Kinetics of Crosslinking of Poly(vinyl Chloride) in the Presence of Tetramethylthiuram Disulfide and Zinc Oxide

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Synopsis

Continuous measurements in a Vuremo curemeter at temperatures from 160°C to 195°C were used to estimate the extent of crosslinking of poly(vinyl chloride) which was plotted against cure time. The linearized forms of the cure curves clearly show that at obvious tetramethylthiuram disulfide–zinc oxide concentrations, the course of crosslinking differs significantly from the first-order rate law. These digressions caused by the degradation crosslinking of poly(vinyl chloride) were diminished by increasing tetramethylthiuram disulfide concentration, which simultaneously increases the ultimate extent of controlled crosslinking. On the basis of the above results, a method of the kinetic analysis of the cure curves is discussed.

INTRODUCTION

A series of chemical compounds which functions as crosslinking agents for poly(vinyl chloride) (PVC) has been described. These are organic peroxides,[1–3] metal oxides[4,5] and hydrosulfides,[6] alkylhydropolysulfides,[7] aminocompounds without[8–11] or with elemental sulfur,[12] copper bis(ephedrine chelate),[13–15] and others.[16–19] In all the cases, PVC is cured at increased temperature, and for this reason the crosslinking reaction controlled by a chemical agent is accompanied by degradation crosslinking.

The thermal degradation of PVC is effected by an autocatalytic dehydrochlorination reaction due to the presence of labile sites in the polymer chains such as allyl chlorines and tertiary hydrogen and chlorine atoms, or by terminal end groups such as double bonds or peroxide residues.[20–22]

Although various mechanism have been suggested for the dehydrogenation process leading to degradation crosslinking, the radical mechanism seems to be supported by most investigators.[23–26] If the degradation in PVC actually proceeds by a radical mechanism, the use of radical scavengers for short-stopping the radical chain degradative process (i.e., antidegradents) would therefore provide an effective method of inhibiting the degradation of the polymer. The work of Yassin and Sabaa[27] with *p*-benzoquinone–tin derivatives supports this view.

Zinc dimethyldithiocarbamate probably has a similar antidegrading effect which is formed in the course of curing of a polymer by a zinc oxide–tetramethylthiuram disulfide (TMTD) system.[28] The use of this crosslinking system for PVC has not been published previously, so far as we know. This is why the goal of the present work is a kinetic study of crosslinking of PVC by the TMTD—ZnO system.

EXPERIMENTAL

Materials

Poly(vinyl chloride): Slovinyl SpS (suspension type of PVC with K-value of 67) is sold by CHZWP n.p. Nováky, Czechoslovakia.

Tetramethylthiuram disulfide: Hermat TMT is sold by CHZJD n.p. Bratislava, Czechoslovakia.

Zinc oxide: Silver Seal zinc oxide is sold by Farby a laky n.p. Košeca, Czechoslovakia.

Stearic acid: Stearin is sold by STZ n.p. Ústí nad Labem, Czechoslovakia.

Compounding

The mix formulation was PVC, 100 parts, stearic acid, 1 part, zinc oxide, 5 parts, TMTD, variable.

PVC was mixed with stearic acid and plasticated for 3 min on a laboratory mill with 200 mm × 100 mm rolls at 150°C. Then TMTD and zinc oxide were added to the batch and mixed on the mill for 5 min at 125°C.

Curemeter Measurements

The PVC compounds were cured at temperatures from 160°C to 195°C on a VUREMO curemeter, an instrument used to measure VUlcanization, RElaxation, and MOdulus. The apparatus and curemeter measurements have been completely described in our recent publication.[29]

In order to preserve the continuity of our quantitative studies,[29] the extent of crosslinking at any time t (modulus in torsion), M, was expressed in VUREMO units (1 VUREMO unit corresponds to 10 kPa) and plotted against time of cure, τ. Thus, the cure curves were obtained. The ultimate extent of crosslinking reaction was calculated as a $(M_{max} - M_{min})$ value. The cure curves have been analyzed by treating them as first-order reactions, following an induction period t_i:

$$M = (M_{max} - M_{min})(1 - e^{-kt}) + M_{min}$$

where k is the first-order rate constant and $t = (\tau - t_i)$.

