Crosslinking of Poly(vinyl Chloride) with Metal Oxides, Sulfur, and Organo Sulfur Compounds

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Synopsis

The crosslinking of poly(vinyl chloride) in the presence of zinc oxide, magnesium oxide, ethylenethiourea (ETU), tetramethylthiuramdisulfide (TMTD), and sulfur at 160 and 180°C has been studied. The effects of ETU and sulfur on the crosslinking of PVC in the presence of TMTD have been individually studied. It has been found that zinc dimethyldithiocarbamate (ZnDMDC) is the actual crosslinking agent and heat stabilizer of PVC, formed in the cured polymer mix.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important and widely used plastics due to its many valuable properties like low price, good processability using conventional technologies, chemical resistance, etc. Its drawbacks, however, are low thermal stability at processing temperatures, unsatisfactory dimensional stability at elevated temperatures, low impact strength, migration of plasticizers, etc. One of the ways to improve the properties of PVC is by crosslinking, which is what our present work deals with.

THEORY

There are several procedures used to obtain crosslinked PVC; the most important among them are[1]: (1) degradation crosslinking; (2) photochemical or radiation crosslinking, particularly in presence of sensibilizers, promoting the efficiency of the crosslinking reaction; (3) chemical crosslinking using a crosslinking agent which can react with (a) the comonomer incorporated in the polymer chain to facilitate the crosslinking of PVC, (b) the grafted side chain which can be crosslinked by means of conventional agents, (c) the main chain of PVC directly.

This last method is the most interesting because of its low cost, possibility to use existing equipment, raw materials, etc. It is, however, the most difficult to realize due to low chemical reactivity of polymer combined with its low thermal stability.

Chemical Structure and Thermal Stability of Poly(vinyl Chloride)

The field of investigation of the chemical structure and thermal stability of PVC is at present so wide that we can give here only a short survey of the

most remarkable information which we believe to be tightly connected with the PVC crosslinking problematics. It has been shown in practice that the poor processing stability of commercial PVC grades is due to the presence of defective sites in the macromolecule, their concentration being increased with both polymerization time and temperature.[2]

During the last several years considerable attention has been given to the investigation of the chemical nature of the above defects and to the determination of their concentration. In the PVC macromolecule internal double bonds, chlorine atoms on the tertiary carbon atom, short chloromethyl side groups in branching sites of main chains, and unsaturated chain ends with allyl or vicinal chlorine atoms have been determined.[2] The effect of end groups on the thermal stability of PVC has been studied by other authors,[3] who have reported the presence of 1,2-dichloroethyl, *trans-* and *cis*-4-chlor-2-butenyl, 2-chloroethyl, and 2-chloroethylidene. Lisitskii et al.[4] found that the concentration of double bonds in the emulsion PVC is not in excess of 2.5×10^{-3} mol/mol of vinyl chloride and the concentration of ketoallylic groups 1.5×10^{-4} mol/mol of poly(vinyl chloride).

Irregularities in the chemical structure of the polymer (esteemed concentration several tenths of percent) are initiation centers of the dehydrochlorination reaction; it is very probable that the mechanism of this reaction is one of zipper type.[5] Danforth[6] has determined the activation energy of the PVC dehydrochlorination reaction as 120 kJ/mol, and Mori and Nakamura[7] have found that the activation energy of its thermal destruction is between 122 and 126 kJ/mol, while the activation energy of chemical crosslinking by substituted triazines is as low as 68 kJ/mol. It can thus be assumed that by reducing the crosslinking temperature it is possible to prefer chemical crosslinking and to limit the polymer degradation, leading to color changes and other undesirable effects.

According to the majority of authors, PVC has, after thermal degradation, a polyenic structure with alternating shorter and longer segments of conjugated double bonds.

Thermal stressing of PVC induces degradation reactions (dehydrochlorination oxidation and scission of primary macromolecules) on one hand and reactions leading to network formation on the other. The mechanism of these reactions is not quite clear yet. The most likely crosslinking reaction seems to be the reversible (Diels–Alder) diene synthesis of conjugated double bonds.[8,9]
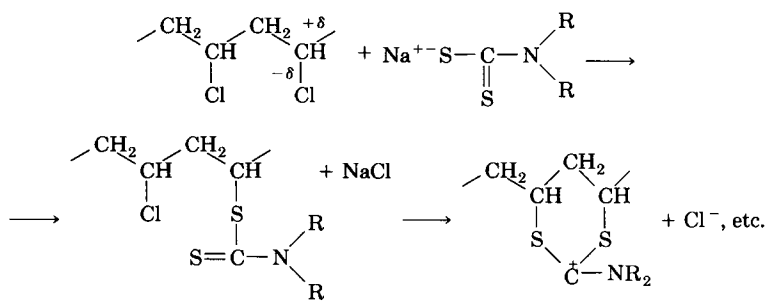
Irregularities in the chemical structure of PVC are the cause of poor thermal stability of the polymer.[10-16] They play, however, an important role in the chemical (nondegradative) crosslinking of PVC, although some authors[17] claim that the PVC macromolecule contains only negligible amounts of these defects which are unlikely to affect the degree of the crosslinking reaction. It is assumed[16] that structural defects accumulate in the low molecular weight fractions of PVC.

