The effect of thermal oxidation on the adhesion properties of chloroprene rubber

M.E. Solov’ev, G.I. Kostrykina, A.A. Zuev, and Kh.A. Pavlova
Yaroslavl State Technical University

Translated by P. Curtis

Elastomeric adhesives based on chloroprene rubbers, owing to a combination of good adhesion properties with a high cohesive strength on account of the ability of polychloroprene to crystallise in the non-stressed state and under strain, are being used in different sectors of engineering and in the home [1–3]. They possess adhesion to a large number of different materials: rubber, metals, wood, glass, concrete, leather, and ceramics.

In the process of manufacture and during storage, and also during the service of adhesive bonds, the adhesives can undergo heat effects, which influences the strength of the bonds [4]. Depending on the conditions of the heat effect, the strength of the adhesive bond can change in a complex way. Adhesives based on chloroprene rubbers comprise elastomer composites that, besides polychloroprene, may contain resins, low-molecular-weight adhesion modifiers, fillers, and other additives.

The aim of this work was to investigate the effect of thermal oxidation of polychloroprene, representing the elastomer base of the adhesive, on its ability to crystallise and on the adhesion strength of chloroprene rubber in rubber–metal bonds.

The investigation was conducted on toluene solutions of chloroprene rubber SN-232 (standard Q/SNYF02.06-2009) of different concentration (3–15 wt%). Solutions prepared at room temperature were heated in air under normal pressure at temperatures of 333–363 K for different times. The structure of the rubber was assessed from IR transmission spectra, which were obtained on an IR Fourier RX1 spectrophotometer (Perkin-Elmer) in the wave number range 400–4000 cm$^{-1}$. Specimens for analysis were prepared by casting toluene solutions of the polymer onto crystals of potassium bromide and subsequent complete removal of the solvent. The spectra were interpreted using correlation tables [5] and literature sources [6, 7]. As elastomeric substrates in bonding to metal, use was made of optimally vulcanised, carbon-black-filled rubber mixes based on BNKS-28 nitrile butadiene rubber. The strength properties of the adhesive were determined by the direct pull method using the procedure described by Baryshev et al. [8]. Tests were conducted on adhesive bonds held at room temperature for 3 days after bonding, and also subjected to a heat effect in air under normal pressure at a temperature of 353 K for different times. After heating, the specimens were cooled and were held for 3 days before testing.

Mercaptan-regulated chloroprene rubbers, including the polychloroprene examined in this work, are statistical polymers of 2-chloro-1,3-butadiene containing units of different microstructure: trans-1,4-, cis-1,4-, 1,2-, and 3,4-, the amount of which amounts to roughly 85–87, 10–12, 1.5–3, and 1–2% respectively. Their reactivity in oxidation reactions may differ considerably. Furthermore, a feature of the oxidation of polychloroprene is the possibility of the participation in the radical reactions taking place during oxidation of the chlorine atoms present in the structure of the polymer units. In connection with the fact that the oxidation of polychloroprene, in contrast to general-purpose rubbers, has been studied comparatively little [9], it was of interest to assess theoretically the reactivity of units of different structure in reactions of initiation of oxidation and separation of chlorine. The thermodynamic functions of the given reactions were calculated by the density functional quantum chemical method [10] DFT B3LYP/6-31G** using the NWChem program package [11]. As molecular models during calculation, use was
made of dyads of two units of chloroprene of different microstructure with end-chain methyl groups instead of chain continuation. By way of example, Figure 1 gives a model of a dyad consisting of chloroprene units in 1,2- and trans-1,4-configurations with end-chain methyl groups (3,5-dichloro-3-ethylocta-1,5-diene).

