Thermovulcanization of Polychloroprene Rubber and Its Blends with Poly(vinyl Chloride)

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Synopsis

Heat and mechanical stressing at higher temperatures effect changes in polychloroprene rubber leading to network formation. During thermovulcanization of polychloroprene rubber in the temperature range of 150–200°C, two reactions have been observed and their kinetic parameters determined. When the rubber is stressed by shearing forces, the rate of degradation crosslinking is fairly high even at relatively low temperatures (90–150°C). Thermovulcanization of polychloroprene rubber/poly(vinyl chloride) blends has been investigated in the entire concentration range at 180°C. Maxima have been observed on the dependences of some kinetic parameters of the thermovulcanization reaction on polymer blend composition.

INTRODUCTION

Polychloroprene rubber (CR) and poly(vinyl chloride) (PVC) are polymers which are particularly sensitive to effects of heat and mechanical stressing.

These effects induce some undesirable reactions in the polymers, such as oxidation of the polymeric chain, dehydrochlorination, chain scission combined with the production of reactive macroradicals, leading eventually to degradation crosslinking. Increased reactivity of these polymers is connected with certain defects in their structure which have been widely discussed in the literature, especially in the case of PVC. In this respect CR was given much less attention.

THEORY

Chemical Structure and Thermal Stability of CR

Properties of a polymer are essentially determined by the type and concentration of the molecular weight regulator (modifier) used and conversion, and polymerization temperature.[1] As to its chemical reactivity, the most important are the structural units in the 1,2-position in which allyl-type rearrangement of the chlorine atoms can occur.

During storage and compounding, ketoallylic

$$\begin{array}{c} O \\ \parallel \\ +C{-}CH{=}CH{-}CHCl + \end{array}$$

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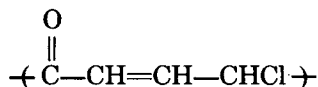
and analogous thioketoallylic chlorine atoms with reactivities approaching chlorine atoms in the 1,2-position[2] are formed. As is the case with PVC, dehydrochlorination reaction takes place in CR, its course is, however, different. During CR dehydrochlorination, three domains have been observed, characterized by different rates of the dehydrochlorination reactions.[3] Chlorine atoms with allylic bonds are eliminated at highest rate and their content was determined to be 1.5% (by weight).

It has been reported[4] that thermal destruction of Nairit P (thiol-modified CR) involving elimination of labile chlorine atoms, occurs in the temperature range 130–140°C.

Amano and Sato[5] have studied CR dehydrochlorination below 150°C and determined its activation energy value of 100 kJ mol^{-1}.

Zhovner et al.[6] have found, however, that dehydrochlorination, thermovulcanization, and vulcanization of CR by metal oxides have similar activation energy values in the 67–76 kJ mol^{-1} range, and their mechanisms under participation of allylic chlorine atoms are also similar. Crosslinking reactions requiring higher activation energies (126 kJ mol^{-1}) take place only at temperatures above 160°C. It is assumed that changes of activation energy with temperature are connected with the presence of reactive sites in the CR macromolecule. Other authors[7] have shown that CR thermovulcanization occurs even when allylic chlorine atoms are hindered by pyridine. Moreover, it was established[8,9] that shearing forces at higher temperatures and in presence of atmospheric oxygen, effect important changes in the CR macromolecule, resulting in gel formation.

Crosslinking of CR in the absence of crosslinking agents (thermovulcanization) is a characteristic feature of this polymer. Little attention was given to quantitative investigation of these reactions, although understanding the polymer degradation and stabilization is of considerable practical importance (e.g., in rubber storage and compounding).

Degradation of CR / PVC Polymer Blends

In spite of increasing attention to polymer blends, little attention was given until now to degradation and stabilization problems, especially in the case of PVC blends with other chlorine-containing polymers (chlorinated polyethylene, chlorsulfonated polyethylene, CR).

It has been established[10] that hydrogen chloride products play an important role in the autocatalytic degradation reaction, particularly in its initial phase. Because HCl removal from the polymer, for example, by means of an inert gas stream, has a pronounced inhibitive effect on the degradation of PVC, it can be assumed that the reaction will be promoted by its presence. Dodson et al.[11] have studied the thermal degradation of PVC mixed with chlorinated natural rubber (Alloprene R 20, produced by ICI) and found that the stability of this blend is inferior to the stability of its individual components. Degradation of the chlorinated elastomer begins at lower temperatures than the degradation of PVC, which is activated by the HCl produced. By using ^{36}Cl as a marker in PVC they have shown that the main part of the hydrogen chloride eliminated during the degradation of the blend comes from PVC.

