crosslinking reactions. The most probable mechanism in this case is the intermolecular dehydrochlorination of the chlorine-containing polymer, leading to crosslinking, and the chlorination or hydrochlorination of the second components of the mixture by the intermediate or final products of dehydrochlorination with the subsequent participation of the chlorine atoms in crosslinking by one or several mechanisms. The rate and degree of modification of the other mix components by chlorine can be varied widely by the choice of formulation and technology. For instance a method has been recommended consisting of multi-stage preparation of rubber mixes based on a combination of chlorine-containing polymer, low-unsaturation elastomer and an unsaturated elastomer. The first stage is the rapid controlled (temperature, pressure, charge volume and time) thermomechanical processing of the composition. During this stage there occurs the transfer of chlorine from the chlorine-containing polymer to the low-unsaturation elastomer and as a result there is an improvement in the covulcanisation of the low-unsaturation elastomer with the diene components of the composition, in the technical properties and particularly in the weather resistance [2].

It is of theoretical and practical interest to show the probability and investigate the patterns of participation of the labile chlorine atoms of the chlorine-containing polymers in reactions of anomalous unrestricted crosslinking between the CP and other components that differ from the CP in their degree of unsaturation.

Reactions of dehydrochlorination of CP have been extensively studied [3 – 12].

The materials studied were engineering chlorinated polymers – PVC, chlorinated natural polyisoprene (CNR), chlorinated polychloroprene (CPCP), chlorinated polyethylene (CPE), 1,4-poly-1,1,2-trichlorobutadiene (PTCB), chlorosulphonated polyethylene (CSPE), polyisobutylene (PIB), sulphur-regulated polychloroprene (PCP-SR), sulphur- and thiol-regulated polychloroprene (PCP-STR), thiol-regulated polychloroprene (PCP-TR), and chlorobutyl rubber (CBR) and also piperidine-treated PCP-TR (PCPTRP). To obtain the PCP-TRP piperidine was introduced into the purified rubber (0.1 mol per mol of rubber, i.e. a known excess in relation to the mobile (allyl) chlorine atom [13 – 115]). The mixture was placed in ampoules into which argon was blown, sealed and
heated at 100 ± 0.2°C for 48 h. Under these conditions the mobile Cl in the PCP was replaced by piperidine [16, 17].

We studied mixtures of several CPs with unsaturated polydiene elastomers (cis-1,4-polyisoprene (SKI-3), a copolymer of butadiene and acrylonitrile (SKN-26), low-unsaturation elastomers (copolymers of isobutylene and isoprene with an isoprene content of up to 2% (BR), terpolymers of ethylene, propylene and unconjugated diene (SKEPT), and unsaturated elastomers (ethylene-propylene copolymer (SKEP) and polyisobutylene).

In a number of cases the polymers being studied were purified by extraction with acetone at 20 ± 3°C in an atmosphere of pure nitrogen for 72 h. Analysis of the purified polymers by IR spectroscopy showed the absence of accompanying substances and products of oxidation. The rate of dehydrochlorination was studied in air and argon in the temperature range of (140 – 200) ± 0.5°C. The rate of feed of the gases through the CP (about 1 g) reduced to particles of 0.5 – 1.0 mm diameter was about 5 dm³/min. For study of dehydrochlorination during heating we used a device described in [18]. The concentration of HCl in the absorption apparatus with distilled water was determined using conductometry, and sometimes for purposes of control, from the results of Folgar determination of chlorine. The concentration of bound chlorine was determined using Schoeniger’s method [19]. The concentration of ZnCl₂ was determined by the method used in [20].

The rate of crosslinking for individual elastomers was studied according to the change in concentration of effective crosslinks (n'c), which was determined by equilibrium swelling of the vulcanisates in m-xylene and calculated by the Flory-Rehner equation. In the case of vulcanisates of blends of CP with other elastomers we used the method of non-equilibrium stress on a tensile testing machine at a rate of movement of the lower clamp of 50 mm/min, and using the Mooney-Rivlin equation we calculated the equilibrium constant C₁, using which we calculated the concentration of effective crosslinks.

Comparison of the change of n’c (Figure 1) during covulcanisation of the blends of PCP-SR, PCP-TR and PCP-TRP with EPR, EPDC and SKI-3 with a sulphur-metallic oxide vulcanising system shows that the rate and degree of covulcanisation depend on the molecular structure of the PCP, the amount and reactivity of the mobile Cl atoms, as is the case with dehydrochlorination reactions. In addition it clear that the rate and degree of covulcanisation of PCP-SR with the second blend components is considerably greater than in the case of PCP-TR and PCP-TRP, and that the rate and degree of covulcanisation in the blends with second components increase in the order EPR, EPDC, SKI-3, i.e. they depend on the molecular structure of the two components of the blend and on the number of active centres. In spite of the substitution of the initial allyl atom of chlorine in the PCP-TR it covulcanisation at fairly high temperatures does not stop but only slows down, as is the case with dehydrochlorination [20].

