Chemical processes following mechanical pulse action on polyepoxide resins doped with cobalt and nickel acetates

A. I. Aleksandrov,[a]* *I. Yu. Metlenkova,*[a] *A. N. Zelenetskii,*[a] *A. I. Prokof'ev,*[b]
S. P. Solodovnikov,[b] *and N. N. Bubnov*[b]

[a]*Institute of Synthetic Polymer Materials, Russian Academy of Sciences,*
70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation.
Fax: 007 (095) 420 2229
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085

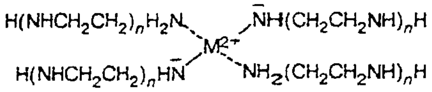
The action of elastic wave pulses from a rheological explosion on solid glassy polyepoxides, including those doped with Co^{2+} and Ni^{2+} complexes, leads to the generation of stable dimethylbenzyl radicals. The structures of the polyepoxides and the concentration of Co^{2+} and Ni^{2+} complexes in them have an effect on the mechanochemical yield of these radicals and on the pressure at which the rheological explosion occurs.

Key words: polyepoxides; cobalt acetate, nickel acetate; rheological explosion, elastic wave pulse.

It is known that uniaxial compression of polymeric plates to a certain pressure results in the generation of short-term acoustic emission in them and in the propagation of an elastic wave pulse (EWP) in the polymer. This process is referred to as rheological explosion (RE).[1,2] Previously,[1,2] a series of polymers was studied, *viz.*, high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), poly(ethylene terephthalate) (PETP), polyamides, poly(vinyl chloride) (PVC), and polystyrene (PS), and the effects of the thickness of the polymeric plate and the type of the polymer on the pressure at which the RE occurs (p_{RE}) were elucidated. The purpose of the present work was to study the chemical processes occurring in glassy polyepoxides during the rheological explosion as functions of their structures.

Experimental

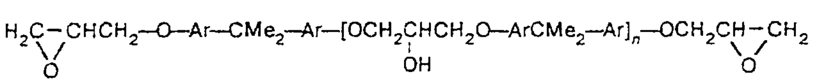
"Chemically pure" grade reagents, anhydrous cobalt and nickel acetates, polyethylenepolyamine [$H_2N(CH_2CH_2NH)_nH$] (PEPA), and ED-20 diane epoxy resin based on 4,4′-(2,2′-propylidenebisphenol) were used in the study. Space-network polyhydroxy-oxyamino ethers, products of the interaction of the epoxy and amino groups in ED-20 and PEPA, both containing metal atoms and not containing them were prepared by a procedure described previously.[3,4] A metal acetate was dissolved in PEPA at various metal/nitrogen ratios. Heating the solution of the salt resulted in the removal of the acetic acid liberated and in the formation of complexes **1** possessing high stability constants (this was shown for model systems containing Ni^{2+} or Co^{2+} and triethylenetetramine[3]).



1

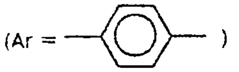
M = Co, Ni

After that, PEPA or solutions of Co^{2+} (or Ni^{2+}) complexes in PEPA were mixed with the epoxide-containing oligomer and thoroughly stirred (see Ref. 5); then the mixture was kept in a thermostat for 8 h at 100 °C. Previously, it was shown that the network polymers thus prepared contain no acetic acid or acetate groups and that metal complexes are uniformly distributed within the material.[6] The procedure described was used to prepare samples of polyepoxides that consisted initially of a curing agent (PEPA or a 0.1 *M* solution of $Co(OAc)_2$ or $Ni(OAc)_2$ in PEPA) and ED-20; the [curing agent]/[resin] ratios were 0.1, 0.2, 0.3, 0.4, and 0.5 (v/v). 1.5-mm thick samples with a diameter of 15 mm were subjected to mechanical treatment in a special setup (Fig. 1) that made it possible to perform uniaxial compression ending with a rheological



$H_2C{-}CHCH_2{-}O{-}Ar{-}CMe_2{-}Ar{-}[OCH_2CH(OH)CH_2O{-}ArCMe_2{-}Ar]_n{-}OCH_2CH{-}CH_2$

ED-20



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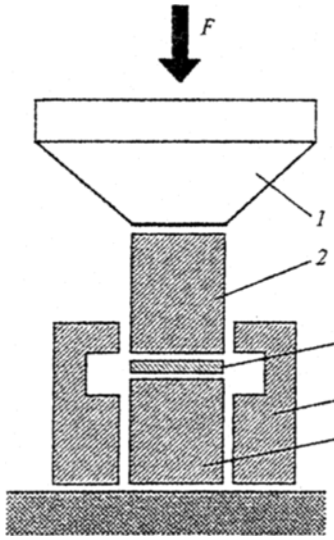

Fig. 1. Scheme of the setup for the action of EWP: Bridgeman anvil (*1*); steel punches (*2*, *3*); holder (*4*); the sample (*5*).

explosion of the polyepoxide sample. After EWP, the samples were placed into liquid nitrogen and studied by ESR spectroscopy on a Varian E12a spectrometer operating in the three-centimeter range.