The rate constants k were calculated from the slopes of linearized cure curves, i.e., time dependences of the logarithm of the extent of crosslinking, $100\ [(M - M_{min})/(M_{max} - M_{min})]$ (%), shown in Figures 2 and 6.

RESULTS AND DISCUSSION

Figure 1 shows a typical shape of the time dependence of crosslinking of PVC. The modulus values show no maximum as well as no limit level. After a certain time, they increase very vehemently. This is caused by increasing of the rate of degradation crosslinking of PVC. Thus, the latter complicates determination of a maximum value of crosslinking of PVC controlled by a ZnO—TMTD system.

Using a modulus value from the time range corresponding to the vehement bend of a cure curve as M_{max}, the time dependence of the logarithm of the extent
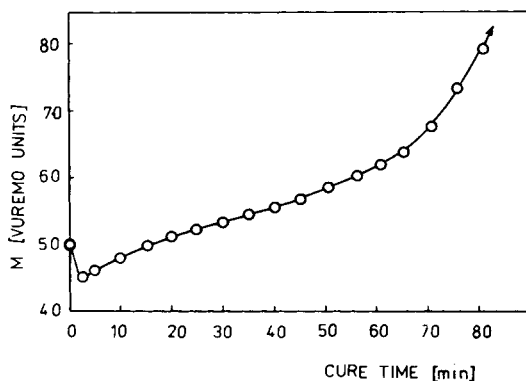
Fig. 1. A typical cure curve for PVC. Mix formulation: PVC, 100; stearic acid, 1; zinc oxide, 5; TMTD, 3. Cure temperature = 170°C.

of crosslinking is not linear as is shown in Figure 2. That is why this M_{max} is lower than the theoretical maximum value of the extent of controlled crosslinking. Thus we can see that the determination of a theoretically correct M_{max} value is of the prime importance for a kinetic analysis.

Although PVC alone does not undergo practically any degradation corsslinking when subjected to cure temperatures in a curemeter (curve 1 in Fig. 3), in the presence of zinc oxide it is crosslinked very extensively (curve 2 in Fig. 3). This is in accord with a generally known fact that degradation of PVC is catalyzed by metal chlorides,[30] in this case namely by $ZnCl_2$.
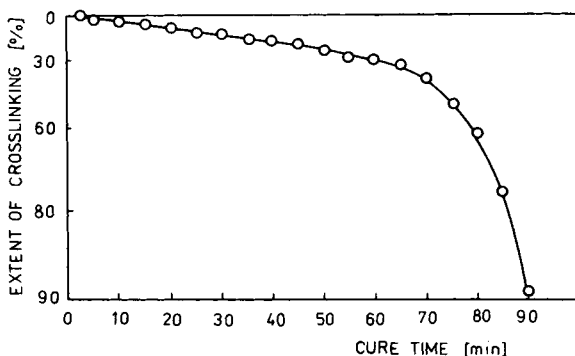

Fig. 2. Increase of extent of crosslinking at 170°C in cure of PVC by ZnO—TMTD system. Mix formulation as in Figure 1.
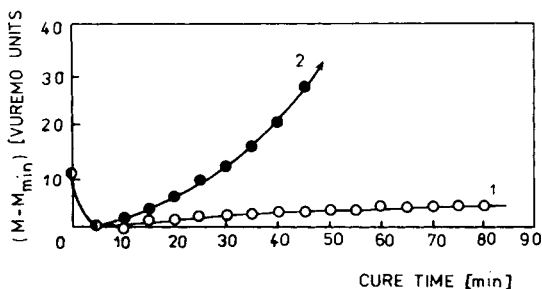