Chemical Reactions of Poly(vinyl Chloride) in the Presence of Sulfur and Tetramethylthiuramdisulfide
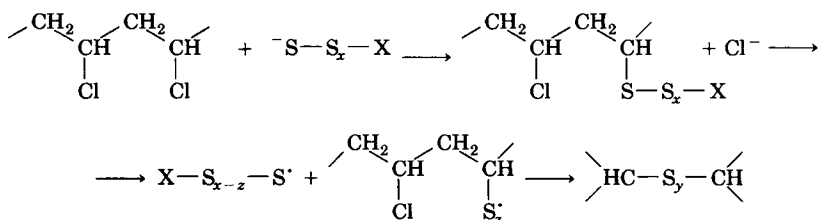
The presence of sulfur impairs the thermal stability of PVC. It has been established that sulfur atoms bonded to the polymeric chain induce activation

of the adjacent chlorine atoms.[7,18,19] These labile chlorine atoms can initiate the PVC dehydrochlorination; they provide, however, reactive sites for the crosslinking reaction in the presence of suitable agents. Mori and Nakamura[20] suggest that the crosslink distribution in the crosslinked sample is unlikely to be a random one. The formation of a crosslink containing a sulfur atom will namely activate the adjacent vinylic chlorine atom and further crosslinks will be grouped around the original initiation site.

Similar conclusions are reported by Okawara and Ochiai,[21] who have investigated the chemical modification of PVC by alkali metal salts of the dithiocarbamic acid. They found, e.g., that the sodium salt of the N,N-dialkyldithiocarbamic acid prefers the nucleophilic substitution to the otherwise much easier elimination, and the sulfur atoms in the residue of the agent bonded in a PVC chain activate the adjacent vinylic chlorine atoms:
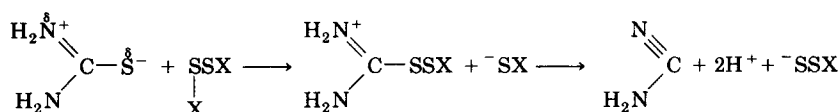
$$
\begin{array}{c}
\underset{\substack{|\\ Cl}}{\overset{\diagup CH_2}{CH}} \quad \underset{\substack{-\delta|\\ Cl}}{\overset{\diagdown CH_2 \; +\delta}{CH}} \; + \; Na^{+-}S-\underset{\substack{\|\\ S}}{C}-N\overset{R}{\diagdown}_{R} \longrightarrow
\end{array}
$$

$$
\begin{array}{c}
\underset{\substack{|\\ Cl}}{\overset{\diagup CH_2}{CH}} \quad \underset{\substack{|\\ S}}{\overset{\diagdown CH_2}{CH}} \; + \; NaCl \qquad \underset{\substack{|\\ S}}{\overset{\diagup CH_2}{CH}} \quad \underset{\substack{|\\ S}}{\overset{\diagdown CH_2}{CH}} \; + \; Cl^{-}, \; etc. \\
\hspace{2cm} S=\underset{\diagdown R}{\overset{\diagup R}{C-N}} \hspace{3cm} \diagdown_{C-NR_2}\diagup
\end{array}
$$

Ducháček and Kuta[22] have crosslinked PVC by tetramethylthiuramdisulfide (TMTD) in presence of zinc oxide. They found that the activation energy of the crosslinking reaction (106 kJ/mol) is very close to the activation energy of the sulfur-free thiuram vulcanization of natural rubber and proposed a similar mechanism of this reaction. In the first step the reaction of ZnO with TMTD yields perthioanion [here X = $(CH_3)_2N$—C(S)—]. The sulfurating agent formed attacks the PVC chain by nucleophilic substitution, and the intermediary product formed is further decomposed, presumably by a radical mechanism, generally under formation of a polysulfidic crosslink.

$$
\underset{\substack{|\\ Cl}}{\overset{\diagup CH_2}{CH}} \quad \underset{\substack{|\\ Cl}}{\overset{\diagdown CH_2}{CH}} \; + \; {}^{-}S-S_x-X \longrightarrow \underset{\substack{|\\ Cl}}{\overset{\diagup CH_2}{CH}} \quad \underset{\substack{|\\ S-S_x-X}}{\overset{\diagdown CH_2}{CH}} \; + \; Cl^{-} \longrightarrow
$$

$$
\longrightarrow X-S_{x-z}-S^{\cdot} \; + \; \underset{\substack{|\\ Cl}}{\overset{\diagup CH_2}{CH}} \quad \underset{\substack{|\\ S_z^{\cdot}}}{\overset{\diagdown CH_2}{CH}} \longrightarrow \; \diagdown HC-S_y-C\overset{\diagup}{\underset{\diagdown}{H}}
$$