An exception to this is the blend of EPR with PCP-TRP, during vulcanisation of which only a small amount of gel is formed. It is not possible to determine n'c of such vulcanisates by the method of arbitrary equilibrium stress.

In this case the basic process of crosslinking with the participation of the initial mobile chlorine, as in the PCP-TR untreated with piperidine, is overlaid by additional reactions ensuring the vulcanisation of the PCP-TRP and its covulcanisation with the second blend components. The kinetic parameters of covulcanisation and dehydrochlorination of the different types of PCP completely coincide. The amounts of HCl released in 24 h at 200°C from the PCP-SR, PCP-TR and PCP-TRP are respectively 50.0, 23.0 and 17 x 10⁻⁴ mol/g, and the activation energy of dehydrochlorination of these elastomers is respectively 92±3, 65±2 and 53±2 kJ/mol [14, 20]. The origin of the reactive chlorine atoms (apart from the allyl atoms) during storage, thermomechanical action in processing and vulcanisation has been partially discussed previously [21, 22]. The correlation of the kinetic parameters of dehydrochlorination of PCP and of covulcanisation confirms the determinant role of the reactive chlorine atoms and the intermediate and (or) final products of dehydrochlorination of PCP in the reactions of covulcanisation. The type of effect shown by the second blend components on the rate of covulcanisation coincides...
With their own rate of vulcanisation. Thus the rate and degree of vulcanisation vary in the order EPR < EPDC < SKI-3, i.e. there is a complete correlation between the processes. It can only be assumed that these components participate with analogous activity in reactions of intermolecular dehydrochlorination and interaction with the intermediate or final products of this reaction [14, 20].

**Kinetics of Dehydrochlorination of Chlorine-Containing Polymers in Binary Blends with Unsaturated Elastomers**

It was shown by studying the rate of dehydrochlorination of blends of PCP-TR with SKI-3 and SKEPT in mass ratio of 0.25 : 0.75 (at 150-200°C for 22 h) that the presence of non-chlorine-containing elastomers influences the rate of dehydrochlorination of the PCP-TR (Figure 2). Depending on the molecular structure, especially the degree of unsaturation of the second elastomer, and its concentration and temperature, the kinetic parameters of dehydrochlorination (rate, amount of HCl released in a time interval $\tau$ ($[\text{HCl}]_\tau$) or the maximum amount of HCl formed under the experimental conditions ($[\text{HCl}]$) can vary enormously.

The kinetics of dehydrochlorination of PCP-TR in blends with other elastomers are affected by all of the studied elastomers. In blends with BR, PIB and SKEPT the rate and degree of dehydrochlorination of PCP-TR increases in the order BR < PIB < SKEPT, whereas in blends with SKI-3 and SKN-26 the kinetic parameters are lower than for the initial PCP-TR. The effect of non-chlorine-containing elastomers on the rate and activation energy of dehydrochlorination increases with increase in their concentration. The effect of the second elastomer on the values of $E$, $[\text{HCl}]$ and $[\text{HCl}]$, may vary quantitatively and qualitatively.

Elastomers not containing chlorine also have an effect on the rate of dehydrochlorination of the other chlorine-containing polymers, PCP-STR and PTCB. The nature of this effect depends on the molecular structure of the chlorine-containing polymer, the amount and reactivity of the labile chlorine atoms and other active centres of the macromolecules taking part in the formation of HCl and secondary reactions of the intermediate and end products of dehydrochlorination.

The effect of the non-chlorine-containing elastomer on the rate of dehydrochlorination is clearly due to secondary reactions of attachment of HCl or Cl to this elastomer. In this case SKI-3 and SKN-26 as expected are more active acceptors of HCl and Cl and BR, PIB and SKEPT are less active acceptors of HCl and Cl than the PCP-TR or other chlorine-containing polymers.

