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B. A. DOGADKIN and A. A. DONTSOV

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Fig. 1

Figure 1: Fig. 1

Abstract

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B. A. DOGADKIN and A. A. DONTSOV

INTERACTION OF POLYETHYLENE WITH SULFUR

(Presented by Academician A. A. Balandin on 28 I 1961)

The study of the interaction of sulfur with saturated polymers is of interest from the standpoint of clarifying the possibility of using this classical vulcanizing agent to increase the heat resistance and improve the mechanical properties of polymers. There are no literature data on this question, with the exception of a number of patents [1], in which technical methods of vulcanization under the combined action of peroxides and sulfur are described.

We investigated the interaction of sulfur with high-pressure polyethylene (PE). As can be seen from Fig. 1, heating PE with sulfur in the range 200-250° is accompanied by the addition of sulfur to the hydrocarbon, the evolution of hydrogen sulfide, an increase in the number of double bonds, the appearance and gradual increase in the number of chemical cross-links between the molecular chains of PE, as a result of which, at a certain stage, an insoluble fraction (gel) is formed. Undoubtedly, as a result of the reaction other structural changes in PE also occur, for example the formation of cyclic structures.

Fig. 1. Kinetics of hydrogen sulfide evolution **(1)**, gel formation **(2)**, sulfur addition **(3)**, change in the swelling maximum **(4)**, and accumulation of double bonds **(5)** in a PE + 7.74% S mixture at 230°.

The kinetic curves for the addition of sulfur to PE are for the most part rectilinear (Fig. 2). The absolute rate of reaction for the rectilinear portion increases linearly with an increase in the initial sulfur content in the mixture; the relative rate, expressed as $S_{\text{bond}}/S_{\text{tot}}$, shows an inverse dependence, and in mixtures with a sulfur content greater than 6% per polymer at a temperature of 230° a constancy of the relative rate is observed, independent of the initial sulfur content. The limiting amount of sulfur added does not depend on the reaction temperature and amounts to 31-37% of the initial content. The moment of maximum sulfur addition coincides with the moment of consumption of free sulfur

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[1] Patent references cited in the article.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

in the mixture. Further heating of the mixtures, in the absence of free sulfur, causes a certain decrease in the amount of bound sulfur. The process of sulfur addition satisfies the equation $K = 1.58 \cdot 10^{15} e^{-44.4/RT}$.

The kinetics of hydrogen sulfide evolution have a more complex character. On the kinetic curves (Fig. 3) one can observe an inflection, which at a given reaction temperature occurs at one and the same amount of bound sulfur, irrespective of its content in the initial mixture. This break occurs the earlier and at the smaller amount of added sulfur, the higher the reaction temperature. Before the inflection on the kinetic curves, the amount of evolved H_2S is approximately equivalent to the amount of bound sulfur. In the further course of the reaction, the H_2S/S ratio increases, reaching by the end of the process, independently of the temperature and the initial sulfur content, a value close to 2. These observations make it possible to consider that H_2S is formed both as a result of primary reactions of sulfur with PE and as a result of secondary reactions in which the added sulfur participates.

Fig. 2. Kinetics of sulfur addition as a function of the reaction temperature and the total sulfur content in the mixture. *a* –mixture PE + 7.74% S: 1–240°, 2–230°, 3–320°; *b* –temperature 230°: 4–10.0%, 5–6.58%, 6–3.98%, 7–2.35% sulfur per polymer

The formation of double bonds proceeds at a constant rate. A linear dependence is observed between the amount of sulfur added and the number of double bonds formed. The total amount of double bonds formed is small: by the end of the process it is 5-7.5% of the equivalent of the evolved hydrogen sulfide.

The rate of gel formation increases with an increase in the reaction temperature and the initial sulfur content in the mixture, but the limiting content of the insoluble fraction changes only slightly when these parameters are varied. The limiting gel content is reached independently of the reaction temperature and the initial sulfur content at a comparatively small amount of bound sulfur (0.6-0.7%), and does not change upon further sulfidation (Fig. 4). At the same time, a further increase is observed in the number of cross-links in the gel, determined from the maximum swelling in boiling toluene. A linear dependence is observed between the maximum swelling and the amount of bound sulfur (see Fig. 4). This gives a basis

Fig. 3. Kinetics of hydrogen sulfide evolution as a function of the reaction temperature and the initial sulfur content during the process of interaction of

sulfur with polyethylene. The designations are the same as in Fig. 2.

it may be considered that crosslinking of molecular chains occurs mainly through sulfur-containing groups. The concentration of crosslinks after completion of the process is 5.9–9.4 $\cdot 10^{18}$ per 1 cm^3, which means a content of 50–80 sulfur atoms per crosslink. To explain this it is necessary to admit the possibility of degradation and the formation of intramolecular rings containing sulfur, as well as other modes of sulfur addition that do not lead to crosslinking reactions.