The supposed radical mechanism of this reaction is in good agreement with the high activation energy value of crosslinking and the observed effect of thiourea on the course of the sulfur-free thiuram vlucanization. In the initial stage, thiourea, as a strong nucleophilic agent, accelerates the formation of a

perthioanion, according to the scheme, suggested previously by Moore:[23]

$$H_2\overset{\scriptscriptstyle\delta}{N}{}^+ \diagdown C-\overset{\scriptscriptstyle\delta}{S}{}^- \quad + \quad SSX \quad \longrightarrow \quad H_2N{}^+ \diagdown C-SSX \;+\;{}^-SX \quad \longrightarrow \quad N \diagdown C \;+\; 2H^+ + {}^-SSX$$

Ducháček[24] observed that the extend of the sulfur-free thiuram vulcanization is, in the presence of thiourea, significantly reduced. Considering that thiourea behaves like a radical acceptor, he assumes, in agreement with other authors,[25,26] that the conversion of the intermediary product of the sulfurating agent reaction with the polymer macromolecule, yielding polysulfidic crosslinks, takes place via radical mechanism.[27]

EXPERIMENTAL

Materials

PVC Polymer. Trademark Neralit 682, producer Chemopetrol k.p. Spolana, Neratovice, Czechoslovakia.

Stearic Acid. Technical grade (Stearin), producer STZ, Ústí n/L, Czechoslovakia.

Magnesium Oxide. Fumed, supplied by Lachema, Brno, Czechoslovakia.

Zinc Oxide. Silver Seal, producer Farby a laky, Košeca, Czechoslovakia.

Tetramethylthiuram Disulfide (TMTD). Trademark Hermat TMT, producer CHZJD, Bratislava, Czechoslovakia.

Sulfur (Powder). Oil-treated (lubricated), elementary sulfur content 93.7%, producer Lachema, Nový Bohumín, Czechoslovakia.

Mercaptoimideazoline (Ethylene Thiourea) (ETU). Trademark Rodanin S 62, producer CHZJD, Bratislava, Czechoslovakia.

Mix Formulations

(a) To study the effect of TMTD concentration on PVC crosslinking

PVC	100	100	100	100	100
MgO	4	4	4	4	4
ZnO	5	5	5	5	5
Stearic acid	1	1	1	1	1
TMTD	—	1	2	4	8

(b) To study the effect of sulfur on the PVC crosslinking reaction rate in the presence of TMTD

PVC	100	100	100
Stearic acid	1	1	1
MgO	4	4	4
ZnO	5	5	5
TMTD	4	4	4
Sulfur	—	1	2

(c) To study the effect of ETU on the PVC crosslinking reaction rate in the presence of TMTD

PVC	100	100	100
Stearic acid	1	1	1
MgO	4	4	4
ZnO	5	5	5
TMTD	4	4	4
ETU	—	1	2

Mix Preparation

Polymer mixes were prepared on an electrically heated two-roll mill, cylinder dimensions 100×200 mm. Individual constituents were added to plasticized PVC at 150°C in the following order: MgO, TMTD, sulfur, ETU, ZnO. The total mixing time was not in excess of 6 min, including fivefold crossing of compounds at a narrow gap between rolls.

Curemeter Measurements

The course of the crosslinking reaction was measured on a Monsanto cone-rheometer with a shear rate of 100 min^{-1} and oscillating angle of 1° at temperatures 160 and 180°C. Before starting the reaction, compounds were preheated for 2 min in the chamber of the apparatus.

A characteristic shape of PVC cure curves has been discussed in our previous publication.[22]

For the description of the crosslinking reaction we have used now the exponential function

$$M - M_{\min} = (M_{\max} - M_{\min}) \cdot (1 - e^{-k(t - t_i)})$$

where $M_{\max}$ and $M_{\min}$ are maximum and minimum torques respectively of the compound being crosslinked, k is the rate constant, and t_i the induction period of the crosslinking reaction. The above function was found to be satisfactory for the description of the crosslinking reaction in the controlled (nondegradation) crosslinking region.

Although we are aware of this definition, we have introduced, for the needs of this work and taking into account the characteristic shape of crosslinking curves, the following concepts: region of controlled (chemical, nondegradation) crosslinking and region of uncontrolled (degradation) crosslinking. Controlled crosslinking is dominant in the initial stage of the reaction and is determined by the type and concentration of the crosslinking agent. The uncontrolled crosslinking can be observed at the end of the reaction as a spontaneous increase of the modulus. The second inflection point on the curve is considered as a boundary between the two regions.