Obviously, the role of free radicals formed during the degradation of chlorinated natural rubber is not negligible.[11] On the other hand, it has been reported[4] that CR/PVC blends have better stability than individual polymer components. We have therefore investigated degradation reactions of CR alone and of its blends with PVC, with respect to the preparation and covulcanization of such blends.

EXPERIMENTAL

Materials

Polychloroprene rubber Baypren 110 modified by thiols (produced by Bayer, Leverkusen, F. Germany), with low tendency to crystallization, Mooney viscosity 45 ML (1 + 4) at 100°C, density 1230 kg/m^3, concentration of allylic chlorine atoms 1.15% (by weight).

Suspension poly(vinyl chloride) Neralit 682 (produced by Spolana k.p. Neratovice, Czechoslovakia), with K-value of 68 and density 1410 kg/m^3.

K-value is related to a viscosity-average molecular weight. It is by the factor of 1,000 greater than the Fikentscher's constant, k, which is done by the equation:

$$\log(\eta_c/\eta_o) = \left(75k^2(1 + 1,5kc)^{-1} + k\right)c$$

where η_o and η_c are the viscosity of a solvent and of a polymer solution, respectively, and c is the concentration of the polymer solution in g/dL.

Preparation of Polymer Blends

CR/PVC blends were prepared in agreement with the results obtained by Nakamura[12] using an electrically heated two-roll mill with dimensions of rolls being 100 × 200 mm (CR/PVC = 50/50, 30/70, 20/80, 10/90, 0/100) and a nonheated two-roll mill with roll dimensions of 150 × 400 mm (CR/PVC = 100/0, 70/30). Temperatures are given in Table I.

Study of Thermovulcanization

Thermovulcanization of CR was investigated using the polymer as purchased (without further treatment). Changes occurring during the thermovulcanization of CR/PVC polymer blends were observed on a Monsanto Oscillating Cone Rheometer, at temperatures between 150°C and 200°C. Effects of

TABLE I
Formulation of Polychloroprene Rubber/Poly(vinyl Chloride) Polymer Blends
and Temperatures of their Preparation
(concentrations in parts by weight)

No	1	2	3	4	5	6	7
CR	100	70	50	30	20	10	—
PVC	—	30	50	70	80	90	100
Stearic acid	1	1	1	1	1	1	1
Mixing temperature (°C)	40	60	80	100	110	130	150

mechanical and thermal stressing were studied using a laboratory kneader, chamber volume 50 cm^3, at temperatures between 90°C and 150°C.

A three-parameter exponential function was used for the description of vulcanization curves with the marching modulus, that is,

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

where M_{min} and M_{max} are the minimum and maximum torque values (Nm) of the vulcanizing mixture, respectively, M is a torque value at any time t (min), k the first-order rate constant of the crosslinking reaction (min^{-1}), and t_i the induction period (min). Parameters of the equation were obtained by nonlinear regression analysis of experimental data, in good agreement with the experiment. Effective degree of the crosslinking reaction, characterized by the polymer volume fraction in vulcanizates after swelling (v_r), was determined from equilibrium swelling of samples in cyclohexanone.

RESULTS AND DISCUSSION

Thermovulcanization of Polychloroprene Rubber

Analysis of vulcanization curves has shown two reactions occurring in CR thermovulcanization in the temperature interval 150–200°C, leading to chemical crosslink formation (see Fig. 1, Table II). Activation energy of the first parallel reaction is in very good agreement with activation energies of CR dehydrochlorination, oxidation, or thermovulcanization (67–76 kJ mol^{-1}).[6,13] It is thus very probable that CR is crosslinked in the initial stage of intermolecular dehydrochlorination via allylic chlorine atoms.
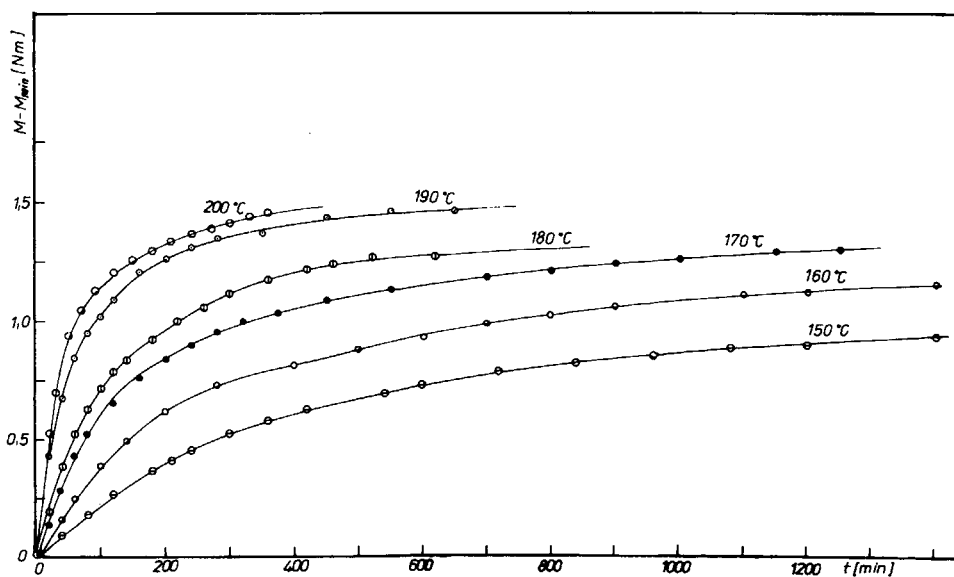