If the assumptions are correct regarding intermolecular dehydrochlorination and secondary reactions of the products of dehydrochlorination involving the chlorine-containing polymer and the second elastomer in blends and adhesive compounds, then the rate of dehydrochlorination should depend on the degree of homogeneity of their mixtures and the complexity of the intermediate diffusion layers between the phases of the colloid system of the blend. By way of example Figure 3
shows the dependence of the basic kinetic constants of dehydrochlorination of PCP-TR on the time of mixing with SKI-3 and SKEPT (0.50:0.50). When \( \tau = 0 \) (absence of mixing, when a mechanical mixture of PCP-TR crumb with SKI-3 or SKEPT is placed in the production reactor to study the dehydrochlorination) there is a decrease in \([HCl]_{8h}\), but \( E \) does not change. This is evidently due to the absence of intermolecular dehydrochlorination, since there is no contact between the phases and no developed transitional diffusion layers. At the same time secondary chlorination and/or hydrochlorination of the SKEPT and SKI-3 takes place. Similar results were obtained for 0.5:0.5 mixtures of PCP-SR with SKI-3 and SKEPT.

The rate of dehydrochlorination of chlorine-containing polymers in blends with other elastomers is also affected by the method of preparation of the homogeneous blends. For example, the rate and degree of dehydrochlorination of PTCB in blends with SKI-3, SKN-26, SKEPT, BR and PIB in a ratio of 0.5:0.5 obtained by co-precipitation from toluene solutions in closed mixers are considerably lower than they are in blends obtained in a mill, an the activation energy on changing over from mixing in a mill to co-precipitation from solutions and mixing in closed mixers increases considerably.

CHANGE IN MOLECULAR STRUCTURE OF UNSATURATED ELASTOMERS IN BINARY MIXTURES AND ADHESIVE COMPOUNDS WITH CHLORINE-CONTAINING POLYMERS

The kinetics of attachment of chlorine to SKI-3, BR, SKEPT and PIB when heated in sandwich specimens is shown in Figure 4. Mill-mixed strips of these elastomers 1 mm thick were placed between two 2 mm thick strips of PCP-STR, placed in a mould and heated. The surfaces of the strips were coated with silicone liquid to prevent them co-vulcanising. The amount of bound chlorine in the elastomers was determined by Schoeniger's method. As is shown in Figure 4, the rate and degree of chlorination decreases in the order SKI-3 > BR > SKEPT > PIB. Under more extreme conditions of the experiment the amounts of chlorine attaching to these elastomers are respectively 12.0, 0.9, 0.6 and 0.4% by mass.

The experiments using sandwich specimens only qualitatively model the processes taking place in the diffusion layers and inside the different phases of colloid systems formed by mixing chlorine-containing polymers with other elastomers and their adhesive compounds during mixing, processing, vulcanisation and ageing. However it has been shown experimentally that an unsaturated elastomer not containing chlorine when mixed with or bonded to a chlorine-containing polymer under widely variable conditions is chlorinated and/or hydrochlorinated. The amounts of bound chlorine are similar to the content of chlorine in the corresponding industrial halogen derivatives.

Chlorination and/or hydrochlorination of an elastomer in sandwich specimens at 173°C such as the SKI-3 shown in Figure 5 is accompanied by profound changes in molecular structure. The intrinsic viscosity of the sol-fraction increases many times more quickly, the gel

![Figure 4](image-url) Kinetics of chlorination of engineering SKI-3 (curves 1 – 4), BR (curve 5), SKEPT (curve 6) and PIB (curve 7) during thermal processing in contact with PCP-TR at 153°C (curve 1), 163°C (curves 2, 5 and 7), 173°C (curve 3) and 183°C (curve 4)

![Figure 5](image-url) Intrinsic viscosity of sol fraction of SKI-3 (curves 1 and 1'), gel fraction content g (curves 2 and 2'), equilibrium swelling of gel fraction Qe (curves 3 and 3') in toluene during heat treatment of purified SKI-3 when isolated (curves 1 – 3) and in contact with engineering PCP-STR (curves 1' – 3') at 173°C vs time of treatment
fraction decreases and there is an increase in the network density of the gel in specimens heated in contact with the chlorine-containing polymer. The greatest changes occur with a heating time < 1 h. The changes in $[n]$, $g$ and $Q_p$ indicate that the process is accompanied by crosslinking of the macromolecules.

In the case of SKI-3 and SKEPT (Figure 6) it is shown that chlorination of these polymers in sandwich specimens increases their rate of vulcanisation by a sulphur – metal oxide vulcanising system. Crosslinking is accompanied by the formation of ZnCl$_2$. The kinetic curves plotting change in the concentration of effective crosslinks $n_c$ and the formation of ZnCl$_2$ are symbatic for the two elastomers. This also points to the participation of Cl atoms in the crosslinking reactions in chlorinated SKI-3 and SKEPT.

A very important fact discovered previously [3] is that ZnCl$_2$ has a qualitatively similar effect on thermo-oxidative ageing of SKI-3 vulcanisates chlorinated in contact with PCP-TR at 173°C in sandwich specimens and on the thermo-oxidative ageing of PCP-TR vulcanisates.