Results and Discussion

The pressure p_{RE} at which the rheological explosion of the solid polyepoxide occurs varies as a function of the quantity of PEPA introduced into the ED-20 resin and of the sort of complex stabilized in the polyepoxide network. Figure 2 shows the dependences of p_{RE} on the [curing agent]/[resin] ratio (below referred to as [CA]/[ED-20] or [PEPA]/[ED-20] for samples containing no cobalt or nickel complex). It can be seen that these dependences pass through a minimum at [CA]/[ED-20] = 0.2 to 0.3 and that the minimum p_{RE} value for the curing agent containing Co^{2+} complexes is larger than that for the Ni^{2+}-containing material; the samples in which PEPA acts as the curing agent are characterized by the lowest p_{RE} values. It is known[7—9] that a [CA]/[ED-20] ratio equal to 0.2—0.3 corresponds to the greatest number of cross-links in the polyepoxides formed (the density of cross-links in a thickly cross-linked polymer is >3.5 kmol m^{-3}). When an excess of PEPA or ED-20 is present, the content of free end groups increases and the concentration of network joints decreases; the presence of Co^{2+} or Ni^{2+} complexes changes the nature of the cross-links. Thus, the experimental results obtained imply that the p_{RE} value is related to the topological structure of the polyepoxide network.

In an ESR study of the chemical changes initiated by rheological explosions in solid samples based on "pure" polyepoxides and in those containing metal complexes in a polymer network, we detected a species whose ESR spectrum (Fig. 3) consisted of seven lines with a binomial distribution of intensities; each of these lines was split additionally into three components. This spectrum refers to the —O—Ar—$\dot{C}Me_2$ radical, because its HFC constants coincide exactly with those found previously[10] for the dimethylbenzyl radical: $a_{CH}(H)$ = 1.65 mT, a(H) = 0.52 mT, and a_m(H) = 0.17 mT.

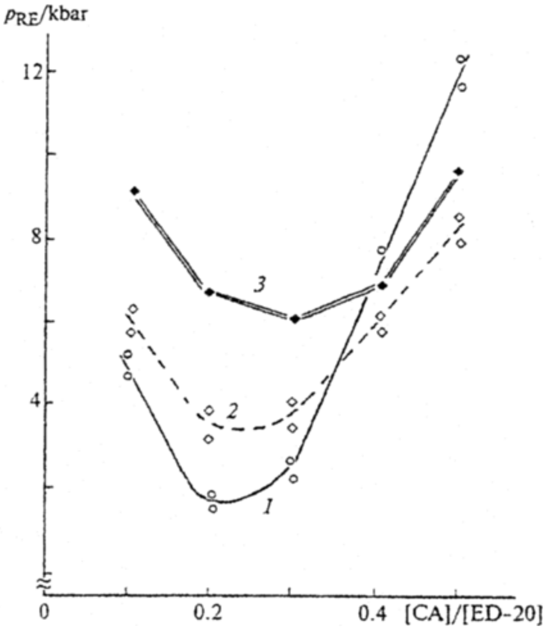

Fig. 2. Dependences of the pressure of the rheological explosion (p_{RE}) on the [CA]/[ED-20] ratio; curing agents: PEPA (*1*); PEPA+Ni^{2+} complex (*2*); PEPA+Co^{2+} complex (*3*).

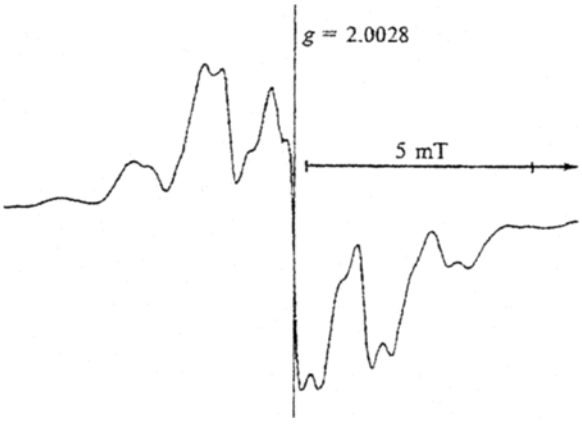

Fig. 3. ESR spectrum of the species arising in polyepoxides after the action of EWP.