Gel Content Determination

Gel content was determined on the basis of equilibrium swelling of cured samples in cyclohexanone. The samples (weight of about 0.2 g, thickness of

1 mm) were swollen at room temperature in separate tubes. Each sample was weighted dry, then swollen in 50 mL cyclohexanone for 24 h, and 20 times transferred to fresh cyclohexanone for a further 24 h. The samples were dried 7 days at a room temperature and 24 h at 100°C. Then deswollen weights were measured. The dry (m_1) and deswollen (m_2) weights were used to calculate the gel content (G) of a cured mix:

$$G = \frac{m_g}{m_p} \times 100 = \frac{m_1 - m_2 \cdot x}{m_p} \times 100 \, (\%)$$

where m_g is a weight of the gel, m_p is a weight of PVC in the dry sample, and x is a weight fraction of nonextractible additives in a polymer mix.

RESULTS AND DISCUSSION

PVC Crosslinking with Tetramethylthiuram Disulfide in Presence of Metal Oxides

Figures 1 and 2 show the cure curves, illustrating the influence of TMTD concentration on the course of the crosslinking reaction at temperatures 160 and 180°C, respectively.

It has been found that the course of the PVC crosslinking reaction is relatively little dependent on the concentration of the crosslinking agent, especially at lower temperatures. This observation supports the assumption that in the PVC chain there is a limited number of sites in which chlorine atom bonds are more labile[17] and thus susceptible to substitution by nucleophilic agents.[21]

The carbamoyl groups bonded seem to promote the reactivity of adjacent chlorine atoms, including higher polymer dehydrochlorination rates and leading finally to spontaneous degradation crosslinking (see Fig. 2, curve 1).

With increasing TMTD concentration this effect is suppressed and the spontaneous degradation shifted towards longer times, in case of sample exposure to the given conditions. This effect has been observed previously.[22]

Unreacted TMTD or zinc dimethyldithiocarbamate (ZnDMDC) formed[22] tends to attack labile chlorine atoms and to block the zipper mechanism of PVC dehydrochlorination.

From the proposed mechanism of TMTD action on the PVC chain in the presence of metal oxides the following can be deduced:

(1) In the absence of heat stabilizers, TMTD or ZnDMDC present act like antidegradants, which, however, tend to intensify and accelerate the PVC dehydrochlorination, and thus the "chemical" PVC crosslinking is to a great extent accompanied by the degradation crosslinking.

(2) The distribution of chemical crosslinks is not a random one, as in case of rubber vulcanization, but there are some kinds of crosslink clusters.[20]