Fig. 1. Thermovulcanization of polychloroprene rubber (Baypren 110) in the temperature interval 150–200°C (curves are calculated functions, points experimental values).

TABLE II

Kinetic Parameters of Thermovulcanization of Polychloroprene Rubber (Baypren 110)
in Temperature Interval 150–200°C

Temperature (°C)	150	160	170	180	190	200
First parallel reaction						
$M_{max}1$ (Nm)	0.82	0.89	0.97	1.04	1.11	1.19
$k_1 \cdot 10^3$ (min^{-1})	3.4	6.3	10.4	12.1	24.2	32.2
t_i1 (min)	10.0	10.4	7.4	2.5	2.1	0.5
$E_1 = 73$ kJ mol^{-1}						
Second parallel reaction						
$M_{max}2$ (Nm)	0.43	0.35	0.45	0.28	0.38	0.36
$k_2 \cdot 10^3$ (min^{-1})	0.38	1.5	1.3	4.7	5.1	5.2
t_i2 (min)	540	450	210	200	105	95
$E_2 = 87$ kJ mol^{-1}						
Ultimate extent of thermovulcanization						
M_{max} (Nm)	1.26	1.24	1.42	1.32	1.49	1.55

It is interesting that the induction period of the first parallel reaction is practically negligible, especially at higher temperatures (Table II). Taking into account that the onset of the chemical destruction of CR, connected very likely with the elimination of allylic chlorine atoms,[4] is in the temperature interval 130–140°C, the reaction rate of CR thermovulcanization in the initial stage can be explained by high mobility of these labile chlorine atoms in the temperature range investigated.

Both degree of vulcanization and gel content in CR vulcanizates are relatively high and comparable with chemically vulcanized CR (Table III). The contribution of the first parallel reaction, which is supposed to be connected with the reaction of allylic chlorine atoms, is of critical importance for the degree of the vulcanization reaction obtained. On the other hand, marching modulus, which is typical for the vulcanization of several synthetic rubbers, is determined by the rate and degree of the second parallel reaction which we consider to be connected with the activities of other reactive sites.[7]

TABLE III

Time Dependence of Degree of Crosslinking (v_r) and Gel Content in thermovulcanized
Polychloroprene Rubber (Baypren 110) at 180°C

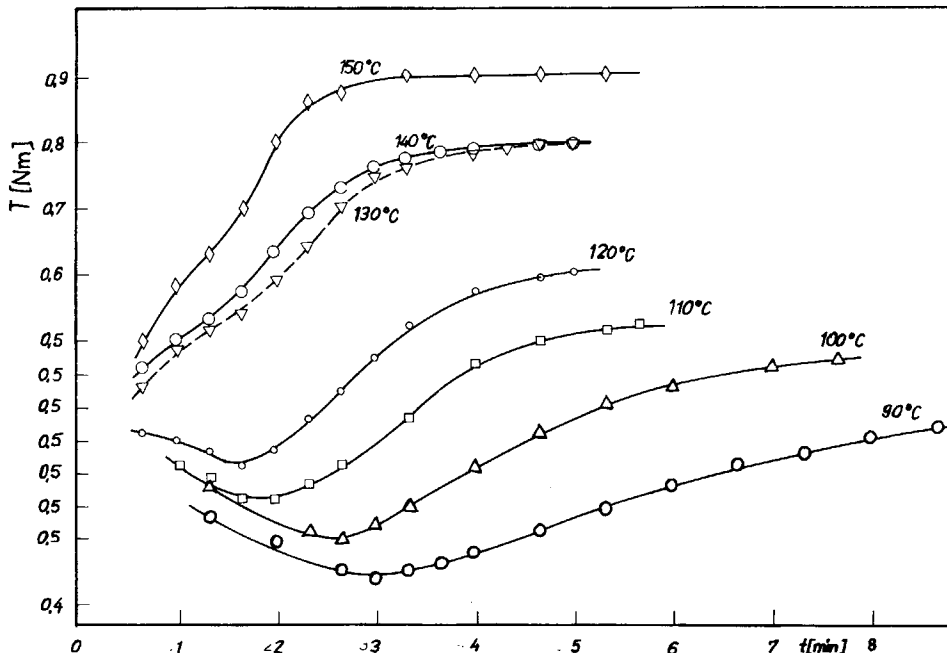| Cure time (min)	v_r	Gel content (%)
10	—	10
22	—	32
40	—	51
85	0.0697	74
145	0.1182	90
280	0.1785	92
595	0.2051	93
1365	0.2649	94
1745	0.3261	94

