Kinetics of the thiokol–epoxy cure process as studied by the e.s.r. spin probe method

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The dependence of the kinetics of the thiokol–epoxy cure process with dimethylaminomethylphenol on the formation of components was studied by the e.s.r. spin probe method. It was found that the copolymerization reaction is characterized by the following stages: the initiation of the epoxy molecules; the appearance of regions of structurized polymer; the activation of polysulphide molecules and the formation of linear polymer chains. No stage division is found when a modifying agent (quinone imide or benzoquinone) is used. The data obtained correspond well to the recently proposed concept of radical copolymerization of thiokol–epoxy compositions.

(Keywords: electron spin resonance; nitroxide spin probe; thiokol–epoxy; kinetics; rotational correlation time)

INTRODUCTION

The chemical modification of polysulphide polymers by epoxy resins is of increasing practical importance due to their unique properties[1]. Different materials are produced for aviation, mechanical engineering and the electrotechnical industry. To obtain the optimal properties of hermetics it is necessary to understand the physical–chemical processes which occur during the cure reaction and their influence on the properties of the products.

Stable radicals are extensively employed[2] as probes in studies of various processes in polymers and liquids (melting, phase transition, structure formation) which are accompanied by changes in the kinetic mobility and flexibility of molecules. For instance, linear and ordered resins were investigated using the spin probe method[3]. This method had not been previously used in studies of thiokol–epoxy compositions.

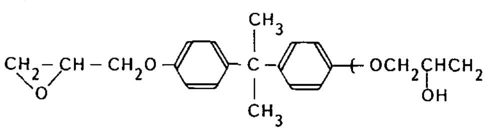
This paper reports the polymerization reaction resulting from the interaction of polysulphide, epoxy resin and aminomethylphenol using the e.s.r. spin probe method.

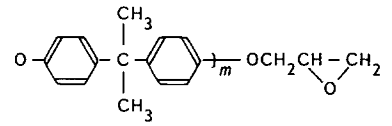
EXPERIMENTAL

The compound studied was the polysulphide polymer LP-2:

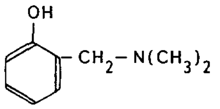
$$HS-CH_2CH_2OCH_2OCH_2-(SSCH_2CH_2OCH_2OCH_2CH_2-)_n-SH$$

and epoxy resin E-40:

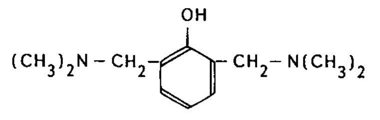




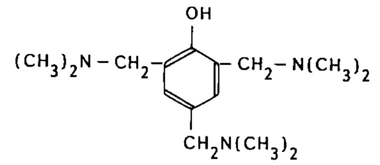
dimethylaminomethylphenol:



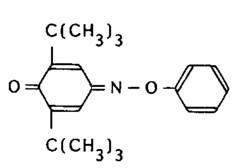
2,6-bi-dimethylaminomethylphenol:



and 2,4,6-tri-dimethylaminomethylphenol:



were used as initiators. In some experiments the curing agent was modified by adding 3,5-di-t-butylquinone imide:



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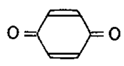
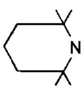
or benzoquinone:



The e.s.r. spectra were recorded on an ER-200 D spectrometer (Bruker, Germany). The e.s.r. kinetics studies were carried out in open tubes at 353 ± 1 K.

Nitroxide radicals of 2,2,6,6-tetramethylpiperidine-1-oxyl:



TEMPO

dissolved in the epoxy resin (concentration: 10^{18} radicals g^{-1}) were used as spin probes.

The required amount of polysulphide was added to the epoxy resin and the components were mixed at 333 K. The components were mixed again for 2 min after adding the curing agent at room temperature and then placed into a tube which was put in the e.s.r. spectrometer cavity.