The first assumption has been further verified experimentally. In the case of PVC crosslinked by TMTD in the presence of metal oxides, we have measured, in addition to the curemeter record, the changes of gel content, as well as color changes during crosslinking, as determined according to the SYN-MERO scale (Fig. 3).
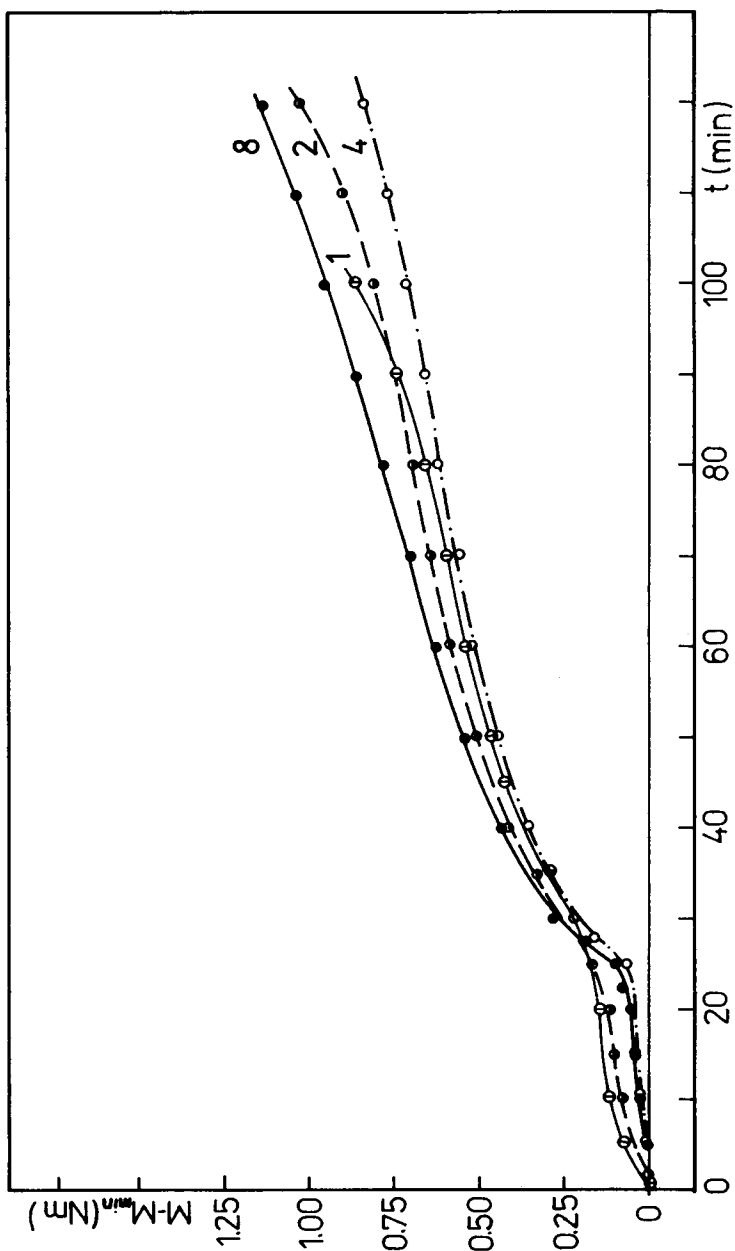
Fig. 1.   Effect of TMTD on cure of PVC at 160°C. Mix formulation: PVC, 100; stearic acid, 1; zinc oxide, 5; magnesium oxide, 4; TMTD, as shown in the figure.
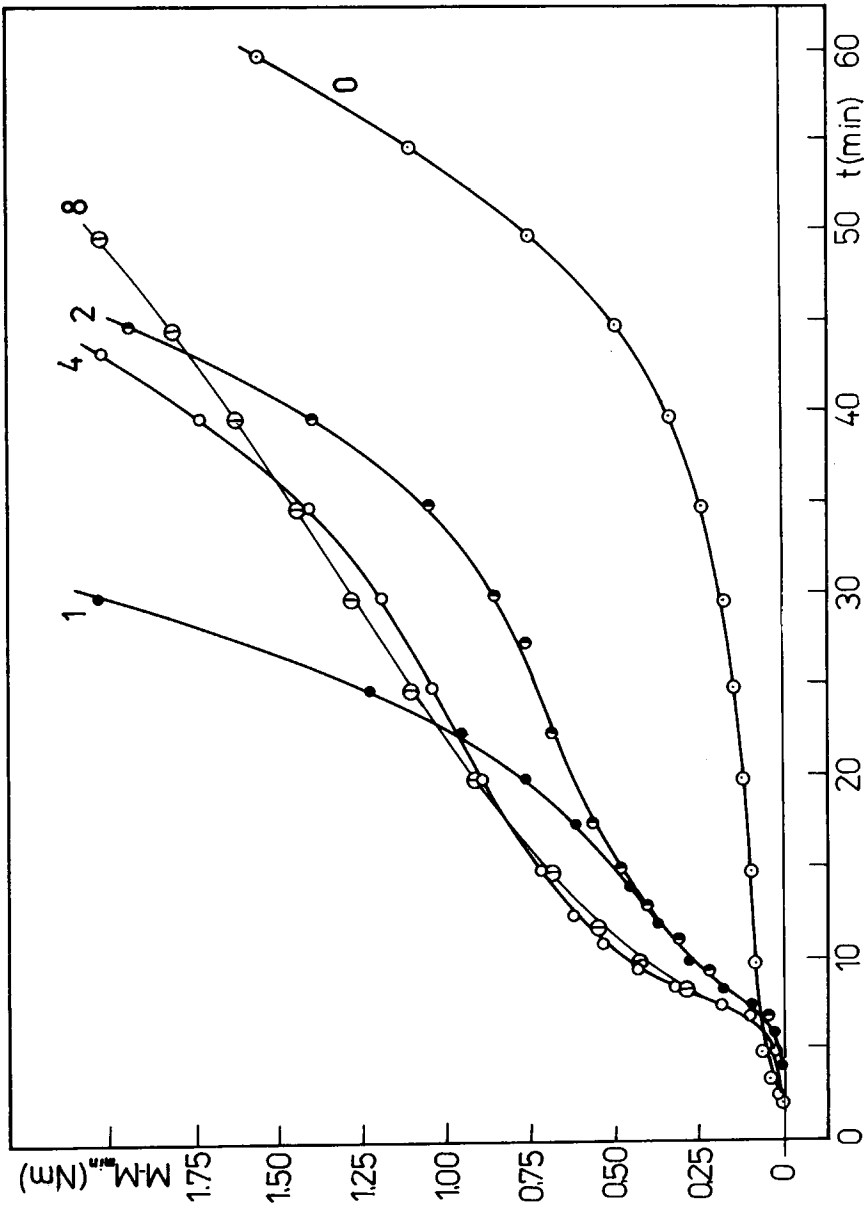
Fig. 2. Effect of TMTD on PVC crosslinking at 180°C. Mix formulation: PVC, 100; stearic acid, 1; zinc oxide, 5; magnesium oxide, 4; TMTD, as shown in the figure.
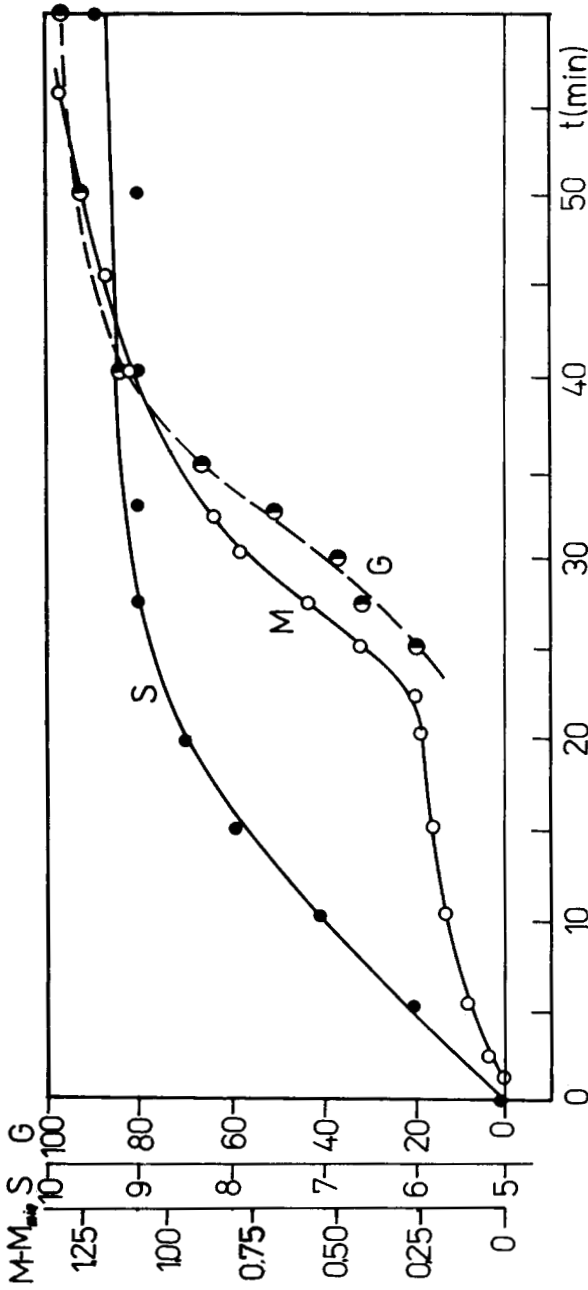
Fig. 3.   Time dependences of M [torque (N/m)], G [gel content (wt%)] and S (SYNMERO scale) for PVC crosslinking at 160°C. Mix formulation: PVC, 100; stearic acid, 1; zinc oxide, 5; magnesium oxide, 4; TMTD, 4.

