INTERACTION OF 2,6-DIMETHYLOL-4-*tert*-BUTYLPHENOL WITH UNSATURATED ELASTOMERS

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Fig. 1

Figure 1: Fig. 1

Abstract

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L. V. GINZBURG, V. A. SHERSHNEV, B. A. DOGADKIN

INTERACTION OF 2,6-DIMETHYLOL-4-*tert*-BUTYLPHENOL WITH UNSATURATED ELASTOMERS

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In recent years the process of structuring elastomers containing double bonds by means of various *p*-alkylphenol-formaldehyde derivatives has been acquiring ever broader importance. The literature contains a considerable amount of patent data, as well as works dealing with the technological side of the question. The mechanism of the processes occurring in this case has been insufficiently elucidated; in particular, there are almost no data on the kinetics of addition of these structuring agents to elastomers during the reaction. In order to study this latter aspect of the process of interaction of phenol-formaldehyde derivatives, we synthesized 2,6-dimethylol-4-*tert*-butylphenol from phenol labeled with C^{14} in position 1, with a specific activity of 0.01 mCi/g.

The phenol alcohol, recrystallized from a petroleum ether—chloroform mixture, was a white crystalline substance with m.p. 75° and contained 28% methylol groups (calculated 29%).

Dimethylolphenol and rubber were mixed in benzene solutions, and the accelerator commonly used in practice, $SnCl_2 \cdot 2H_2O$, was introduced in microquantities into films of these mixtures obtained from the solutions.

The mixtures were heated in an electropress at 160 and 180°; the amount of labeled dimethylolphenol was determined before and after extraction of the unreacted portion with acetone, by activity on a type B-2 apparatus. Counting was carried out on both sides of circular specimens (two parallel ones) of thickness above the limiting value (100 mg/cm^2).

Fig. 1. Kinetics of structuring of SKD rubber and addition of dimethylolphenol (DMF) during heating at 160° (*1, 2*) and 180° (*1′, 2′*). Solid curve—added DMF; dotted curve—maximum swelling in *m*-xylene. *1*—concentration of phenol alcohol 1.506%, *2*—same, 2.660%.

The time required for counting the activity of the specimens was determined by statistical methods (^{1}). A Poisson distribution of the counting rate had first been established. The formation of crosslinks during the reaction was determined from swelling data (Q_m) for the specimens in *m*-xylene and was calculated from nomograms on the basis of the Flory-Rehner equation (^{2}). In doing so, allowance was made for the slight purely thermal structuring of cis-1,4-polybutadiene (SKD) that occurs.

As can be seen from Fig. 1, addition of dimethylolphenol to the rubber proceeds very rapidly (already after 20–30 min the maximum amount is reached: ~80% at 180° and ~75% at 160°). The character of the kinetic curve

within the accepted limits does not depend on the concentration of the introduced dimethylolphenol. The structuring of rubbers that occurs simultaneously upon heating proceeds at a considerably lower rate than the addition of the structuring agent. This indicates the presence of two stages in the interaction of rubbers with dimethylolphenols: (a) primary addition of it to the rubber molecule, and (b) formation of a cross-link in the reaction with the next polymer molecule. The addition reaction obeys a first-order equation with an activation energy of about 17 kcal/mole.

Fig. 2. Dependence of the number of phenol alcohol molecules per one cross-link on the duration of heating at 160° (**A**) and 180° (**B**). The contents in the mixture of phenol alcohol and $SnCl_2 \cdot 2H_2O$, respectively, in percent: *a* –1.435; 2.90; *b* –2.707; 2.84; *v* –1.431; 5.58, *g* –5.600; 2.750.

In the presence of $SnCl_2 \cdot 2H_2O$, the rates of the addition and structuring reactions increase sharply. The rate of addition is so high that practically after only 10 min (at 180°) and 20 min (at 160°) the limiting amount of dimethylolphenol has added. The maximum amount of added structuring agent increases somewhat in comparison with mixtures without accelerator (to 85%, independently of temperature). Increasing the concentration of stannous chloride has practically no effect on the rate of addition, but somewhat increases the rate of structuring and the relative amount of added dimethylolphenol. The dependence of the number of dimethylolphenol molecules per one cross-link on the duration of heating at 160 and 180° is presented in Fig. 2. As can be seen, at different concentrations of dimethylolphenol and accelerator, at first only addition of dimethylolphenol to the rubber takes place, without visible formation of cross-links. The initially recorded number of alcohol molecules per one cross-link is more than 8. As the density of the network increases, this value decreases and, in the limit, tends to unity.

Fig. 3. UV spectra of the products of the interaction of SKD rubber and 2-methylol-4-tert-butyl-6-methylphenol (11% based on rubber) at 160°. 1 –90 min heating, 2 –50 min heating.

Butyl rubber under the same conditions is structured in the presence of stannous chloride somewhat more slowly, but nevertheless the number of phenol alcohol molecules used to form one cross-link likewise falls to 1.

To elucidate the mechanism by which phenolic alcohol is added to rubber, we investigated the UV spectra of the product of the interaction of monomethylolphenol (2-methylol-4-*tert*-butyl-6-methylphenol) with SKD rubber under vulcanization conditions. The reaction product was dissolved in cyclohexane, and UV spectra were recorded in the region of 230–300 mμ. As can be seen from Fig. 3, the spectrum obtained coincides completely with the chroman spectra reported in the literature (^{3}). Rubber gives no absorption bands in this region. The absorption intensity of the chroman groupings increases with increasing heating time of the mixture of phenolic alcohol with rubber.

From the foregoing it may be concluded that, in the first stage of the reaction of phenolic alcohol with rubber, its addition occurs predominantly to one rubber molecule, with formation of a chroman ring according to the scheme:

[reaction scheme: a rubber-chain fragment reacts with dimethylol-*tert*-butylphenol to form a chroman ring attached to the chain, with elimination of H_2O]

Crosslinking with formation of two-sided chroman structures (^{4}) requires condensation of two added dimethylolphenol molecules via the methylol groups (or their preliminary condensation). The data presented above, however, show that formation of a crosslink is ultimately provided by one molecule of dimethylolphenol. Consequently, crosslinking must occur by another reaction, which may be the interaction of the methylol group of the addition product with an α-methylene hydrogen of the polyolefin chain:

[reaction scheme: a chroman-containing rubber-chain fragment bearing a CH_2OH group reacts with a second polyolefin-chain fragment to form a methylene bridge]

Thus, in the reactions of addition of dimethylolphenol to rubber and of subsequent structuring, the methylol groups of the structuring agent participate. Therefore, the more of them introduced into the mixture, the more crosslinks should be formed. It follows from this that monomeric dimethylolphenol, introduced into the mixture with rubber in the same weight amount as its tri- or tetramer (resin 101), should be a more effective structuring agent. This was indeed observed by us experimentally.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

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