During ageing of rubbers vulcanised with sulphur, Thiuram D and zinc oxide an induction period is observed (Figure 7), after which breakdown of the chains occurs at the same rate as in sulphur-Thiuram vulcanisates. After elimination of ZnCl$_2$ the vulcanisate with ZnO undergoes marked degradation at the beginning of ageing. After 6 h ageing stabilisation is observed. The degradation stops for a period of time equal to the induction period of ageing of the unextracted vulcanisates. Then ageing continues once again. Elimination of the ZnCl$_2$ also leads to a marked increase in the rate of structurisation in ageing (Figure 7). Hence ZnCl$_2$, by slowing down structurisation and degradation, stabilises the vulcanisate during ageing.

To find out the reason for this phenomenon we studied by IR spectroscopy the kinetics of oxidation of the vulcanisates during ageing. The shape of the kinetic curves of change in the content of COO groups (the band at 1715 cm$^{-1}$) (Figure 8) is similar to that of the degradation curves (see Figure 7). Apparently the stabilising action of the ZnCl$_2$ is due to inhibition of oxidation. Analogous data were obtained when studying the kinetics of build-up of C=O groups. The existence of a second (induction) section on the curves of oxidation and degradation during ageing of vulcanisates extracted with an ethanol-toluene mixture appears to be due to the stabilising effect of the ZnCl$_2$ formed during intensive oxidation on the first section.

The intensive ageing and oxidation after the induction period and after the second section of the curve in the case of ageing of extracted vulcanisates may by analogy with the effect of typical antioxidants be due to two things: 1) the ZnCl$_2$ is completely used up; 2) the ZnCl$_2$ is accumulated in the vulcanisates up to concentrations exceeding the optimum value, after which it initiates oxidation.
We studied the oxidation of vulcanisates containing different amounts of zinc oxide. Initially it was found that during ageing the ZnO is used up, but ZnCl₂ accumulates in the vulcanisate. Increase in the amount of ZnO, which ultimately causes an increase in the ZnCl₂ concentration, leads to a lengthening of the induction period and to a reduction in the rate and degree of oxidation (see Figure 7).

Evidently the acceleration of ageing after the induction period occurs because of the exhaustion of the ZnCl₂, possibly by the formation of complex compounds with oxygen-containing functional groups formed by oxidation of the polymer, and also with reactive chlorine atoms of the polymer chains.

The well-known fact that vulcanisates of chlorine-containing polymers with an increased content of zinc oxide have high heat resistance may be explained by the inhibiting effect of ZnCl₂ on the processes of ageing and oxidation. The mechanism of this phenomenon may be explained as follows. It has been shown [23] that the mobile atoms of chlorine in PCP (allyl units) initiate oxidation. This is understandable if we remember that the detachment of chlorine is a free radical process [2, 3], as a result of which macroradicals are formed which are capable of attaching oxygen. Zinc chloride may in the first place facilitate the separation of chlorine by an ionic mechanism and secondly may stabilise the reactive chlorine atoms by the formation of coordinating bonds ([3]. Ultimately this leads to the inhibition of oxidation during the initiation stage of the process. However, the ZnCl₂, being a Lewis acid, may evidently cause breakdown of hydroperoxides by an ionic mechanism and terminate the chain processes of oxidation at the stage of growth of the reaction chain.

Thus, the correlation of the kinetic parameters of dehydrochlorination and vulcanisation of polychloroprene and of its covulcanisation with other elastomers having different degrees of unsaturation confirms the determining role played by reactive chlorine atoms and intermediate or end products of dehydrochlorination of the chlorine-containing polymers in covulcanisation reactions. The other elastomers, depending on their degree of unsaturation, have a marked effect on the kinetic parameters of dehydrochlorination of the chlorine-containing polymers in binary mixtures. The nature of this effect can be easily explained if we assume that in binary mixtures what takes place firstly is intermolecular dehydrochlorination involving the chlorine-containing polymer and the second elastomer and that this is followed by attachment of the HCl or Cl to the other elastomer. This hypothesis is confirmed by direct experiments on sandwich specimens. For example, we prepared halogenated SKI-3, BR, SKEPT and PIB containing 12.0, 0.9, 0.6 and 0.4% by mass of chlorine respectively. Chlorination is accompanied by profound changes in the molecular structure of these elastomers. They acquire the physico-chemical and engineering properties characteristic of the corresponding engineering chlorinated products. The chlorine atoms in such elastomers take part in the reactions of vulcanisation, covulcanisation and ageing according to any more or less probable mechanisms suggested for the corresponding chlorinated engineering products. The effect of ZnCl₂ in the chlorinated elastomers during vulcanisation and ageing is analogous to its effect in polychloroprene.

REFERENCES