All the e.s.r. spectra showed a well resolved triplet characteristic of the rapidly tumbling nitroxide spin probe:

$$g_{\text{iso}} = 2.0059 \pm 0.0005 \qquad a_{\text{iso}} = 1.57 \pm 0.05\ \text{mT}$$

$$g_{zz} = 2.0031 \pm 0.0005 \qquad a_{zz} = 3.44 \pm 0.05\ \text{mT}$$

(g_{zz} and a_{zz} were measured at 77 K). Changes in the rotational mobility of the nitroxide spin probes during the course of the polymerization reaction, which influence the e.s.r. spectrum line shape, were investigated.

Since TEMPO remained in the fast motional regime throughout the cure reaction, a quantitative analysis was carried out of the changes in probe mobility during the process. Analyses as reported in reference 3 allowed us to conclude that the character of rotational motions of the radicals is near isotropic, and the values of the hyperfine coupling constants (a and g factors) allowed us to use the rotational correlation time τ quantities based on an equation from references 2 and 3:

$$\tau = 6.65 \times 10^{-10}\, \Delta H_{+1}[(I_{+1}/I_{-1})^{1/2} - 1]$$

where ΔH_{+1} is the width of the low-field component of the spectrum, and I_{+1} and I_{-1} are the intensities of the low- and high-field components, respectively. The relative error of τ did not exceed 5–10%[3].

RESULTS AND DISCUSSION

The main peculiarity in the process studied is the presence of reactions in which the nitroxide spin probe takes part. General conclusions may be drawn from the cured compositions. The addition of polysulphide to the epoxy resin leads to the decrease and decay of the nitroxide radical e.s.r. signal. In the cure reaction process in the presence of curing agents the paramagnetism is recovered: the intensity of the e.s.r. signal increases, reaches saturation and then slowly decreases. The copolymerization products contain <0.5% of the initial concentration of radicals, and an appreciable amount of amino groups (>NH) is found. The presence of >NH groups is confirmed by i.r. spectra which are recorded in the region of 400–4000 cm^{-1}. A wide band is observed near 3550–3450 cm^{-1} with a maximum at 3461 cm^{-1}. This band can be attributed to the stretching vibrations of OH, NOH and NH groups. Moreover, the intense band at 1606 cm^{-1} can be ascribed[4] to the deformation vibrations NH.

The mechanism of chemical transformation of the components is not well understood at present. It is possible that a significant contribution to the formation of thiokol–epoxy compositions is provided by a radical copolymerization mechanism in accordance with published results[5–7]. This theory enables us to suppose that a relationship exists between this process and the polymerization reactions of rubbers. On the other hand, the interaction mechanism between nitroxide radicals and vulcanizate is well known[8–10]. Taking into account the data of others[5–10] and data from our study, the scheme shown in *Figure 1* may be proposed.

In the presence of polysulphide the nitroxide radicals (TEMPO) reduce to the corresponding hydroxy amines with the hydrogen atom being removed from the thiol group (*Figure 1*, route A). As a result, thiol radicals ($\sim R - \dot{S}$) are formed. The activity of polysulphides in the transfer of radicals ($\sim R–S$) in the chains of macromolecules is high[11], so the recombination of thiol radicals occurs rather rapidly:

$$R_1\text{–}\dot{S} + \dot{S}\text{–}R_2 \rightarrow R_1\text{–SS–}R_2$$

Therefore the e.s.r. signal of these radicals is not observed.

It was found that polysulphide polymerizes in a mixture of TEMPO and polysulphide in equimolar ratio without any epoxy resin. From the i.r. data it can be seen that the cured polymer contains hydroxy amine groups (>N–OH).

The addition of dimethylaminomethylphenol to the mixture of polysulphide and epoxy polymers leads to the oxidation of hydroxy amines to nitroxide radicals. This is confirmed by the detection of the e.s.r. signal. It should be noted that in the absence of epoxy resin no e.s.r. signal is observed.