The experimental data presented make it possible to regard the interaction of sulfur with PE as a radical process, analogous to the reaction of sulfur with low-molecular-weight compounds[2]. In accordance with the data of the studies by Gee, Gardner, and others[3,4], it may be considered that under the temperature conditions of the reaction thermal dissociation of the eight-membered sulfur ring occurs according to the scheme:

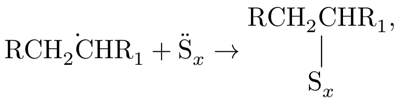
$$S_8 \rightleftarrows \ddot{S}_8 \rightarrow \ddot{S}_x + \ddot{S}_y. \qquad (1)$$

Fig. 4. Dependence of the amount of gel (1) and of the swelling maximum of the gel (2) on the amount of bound sulfur in polyethylene

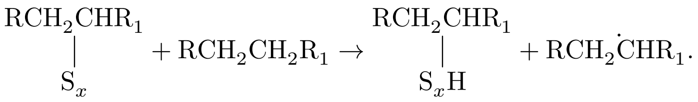
The dissociation of sulfur into radicals is the initial and, at the same time, controlling stage of the process of interaction of sulfur with PE. Sulfur biradicals abstract hydrogen atoms from methine or methylene groups; as a result, polymeric and persulfhydryl radicals are formed

$$RCH_2CH_2R_1 + \ddot{S}_x \rightarrow RCH_2\dot{C}HR_1 + HS_x^{\cdot}. \qquad (2)$$

Recombination of the polymeric $RCH_2\dot{C}HR_1$-radicals at the first stage of the reaction is hindered. It is more probable to assume a sulfidation reaction with subsequent dehydrogenation of the polymer molecules:



$$RCH_2\dot{C}HR_1 + \ddot{S}_x \rightarrow \underset{S_x}{\underset{|}{RCH_2CHR_1}}, \qquad (3)$$



$$\underset{S_x}{\underset{|}{RCH_2CHR_1}} + RCH_2CH_2R_1 \rightarrow \underset{S_xH}{\underset{|}{RCH_2CHR_1}} + RCH_2\dot{C}HR_1. \qquad (4)$$

At all stages it is necessary to allow for the occurrence of decomposition reactions of polysulfide groups with liberation of radicals containing a smaller number of sulfur atoms:

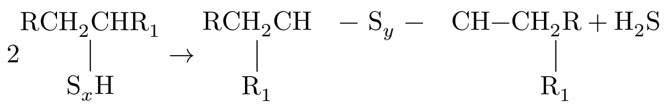
$$\ddot{S}_x \rightarrow \ddot{S}_y + \ddot{S}_z + \ddot{S}, \qquad (5)$$

$$\dot{S}_xH \to \dot{S}_yH + \dot{S}_zH + \dot{S}H. \tag{6}$$

The formation of hydrogen sulfide evidently occurs as a result of the interaction of sulfhydryl radicals with one another:

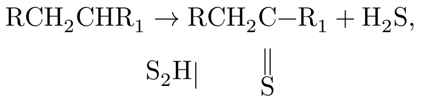
$$2\dot{S}_xH \to \ddot{S}_y + H_2S. \tag{7}$$

The accelerated evolution of hydrogen sulfide, observed in the final stage of the process, is a consequence of the reaction of sulfhydryl groups contained in the molecular chains of PE:

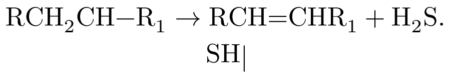


$$2\,\mathrm{RCH_2}\underset{\substack{|\\ \mathrm{S}_x\mathrm{H}}}{\mathrm{CH}}\mathrm{R_1} \to \mathrm{RCH_2}\underset{\substack{|\\ \mathrm{R_1}}}{\mathrm{CH}} - \mathrm{S}_y - \underset{\substack{|\\ \mathrm{R_1}}}{\mathrm{CH}}\mathrm{-CH_2R} + \mathrm{H_2S} \tag{8}$$

Along with the intermolecular reaction (8), intramolecular reactions may occur:



$$\mathrm{RCH_2}\underset{\mathrm{S_2H}|}{\mathrm{CH}}\mathrm{R_1} \to \mathrm{RCH_2}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{-R_1} + \mathrm{H_2S}, \tag{9}$$



$$\mathrm{RCH_2}\underset{\mathrm{SH}|}{\mathrm{CH}}\mathrm{-R_1} \to \mathrm{RCH{=}CHR_1} + \mathrm{H_2S}. \tag{10}$$

These reactions proceed without the participation of free sulfur and are characteristic of the final stage of the process.