Whereas the gel content is in good agreement with the cure curve, it can be seen that the most important color change occurs just during the induction period of PVC crosslinking. For this reason, efficient heat stabilizers noninterfering with crosslinking should be found.

Effect of Sulfur on PVC Crosslinking in the Presence of TMTD

Sulfur has only a negligible effect on PVC crosslinking in the presence of TMTD (Table I). We have attempted to incorporate sulfur into the PVC chain by kneading the plasticized polymer with sulfur in a laboratory kneader at conditions given in Table I.

The effect of mechanical stressing of PVC in the presence of sulfur is manifested after 5 min of kneading by an increase of the crosslinking reaction rate (i.e., by a sharp change of the cure curve slope); the extent of crosslinking is, however, slightly reduced (Table I).

We have observed that with increasing sulfur concentration the degradation crosslinking is significantly suppressed and the interval of controlled crosslinking is prolonged (Fig. 4).

Scheele[25] has shown that in the presence of sulfur in a rubber mix, a much higher portion of TMTD present initially is converted to ZnDMDC (up to 90%). This interpretation of data acquired leads to the conclusion drawn previously,[22] namely, that the actual crosslinking agent and simultaneously an efficient PVC stabilizer is the ZnDMDC formed, i.e., that the presence of sulfur tends to increase the stabilizing effect of the crosslinking system. On the other hand, sulfur is with high probability attacked by dithiocarbamate anions and thus directly involved in the crosslinking reaction. A detailed investigation of the mechanism of sulfur effect on PVC crosslinking in the presence of TMTD would require additional study. The resulting effect is, however, unambiguous. Sulfur increases the stabilizing effect of the TMTD/ZnO crosslinking system, and thus the interval of controlled crosslinking is prolonged.