According to the obtained results and other data[5,7] the reaction of hydroxy amines with the matrix can be presented as shown by route B in *Figure 1*. In the case

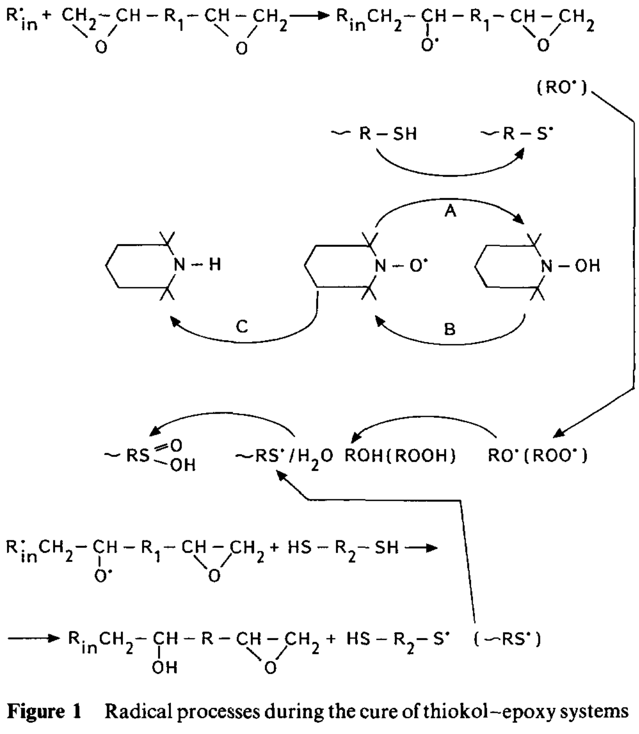


Figure 1 Radical processes during the cure of thiokol–epoxy systems

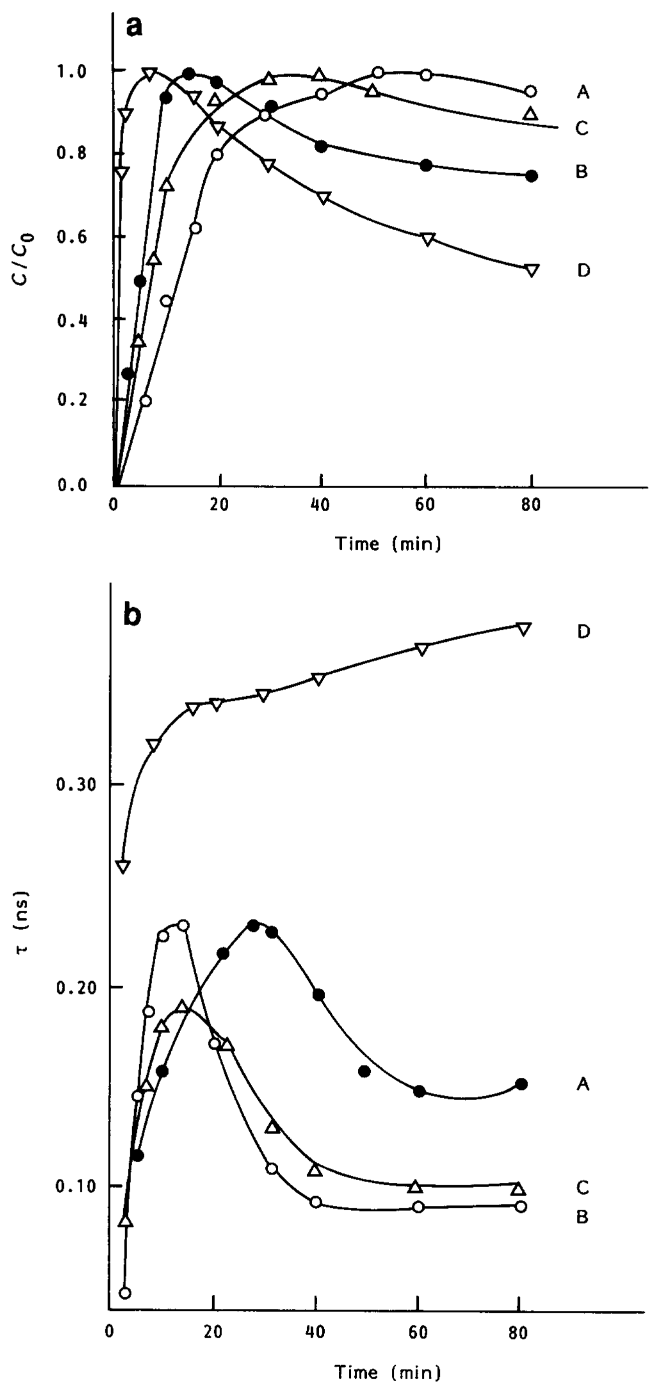


Figure 2 Time dependence of the relative concentration of radicals (a) and their mobility (b) in the cure reaction of polysulphide polymer (60 mass), epoxy resin (60 mass), dimethylaminomethylphenol (2 mass) (A) or 2,6-bi-dimethylaminomethylphenol (2 mass) (B) or 2,4,6-tri-dimethylaminomethylphenol (2 mass) (C) and the cure reaction of polysulphide polymer (20 mass), epoxy resin (100 mass) and 2,6-bi-dimethylaminomethylphenol (2 mass) (D)

of homolytic decay of dimethylaminomethylphenol short-lived free radicals occur, which initiate the epoxy ring decomposition with the formation of alkoxyl radicals. The high activity of alkoxyl radicals in the oxidation reactions of hydroxy amines to nitroxide radicals is well known[8–10].

The above reaction scheme is supported by the following kinetic data. The dependence of the relative concentration of nitroxide radicals in the thiokol–epoxy hermetics on different compositions is shown in *Figures 2a* and *3a*. Analysis of the data shows that the rate of spin probe formation in the first stage of curing increases with epoxy resin content. This rate is proportional to the cure agent content. On the other hand, it follows from the comparison of the reaction rates for mixtures with different ratios of functional groups in the curing agent that the rate of the process increases with increase in number of $-CH_2N(CH_3)_2$ groups in the curing agent from one to two or three. In this case the number of OH groups in the curing agent decreases. These results show that the activation process of epoxy resins is determined by the amine groups rather than the hydroxy groups, and this coincides with the conclusions of this study[7].

A decrease in the activity of the 2,4,6-tri-dimethylaminomethylphenol compared to 2,4-bis-dimethylaminomethylphenol can apparently be explained by the increase in viscosity (~15 times).