Fig. 3. Effect of ZnO on cure of PVC at 170°C. Mix formulation: PVC, 100; stearic acid, 1; zinc oxide, 0 (curve 1) and 5 (curve 2).
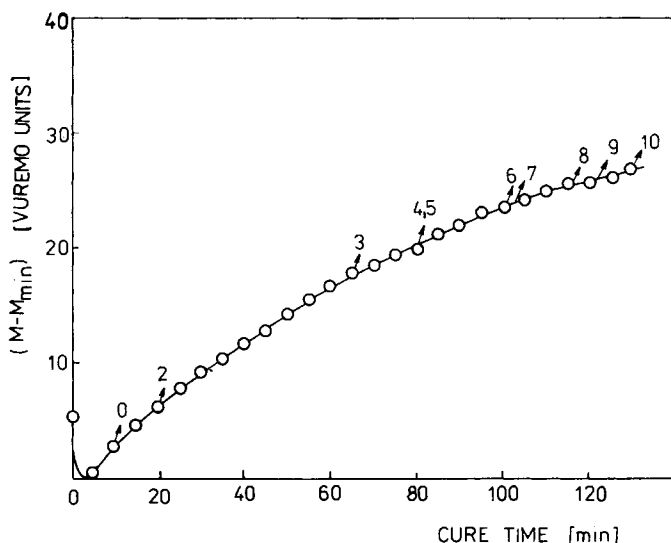
Fig. 4. Cumulative curve of the individual cure curves. Mix formulation: PVC, 100; stearic acid, 1; zinc oxide, 5; TMTD, variable. Numbers on the curve are concentrations of TMTD in parts per 100 parts by weight of PVC. Darts show the moment of a spontaneous degradation of PVC. Cure temperature = 170°C.

The start of a degradation of PVC during its crosslinking by ZnO—TMTD system depends on TMTD concentration. As long as the degradation reaction does not apply significantly, the course of controlled crosslinking is practically independent on the concentration of TMTD. This can be clearly seen from Figure 4, in which the cure curves are drawn up to a moment of the spontaneous degradation. The latter is indicated on a cumulative curve by a dart and a number corresponding to the concentration of TMTD in the polymer mixture.

Increasing TMTD concentration the stage of controlled crosslinking also increases, probably due to an antidegrading effect of zinc dimethyldithiocarbamate formed from zinc oxide and TMTD during the crosslinking reaction.[28] That is why we have extrapolated the curve drawn in Figure 4 to the infinite time of cure by a method shown in Figure 5. We have used the M_{max} value obtained like this for a kinetic analysis. The result is shown in Figure 6. The rate constant of crosslinking has been calculated from the slope of the linearized curve in the same way we have used for the analysis of all the cure curves obtained in the temperature range from 160°C to 195°C.

Logarithmic plot of the first-order rate constants of crosslinking of PVC gives a straight line (Fig.7), allowing calculation, from the slope, of the activation energy of 106 kJ/mol. This value is in very good accordance with the activation energy of sulfur-free thiuram vulcanization of natural rubber (110 kJ/mol).[31] This finding allows to propose that the crosslinking action of ZnO—TMTD system on PVC is based on a similar mechanism as its vulcanizing action on natural rubber.[29]

The initial step of crosslinking is based on the nucleophilic attack of a basic oxyanion (from $\cdots Zn^{2+}\cdots O^{2-}\cdots$) on the electrophilic thiocarbon atom of TMTD:

$$Zn^{2+} \cdots O^{2-} \cdots X\text{—}SSX \rightarrow Zn^{2+} \cdots {}^{-}OX + {}^{-}SSX$$
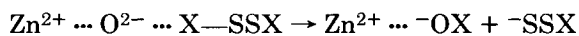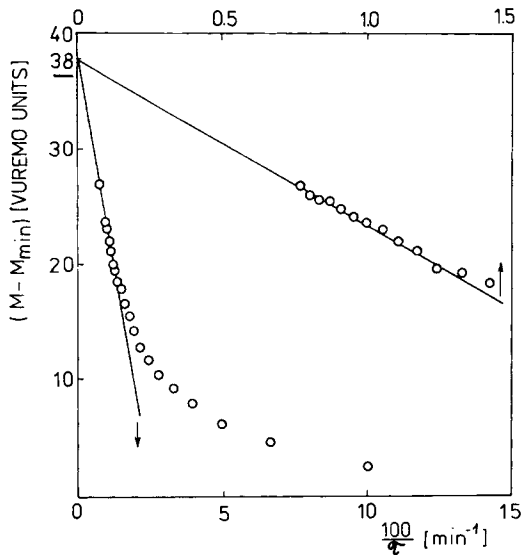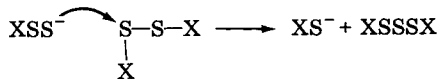
Fig. 5. Extrapolation of the cumulative curve from Figure 4 to the infinite time of cure.

where X represents $(CH_3)_2N$—$C(:S)$—.