Fig. 2. Torque (T) of polychloroprene rubber as function of plasticization time in a laboratory kneader in the temperature interval 90–150°C.

CR Degradation under Thermal and Mechanical Stressing

Investigation of CR behavior under processing conditions is of considerable practical importance. We have therefore measured torque changes during CR plasticization in a laboratory kneader in the temperature range 90–150°C (Fig. 2).

The rate of degradation crosslinking was, in the conditions investigated, an order of magnitude higher then CR thermovulcanization rate under static conditions, in spite of much lower temperatures at which rubber was stressed. Above 130°C, notable increase of CR degradation crosslinking rate could be observed which corresponds to the onset of the thermal destruction of CR.[4] Of course, rubber is crosslinked at a high rate even at relatively low temperatures (e.g., at 90°C, Fig. 2). It could be possible, however, that vigorous kneading induces the formation of further keto- and thioketoallylic groups, contributing to the crosslinking reaction.[7]

These conditions are important with respect to the preparation of CR compounds, as well as of its blends with other polymers, requiring higher processing temperatures (e.g., PVC).

Thermovulcanization of CR / PVC Polymer Blends

The rate of crosslinking reaction of CR/PVC blends in the absence of crosslinking agents is higher than the crosslinking of each polymer alone under the same conditions (Fig. 3). Rate constants of both first- and second-parallel reactions reach their maxima in the concentration range of CR/PVC = 50/50–30/70% (by weight). The extent of the crosslinking reaction is,
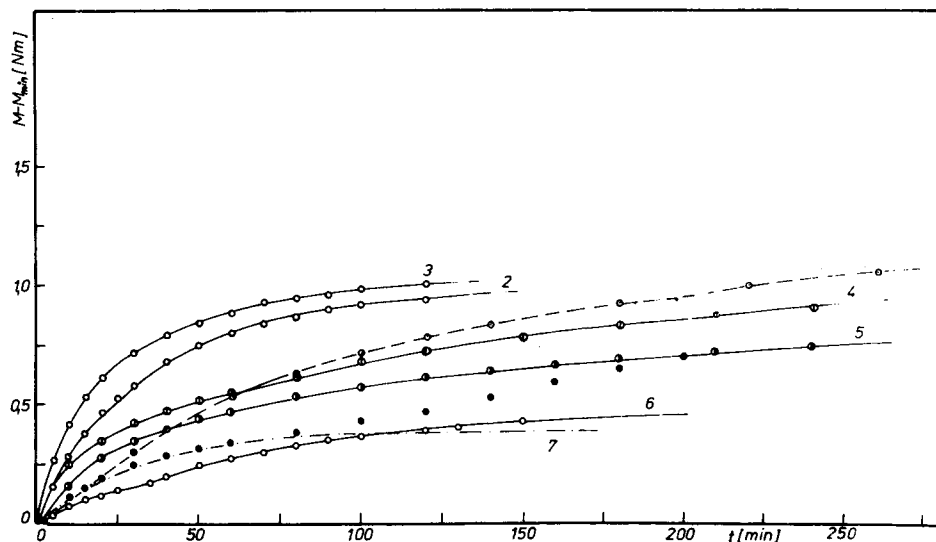
Fig. 3. Thermovulcanization curves of polychloroprene rubber/poly(vinyl chloride) blends at 180°C. Designation and formulation of polymer blends is given in Table I (curves are calculated functions, points experimental values).

however, almost unchanged and remains practically constant up to CR/PVC weight ratio of 30/70% and then rapidly decreases (Fig. 4).