The e.s.r. parameter of the nitroxide radicals formed

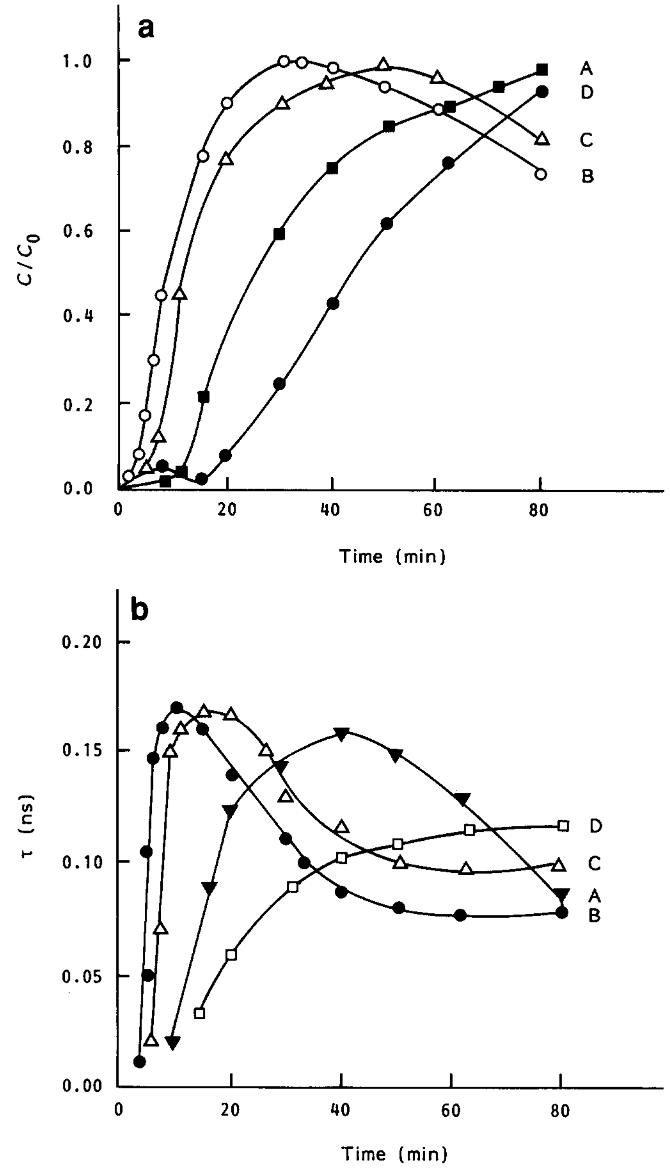


Figure 3 Change in the relative concentration of radicals (a) and their mobility (b) in the cure reaction of polysulphide polymer (100 mass)–epoxy resin (20 mass) compositions by dimethylaminomethylphenol (A), 2,6-bi-dimethylaminomethylphenol (B), 2,4-6-tri-dimethylaminomethylphenol (C) and dimethylaminoethylphenol with the addition of quinone imide (D). The content of 2,6- and 2,4,6-dimethylaminoethylphenols is 2 mass, and that of quinone imide is 0.03 mass

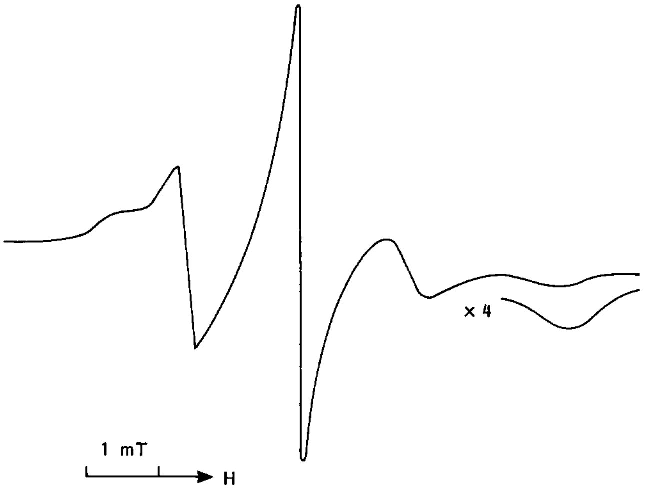


Figure 4 E.s.r. spectrum of the TEMPO probe in the vulcanizate at room temperature

in the cure reaction depends on molecular mobility. It is known[3] that the rotational diffusion process of the spin probes in solution is governed by the microviscosity of the media. The dependence of the time τ of the probes on the time of the cure reaction of thiokol–epoxy mixtures is shown in *Figures 2b* and *3b*. In the case of low polysulphide content (*Figure 2b*, curve D), and in its absence, the change in τ is similar to the change in τ obtained in the cure reaction of epoxy resins with amines[12,13]. It is found[13] that the τ of the TEMPO probes in the polymerization reactions of epoxy resins does not practically change after the transition of the polymer to the pre-gel state, which occurs during the connection of two molecules of epoxy resin: according to reference 13 this transition is analogous to the temperature transition T_{11} in polymers from liquid-like behaviour ('true' solution) to a polymer melt exhibiting short-range order ('weak' ordered state).