It can be assumed that the action of EWP on solid polyepoxides results in cleavage of the polymer chains according to the following scheme

$$\text{—O—Ar—CMe}_2\text{—Ar—O} \xrightarrow{\text{EW}} \text{—O—Ar—}\dot{\text{C}}\text{Me}_2 + \dot{\text{A}}\text{r—O}.$$

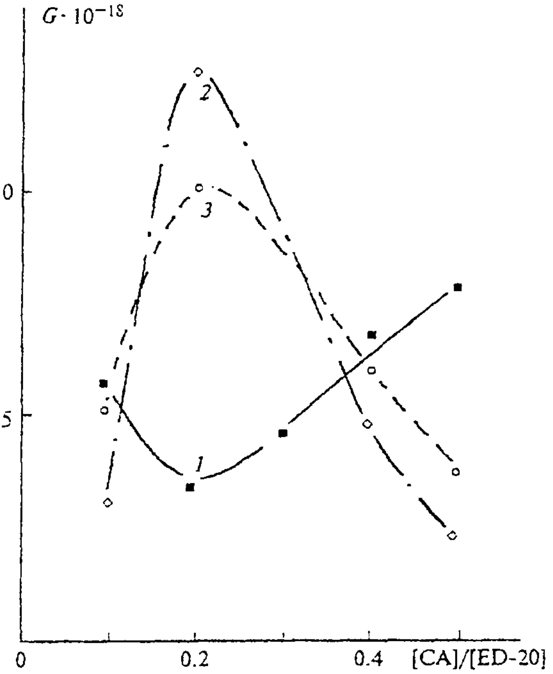

Fig. 4. Dependences of the yield of —O—Ar—$^{\cdot}$CMe$_2$ radicals on the [CA]/[ED-20] ratio; curing agents: PEPA (*1*), PEPA+Ni^{2+} complex (*2*); PEPA+Co^{2+} complex (*3*).

This affords end radicals, *viz.*, stable —O—Ar—$^{\cdot}$CMe$_2$ radicals and unstable phenyl radicals. The latter abstract H atoms from the polymeric chain thus generating unstable alkyl radicals, which are destroyed through the sequential transfer of electron density along the polymer chains, and this gives rise to double bonds and H_2 molecules.[11]

The dependences of the yields of —O—Ar—$^{\cdot}$CMe$_2$ radicals on the [CA]/[ED-20] ratio also pass through extrema (Fig. 4) (*G* is the number of radicals in 1 g of polyepoxide after the action of EWP). For PEPA—ED-20 samples, there is a minimum at [PEPA]/[ED-20] = 0.2, while the curves for the samples containing Co^{2+} or Ni^{2+} complexes exhibit maxima (also at [CA]/[ED-20] = 0.2).

These dependences can be explained by assuming that the relaxation properties and, hence, the structure of the matrix have an effect on the formation of —O—Ar—$^{\cdot}$CMe$_2$ radicals during the action of EWP. In fact, the minimum of *G* coincides with the maximum of rigidity, which corresponds to the most dense cross-linking in polyepoxide; this, obviously, decreases the conformational mobility of the radical fragments and accelerates their recombination. In a looser matrix, radicals have no time to recombine during the action of EWP, since the smaller number of cross-links facilitates the movement of the polymer chains; therefore, they can migrate apart from one another, and their recombination is thus prevented. The sharp change in the form of the dependence of *G* on the [CA]/[ED-20] ratio in the presence of metal complexes in the polyepoxide cannot be explained only by changes in the relaxation properties of the resulting matrices. This can be caused by the fact that Co^{2+} and Ni^{2+} ions participate in the radical generation and destruction through redox processes in which the —O—Ar—$^{\cdot}$CMe$_2$ radical is apparently an intermediate. The appearance of the maximum in the curve actually reflects the variation of the concentration of this radical as a function of the quantity of Co^{2+} or Ni^{2+} complexes in the polyepoxide.

Thus, our studies demonstrated that the pressure at which the rheological explosion occurs in a polymeric matrix is determined by its structure. The action of elastic waves from the rheological explosion in a polyepoxide matrix generates dimethylbenzyl radicals, whose yield depends on the structure of the polymeric network and on the presence of Co^{2+} or Ni^{2+} complexes in it.

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