TABLE I
Effect of Sulfur on Kinetic Parameters of PVC Crosslinking at 180°C

	Mix formulation					
PVC	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1
MgO	4	4	4	4	4	4
ZnO	5	5	5	5	5	5
TMTD	4	4	4	4	4	4
Sulfur	—	1	1[a]	1[b]	2	4
	Kinetic parameters					
$M_{max} - M_{min}$ (N m)	0.756	0.648	0.648	0.486	0.567	0.513
k (min^{-1})	0.22	0.24	0.25	0.48	0.35	0.40
t_i (min)	5.9	4.9	4.9	4.6	5.3	5.2

[a,b]The plasticized polymer has been kneaded with sulfur before completely compounding: [a]1 min at 145°C and [b]5 min at 145°C in a laboratory kneader.
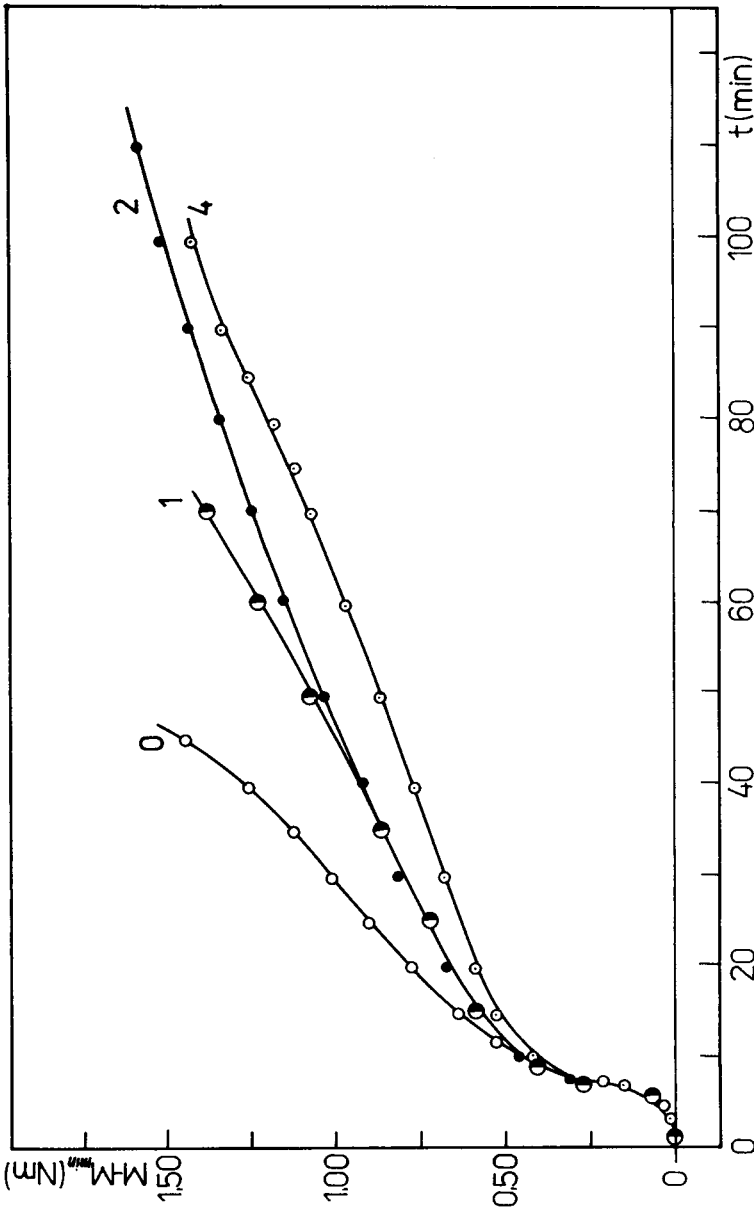
Fig. 4.   Effect of sulfur on cure of PVC at 180°C in the presence of tetramethylthiuram disulfide. Mix formulation: PVC, 100; stearic acid, 1; zinc oxide, 5; magnesium oxide, 1; TMTD, 4; sulfur as shown in the figure.
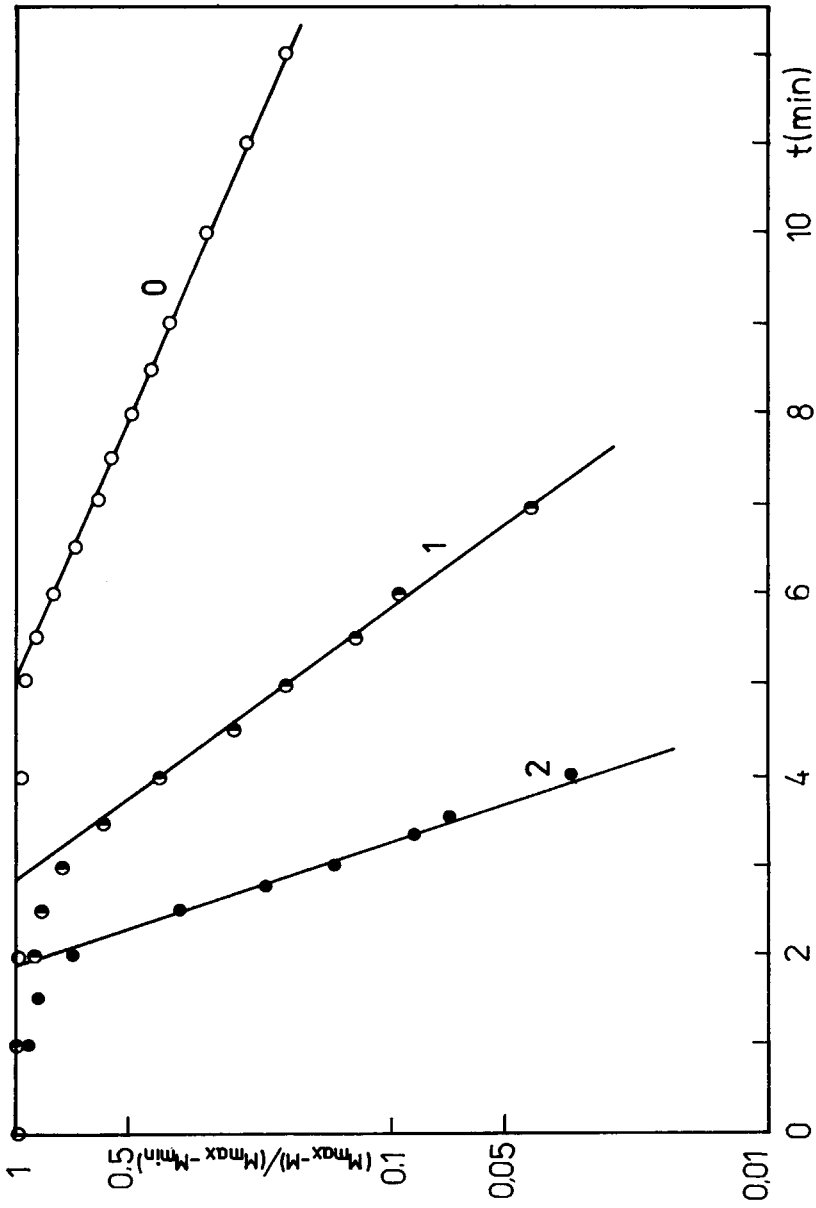
Fig. 5. Increase of extent of PVC crosslinking at 180°C according to first-order reaction. Mix formulation: PVC, 100; stearic acid, 1; zinc oxide, 5; magnesium oxide, 4; TMTD, 4; ethylenethiourea, as shown in the figure.