The increase in τ of the probes in the initial phase of the cure reaction of the polysulphide–epoxy compositions is also detected in the case of high polysulphide content (*Figures 2b* and *3b*). The correlation time τ passes through a maximum. Such unusual behaviour of the probe rotational diffusion is not observed in the polymerization reaction of epoxy resins. This can be explained as follows. As noted above, dimethylaminomethylphenol initiates the epoxy ring decomposition. Some of the molecules of epoxy resin take part in the process of connecting molecules and pre-gel formation with a sharp increase in τ. As a result,' areas of ordered epoxy resin subsequently occur and radicals partially recombine and are partially redistributed to regions with smaller microviscosity. It is observed[14] that 10% epoxy resin takes part in the formation of 'homo' epoxy polymer network.

The existence of different physical structural regions can also be confirmed by the following data. The e.s.r. spectra of spin probes detected in the cured composition at room temperature show evidence of slow ($\tau \geqslant 10$ ns) and fast ($\tau \leqslant 5$ ns) rotating radicals (*Figure 4*) due to the heterogeneity of the system.

In the regions enriched with polysulphide, the process of epoxy ring decomposition and alkoxide radical formation results in the initiation of the $\sim$S–H groups of the polysulphide molecules (*Figure 1*)[5]. This process leads to the formation of thiokol radicals ($\sim$R–$\dot{S}$) which can actively reduce the nitroxide radicals to amines[8]. Hence, the signal intensity decreases (*Figures 2a* and *3a*). Alkoxide radical recombination leads to an increase in hermetic elasticity because the crosslink density and consequently the brittleness of the polymer decreases.

The molecular mobility of spin probes in the polymer is determined by the local segmental mobility of the macromolecules[3]. It is known that the latter significantly depends on the crosslink concentration in the macromolecular chains. As shown in *Figure 3b*, τ becomes constant after a certain period of the cure reaction. It can be concluded from these data that the distances between the crosslinks of the polymer formed are so large that they do not affect the kinetic flexibility of the macromolecules.

The spin probe method makes it possible to distinguish the stages in the copolymerization process of thiokol–epoxy systems. In the initial stage the radicals formed in the homolytic decay process of dimethylaminomethylphenol initiate epoxy ring decomposition with the formation of alkoxide radicals. Some of these take part in the formation of regions of a structured polymer, and others activate the $\sim$S–H groups of polysulphide. The stage of thiol radical formation is the longest one. This can be explained in terms of the diffusion restrictions. The process is completed by the formation of linear chains of the hermetic.

These stages cannot be found for compositions cured in the presence of modifying additions (for instance, quinone imide). In this case a continuous increase in the concentration of TEMPO radicals (*Figure 3a*, curve D) together with their lower content (one-tenth of the value for the composition without quinone imide) can be observed. The cure reaction itself goes on more steadily: a continuous increase in the time τ of the spin probe is detected (*Figure 3b*, curve D).

As it is known[7], the action of quinone imide results in a decrease in the activation energy of homolytic decomposition of the $H_2C{-}N(CH_3)_2$ bond of dimethylaminomethylphenol. This leads to the formation of an order of magnitude larger number of radicals. These radicals initiate the homopolymerization reaction. Apparently the probability of formation of the polysulphide thiol radicals increases and consequently increases the competition between the B- and C-type reactions in the initial stage of the cure reaction (*Figure 1*).

Figure 1 contains reactions which probably take place in the systems studied; the participation of other non-radical particles and products formed in the process is not eliminated.

In conclusion, it should be noted that the kinetics laws established for the cure reaction of thiokol–epoxy compositions will apparently be valid for other hermetics as well. As noted in reference 13, a filler content of up to 5 wt% can essentially change the macroscopic properties of the polymer (viscosity, mechanical strength), but does not influence matrix properties such as the crosslinking density and microviscosity.

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