The main factor determining the oxidation rate of unsaturated carbon-chain rubbers is the reduction by comparison with saturated polymers in the energy of detachment of the hydrogen atom from the carbon in the α-position to the double bond [12], which is 50–80 kJ/mol lower than for alkanes [13]. Quantum chemical calculation within the framework of the level of theory adopted in this work indicates good agreement with these values. In particular, the calculated values of the enthalpies of reactions of hydrogen detachment at carbon atoms C2 and C4 in the model presented in Figure 1 amounted to 418 and 368 kJ/mol respectively. The latter value is roughly 30 kJ/mol higher than the calculated value of enthalpy of the reaction of hydrogen detachment from carbon in the α-position to the double bond for the model of cis-polyisoprene. That is, the α-C–H bond in polychloroprene, although slightly less active than in polyisoprene, is nonetheless a potential reactive centre during oxidation. Chlorine atoms are second centres of this type. Calculation of the enthalpies of reactions of chlorine detachment at atoms C2 and C4 in the examined model gave values of 241 and 378 kJ/mol respectively. Similar results are obtained for other types of dyad where units are present in 1,2-addition. Consequently, the chlorine atom in a chloroprene 1,2-unit is the most active reaction centre, and chlorine detachment from units in 1,4-addition will occur at a much lower rate. This is in agreement with known experimental findings indicating the extreme activity of chlorine in 1,2-units in radical reactions of polychloroprene [9]. Further development of chain reactions of oxidation of rubber is connected with the acceptance of molecular oxygen by the alkyl radicals formed. According to calculation, the enthalpy of reactions of addition of oxygen to alkyl radicals of polychloroprene for 1,2- and 1,4-trans-units amounted to −47 and −68 kJ/mol respectively. That is, the activity of the radicals lies in reverse relation to the activity of initial reaction centres, which is a general rule in radical reactions. Thus, quantum chemical calculation indicates that, during the oxidation of polychloroprene, along with the standard mechanism for unsaturated hydrocarbons, which is accompanied with the build-up and subsequent decomposition of hydroperoxides, a considerable role is played by a mechanism associated with chlorine detachment, the result of which will be the accumulation in the system of hydrogen chloride as a result of the dehydrogenation of hydrocarbon fragments of the rubber by chlorine radicals.

Experimental data on the oxidation of polychloroprene solutions of 3% concentration are in agreement with these conclusions. Thus, by iodometric titration it was established that, at a temperature as low as 333 K, after 20 min of oxidation, the build-up of hydroperoxides is observed in the system, the maximum concentration of which is achieved at an oxidation time of 30–50 min and increases with increase in oxidation temperature. Here, a considerable reduction in the viscosity of the solution is observed. At the maximum hydroperoxide concentration, the reduction in viscosity in some cases is accompanied with opalescence of the solution, which indicates microphase separation. As shown by investigations, this reduction in viscosity is not connected with degradation of the rubber, while the gel formed by microphase separation is not chemical but physical. It is reversible and disappears during the titration of the solution by isopropyl alcohol. The results of experiments

Figure 1. A structural model of 1,2- and 1,4-trans-units of polychloroprene (3,5-dichloro-3-ethylocta-1,5-diene)
on the acid-basic titration of solutions indicate that, apart from hydroperoxides, hydrogen chloride also builds up in the system during oxidation. The rate of formation of hydrogen chloride is slightly lower than the rate of build up of hydroperoxides and reaches its maximum value after the maximum hydroperoxide concentration is reached. It is remarkable that, at the moment of achievement of the maximum rate of hydrogen chloride formation, in those cases where opalescence was observed in the solution before this, it disappears, the solution becomes completely transparent, and its viscosity increases. That is, the physical microgel formed in the course of oxidation breaks down as a result of hydrogen chloride formation. It can be assumed that the formation of a physical microgel is connected with complexing of hydroperoxides, which are generally capable of forming fairly strong hydrogen bonds [14]. Its breakdown is the consequence of a reduction in the hydroperoxide concentration, and also in the complexing of hydroperoxides with low-molecular-weight hydrogen chloride, which leads to breakdown of the physical network. It must be noted that the formation of physical gels during the preparation of adhesives based on polychloroprene is known in factory practice as “gelation” of the adhesive. Factory procedures combat this by adding a small quantity of water to the composition of the adhesive. In this case, the water seems to act similarly to the above-described effect of titration of gel by isopropyl alcohol – it forms complexes of hydrogen bonds with hydroperoxides, breaking down the three-dimensional structure of the physical gel.

Investigation of the changes in the IR spectra during oxidation of the rubber on the whole is in agreement with the picture described above. Thus, during the oxidation of films of rubber at 353 K there is a monotonic reduction in the content of vinyl groups in units in 1,2- and 3,4-configuration, recorded from the 926 and 889 cm\(^{-1}\) absorption bands respectively. Here, the rate of consumption of units in 1,2-configuration is considerably higher. The concentration of units in 1,4-trans-configuration, recorded from the 1660 and 825 cm\(^{-1}\) absorption bands, likewise decreases; however, the rate of their decrease is reduced at an oxidation time of about 40 min. In this period, a maximum is observed on the curves of the dependences of the concentration of OH- groups recorded from the 3347 cm\(^{-1}\) band. The content of C–Cl groups was judged from the 657 and 602 cm\(^{-1}\) bands. Reduction in their intensity during oxidation is consistent with the recorded formation of hydrogen chloride in solutions of the rubber.