It is well known that PVC dehydrochlorination is an autocatalytic process in which HCl elimination plays an important role.[11] It is possible that the presence of CR, easy elimination allylic chlorine atoms, initiates the PVC degradation reaction. These become then increasingly involved in the cross-linking reaction.

Spontaneous degradation crosslinking of PVC and its blends with rubber cannot be observed in Figure 3 (except of crosslinking of PVC alone), even after prolonged exposure to high temperatures (e.g., no spontaneous degradation of CR/PVC polymer blend 30/70% by weight was observed even after 720 min at 180°C; in Figure 3 we can see only the beginning of the curve). However, thermovulcanization rates of polymer blends show pronounced maxima depending on the blend composition and corresponding with the highest extent of the vulcanization reaction (Fig. 4). Mutual influence of the two polymers[7] during thermovulcanization can therefore be supposed. With increasing PVC concentration in the blend, more of its macromolecules are becoming involved in the crosslinking reaction. While the rate of crosslinking increases, modulus remains practically constant, owing to the matrix formed by rubber. Beyond a certain critical PVC concentration in the blend phase, inversion occurs (rubber becomes the dispersed phase) and a sharp drop of both rate and extent of thermovulcanization reaction can be observed.

It would be interesting to focus further study of the vulcanization of polymer blends to investigate the relationship between morphology, given by the processing conditions, and kinetic parameters of the vulcanization reaction.
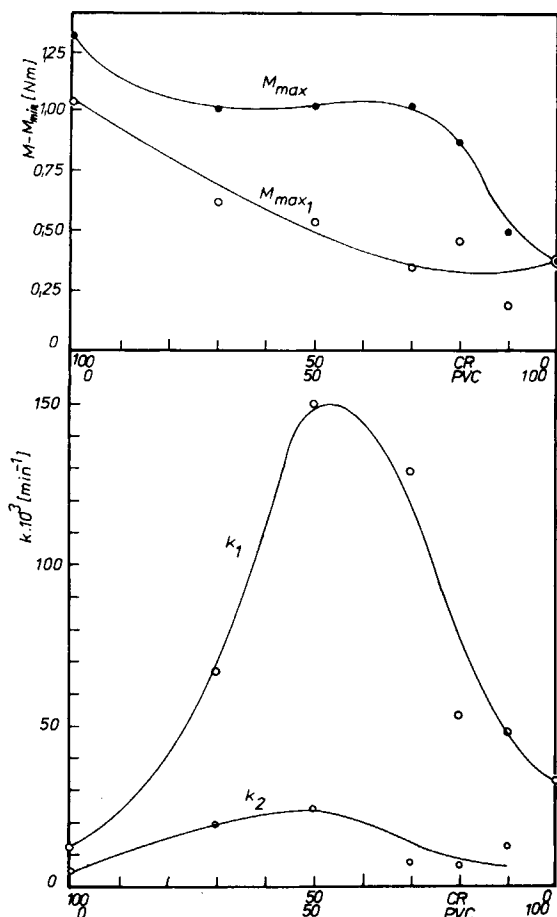
Fig. 4.   Concentration dependences of kinetic parameters of polychloroprene rubber/poly(vinyl chloride) blends thermovulcanization at 180°C.

CONCLUSION

There are various types of reactive sites in polychloroprene rubber, depending on the particular conditions which are involved in the crosslinking reaction. Very reactive allylic chlorine atoms enable rapid CR vulcanization, they are, however, the cause of generally poor processing safety (scorching) of CR compounds. They also negatively affect the CR thermovulcanization activity, which is important in connection with polymer compounding at higher temperatures. The content of allylic chlorine atoms is thus an important criterion in the study of CR vulcanization. In the polymer used in this study (Baypren 110) their concentration was 1.15% (by weight). Other sites with lower reactivities formed even during rubber storage, compounding, and so forth are becoming involved in the crosslinking reaction later and result in the so-called marching modulus.

Plasticization of CR at higher temperatures and in presence of atmospheric oxygen induces much higher rates of degradation crosslinking, possibly due to

higher concentration of reactive fragments and newly formed reactive sites in the rubber macromolecule.

Thermovulcanization of CR/PVC polymer blends progresses at a much higher rate than crosslinking of individual polymers. Maximum values of some kinetic parameters of the crosslinking reaction in the concentration range of CR/PVC = 50/50–30/70% (by weight) are a result of mutual influence (interaction) of both polymers and suggest the possibility of common network formation. The shape of these concentration dependences is determined by different reactivities of the two polymers on the one hand, and by polymer blend morphology on the other.

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