The linear dependence of the number of cross-links on the sulfur content shows that structuring reactions are carried out chiefly with the aid of sulfur:

$$RSH + R_1SH \to RSR_1 + H_2S; \tag{11}$$

$$R\dot{S}_x + R_1\dot{S}_y \to RS_zR_1; \tag{12}$$

$$R\dot{S}_x + \dot{R}_1 \to RS_xR_1. \tag{13}$$

If the primary polymer radical is formed at a branching point of the PE molecule, then the subsequent action on it of $\ddot{S}_x$ or $\dot{H}S$ (to a lesser extent) may cause destruction of the chain:

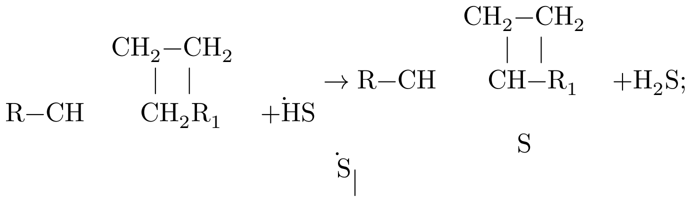
$$\mathrm{R_1{-}C({-}R_2)({-}\dot{S}){-}CH_2CH_2R_3} + \ddot{\mathrm{S}}_\mathrm{x} \xrightarrow[-\dot{\mathrm{H}}\mathrm{S_x}]{} \mathrm{R_1{-}C({-}R_2)({-}\dot{S}){-}CH_2{-}\dot{C}HR_3}$$

$$\to \genfrac{}{}{0pt}{}{\mathrm{R_1}}{\mathrm{R_2}} > \mathrm{C{=}S} + \mathrm{CH_2{=}CH{-}R_3}. \qquad (14)$$

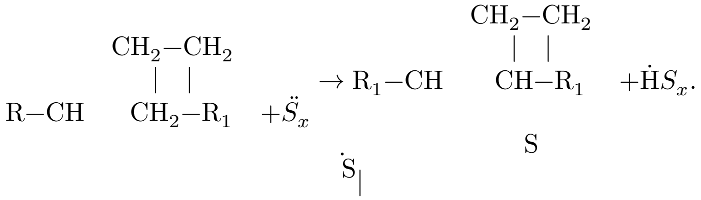
The formation of double bonds occurs mainly as a result of destruction (scheme 14), and also of direct dehydrogenation by sulfur:

$$\ddot{\mathrm{S}}_\mathrm{x} + \mathrm{RCH_2CH_2R_1} \to \underset{\dot{\mathrm{S}}_\mathrm{x}|}{\mathrm{RCHCH_2R_1}} + \dot{\mathrm{H}}\mathrm{S} \to \mathrm{RCH{=}CHR_1} + \mathrm{H_2S} + \ddot{\mathrm{S}}_\mathrm{x-1}. \qquad (15)$$

In accordance with the accepted schemes for the formation of hydrogen sulfide (equations 7, 8, 9, 10, 11, 15), the amount of H_2S should be equivalent to the sum of the cross-links, double bonds, and thione groups formed. A rough calculation shows that this sum is substantially smaller than the equivalent of the hydrogen sulfide formed. In this connection it is necessary to assume that, along with the processes indicated above, formation of cyclic intramolecular structures takes place:



$$\mathrm{R{-}CH} \quad \begin{matrix} \mathrm{CH_2{-}CH_2} \\ | \quad | \\ \mathrm{CH_2R_1} \end{matrix} \quad + \dot{\mathrm{H}}\mathrm{S} \quad \underset{\dot{\mathrm{S}}|}{} \to \mathrm{R{-}CH} \quad \begin{matrix} \mathrm{CH_2{-}CH_2} \\ | \quad | \\ \mathrm{CH{-}R_1} \\ \mathrm{S} \end{matrix} \quad + \mathrm{H_2S}; \qquad (16)$$



$$\mathrm{R{-}CH} \quad \begin{matrix} \mathrm{CH_2{-}CH_2} \\ | \quad | \\ \mathrm{CH_2{-}R_1} \end{matrix} \quad + \ddot{S}_x \quad \underset{\dot{\mathrm{S}}|}{} \to \mathrm{R_1{-}CH} \quad \begin{matrix} \mathrm{CH_2{-}CH_2} \\ | \quad | \\ \mathrm{CH{-}R_1} \\ \mathrm{S} \end{matrix} \quad + \dot{\mathrm{H}}S_x. \qquad (17)$$

As was shown by Gee (3), at temperatures above 159° radical polymerization of sulfur occurs; therefore it must be assumed that sulfided PE contains some quantity of polymeric sulfur.

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

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Note: Figure translations are in progress. See original paper for figures.