	Mix formulation		
PVC	100	100	100
Stearic acid	1	1	1
MgO	4	4	4
ZnO	5	5	5
TMTD	4	4	4
ETU	—	1	2
	Kinetic parameters		
$M_{max} - M_{min}$ (N m)	0.756	0.378	0.297
k (min^{-1})	0.22	0.76	1.39
t_i (min)	5.9	2.9	1.7

Effect of Ethylenethiourea on PVC Crosslinking by TMTD

The presence of ethylenethiourea (ETU) increases the rate of the PVC crosslinking reaction with TMTD and reduces the induction period (Fig. 5, Table II). The effect of ETU, as a strong nucleophilic agent, on the scission of TMTD molecule can be interpreted according to a mechanism proposed previously for rubber vulcanization.[23] The presence of ETU accelerates the conversion of TMTD to ZnDMDC, and the increased concentration of this latter agent is in agreement with the higher reaction rate of PVC crosslinking. This explanation supports the assumption[22] that the actual crosslinking agent is ZnDMDC formed in a cured polymer mix.

CONCLUSIONS

PVC can be crosslinked by TMTD in the presence of ZnO and/or MgO. Crosslinking of polymers using the above crosslinking system induces, however, pronounced color changes, suggesting the occurrence of structural changes in polymeric chains and uncontrolled degradation crosslinking of PVC.

The course of the crosslinking reaction is only slightly dependent on the TMTD concentration, and this supports the assumption that on the polymer chain there is a limited number of reactive sites available for crosslink formation.

Sulfur has only a little effect on the rate of crosslinking of PVC by TMTD; its presence induces, however, significant inhibition of degradation crosslinking. On the other hand, ethylenethiourea increases the reaction rate and reduces the induction period of the crosslinking reaction.

These conclusions, together with the knowledge available as to the chemistry of thiuram vulcanization, support the assumption that the actual crosslinking agent and simultaneously heat stabilizer of PVC is ZnDMDC, formed in a cured polymer mix.

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