Crystallisation of the rubber was conducted at a temperature of 297 K over a 7 day period. The film thickness on a potassium bromide crystal amounted to 25 \(\mu\)m. The spectra were measured every 24 h. Qualitative analysis of IR spectra of crystallised and amorphous polychloroprene specimens indicates that changes in the spectra during crystallisation of the rubber correspond to positions adopted in the literature [6, 7]. In particular, in the IR spectrum of the crystallised specimen, a so-called “crystalline band” appears at 955 cm\(^{-1}\), from which it is possible to assess only the comparative degree of crystallinity. The absolute magnitude of the degree of the crystallinity can be determined from the change in absorption of the “amorphous” band at 1226 cm\(^{-1}\). Other changes in the spectra of crystallised rubber, described in the literature, are also observed. The calculated degree of crystallinity (with account taken of the change in film thickness according to the 1660 cm\(^{-1}\) band) for the investigated specimen amounts to 25.6%.

It is important to note that, during oxidation at 353 K for 30 min, the ability of the polymer to crystallise not only does not decrease but even slightly increases. Thus, the maximum degree of crystallinity, calculated from the “amorphous” 1226 cm\(^{-1}\) band, amounts to 28.7%, which is slightly higher than the degree of crystallinity of the initial specimen. Crystallisation is accompanied with change in the conformation of the methylene groups, namely with transition from a convoluted gauche-conformation to a trans-conformation (the ratio of absorption of the 1443 and 1430 cm\(^{-1}\) bands increases monotonically). Here there is an increase in the proportion of the “crystalline band” of CCl (669 cm\(^{-1}\)). These data make it possible to conclude that the low degree of chain modification by oxygen-containing groups does not lower the degree of crystallinity of the polymer. Assessment of the solubility of the polymer showed that oxidation in this regime is not accompanied with any change in configuration: the polymer is soluble in toluene, i.e. it retains a practically linear chain structure. However, with increase in the duration of oxidation, and during oxidation in a more severe regime, the picture changes. For example, in specimens oxidised at 403 K for 210 min, the ability to crystallise over a 7 day period is lost entirely. Here, the polymer loses its solubility in toluene completely, and the crosslink concentration amounts to \(4.6 \times 10^{-6}\) mol/g. It may be assumed that the determining factor for crystallisation suppression is the loss of regularity of structure on account of modification by oxygen, as thermal structure formation to a crosslink concentration of \(5 \times 10^{-6}\) mol/g, which occurs practically without oxidation, not only does not lower but even slightly increases the degree of crystallinity (roughly by 20%).

The above-examined structural changes in the process of oxidation of polychloroprene can have different effects on its adhesion properties. As shown by investigations, the dependences of the adhesion strength on the heating time of the solution of rubber and bonded specimens have maxima (Figure 2). The position of the maximum on the curve of adhesion strength versus rubber solution heating time corresponds in time roughly to the maximum hydroperoxide concentration during oxidation of the solution. During the heating of bonded specimens, the
position of the maximum on the curve is displaced slightly towards a greater time, and here the maximum value of adhesion strength itself is slightly higher than during heating of the solution. It seems that, during heating of the bonded specimens, the adhesion strength increases in connection with reactions of thermal structure formation, which occur during heating. Furthermore, during heating, interaction by functional groups between the chloroprene rubber of the adhesive and the nitrile butadiene rubber of the substrate is possible. Increase in the heating time above the optimum has an adverse effect on the adhesion strength, in all likelihood because the degree of crystallinity starts to decrease under the influence of functionalisation of the elastomer during oxidation.

Thus, the reactions occurring during oxidation of chloroprene rubber in solution and in films may lead to non-monotonic changes in the rheological properties of the solution and in the adhesion properties of the films. Here, an important feature in these effects is the participation in radical reactions of the chlorine atoms splitting away during heating from chloroprene units in 1,2-configuration.

REFERENCES


Received 24.12.2013