The perthioanion XSS^- then attacks a disulfidic sulfur atom in TMTD to give thioanion XS^- and tetramethylthiuram trisulfide:

$$XSS^- \quad S-S-X \longrightarrow XS^- + XSSSX$$
$$\underset{X}{\mid}$$

Further attack by the oxyanion from ZnO yields higher polysulfides. Interchange between these polysulfides and zinc dimethyldithiocarbamate would then yield the sulfur-donating reagents which react with PVC macromolecules to give PVC-bound intermediate compound:
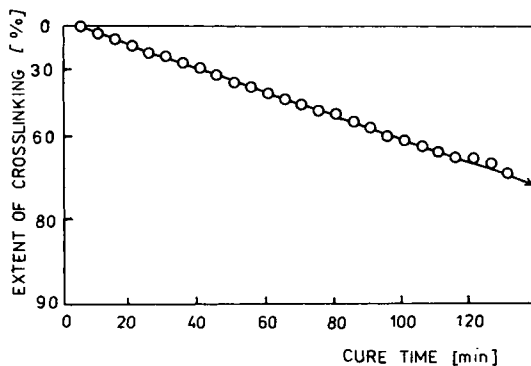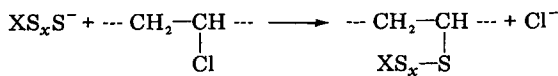
$$XS_xS^- + \text{---} CH_2\text{---}\underset{Cl}{\underset{\mid}{CH}} \text{---} \longrightarrow \text{---} CH_2\text{---}\underset{XS_x\text{---}S}{\underset{\mid}{CH}} \text{---} + Cl^-$$

Fig. 6. Increase of extent of controlled crosslinking at 170°C as first-order reaction in cure of PVC by ZnO—TMTD system. Mix formulation as in Figure 4.
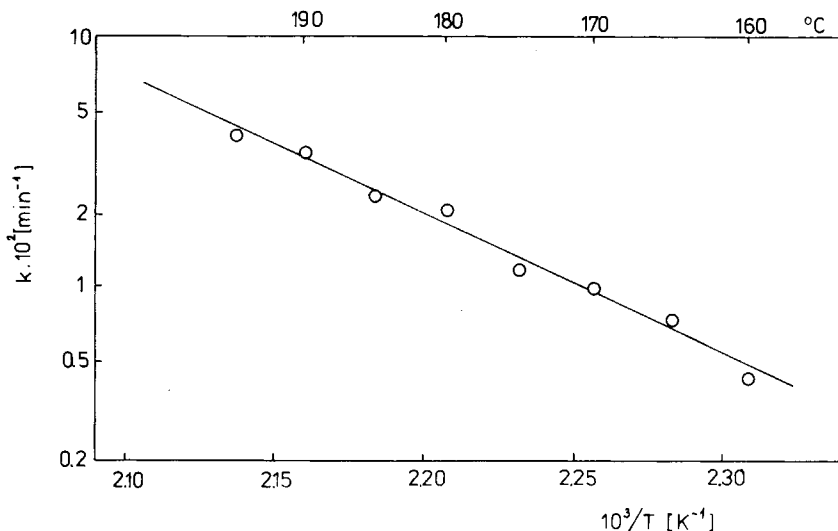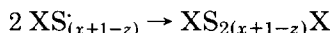
Fig. 7. Temperature dependence of first-order rate constant of controlled crosslinking in cure of PVC by ZnO—TMTD system.   Mix formulation as in Figure 4.

A probable route for the conversion of the intermediate compound RS_xSX into crosslinks is by the radical reactions:

$$2 RS_xSX \rightarrow 2 RS_z + 2 X^{\cdot}_{(x+1-z)}$$

$$2 RS^{\cdot}_z \rightarrow RS_{2z}R$$

$$2 XS^{\cdot}_{(x+1-z)} \rightarrow XS_{2(x+1-z)}X$$

This mechanism explains the inhibiting effect of TMTD on the degradation (dehydrochlorination) of PVC and is in accordance with the experimental results shown in Figure 4.   The radical mechanism of reactions taking place in the latter stage of crosslinking is in a good agreement with the relatively high value of the activation energy of crosslinking.   The assumption that sulfur is bounded in a polymer network is supported by finding that crosslinked PVC after its extraction by cyclohexanone contains about 35% of sulfur presented originally in the polymer mix.

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