

Reactive oligomers based on a cyanuric epoxy resin

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Reactive oligomers with free epoxy and peroxy groups based on a cyanuric epoxy resin and *tert*-butylhydroperoxide (PDCER) have been synthesised in the presence of 18-Crown-6 + ZnCl₂ as a catalytic system. The effect of temperature and process time on the PDCER properties has been determined. The PDCER structure has been confirmed by chemical and IR-spectroscopic analyses. Using ED-20 commercial epoxy resin (70 mass parts), petroleum resin (5 mass parts), TGM-3 oligoesteracrylate (10 mass parts), PDCER (25 mass parts), and polyethyleneamine as a hardener, the stepwise cross-linking has been performed at room temperature for 24h and then at 383, 403 or 423K for 15, 30, 40 and 60min. Three-dimensional films containing both epoxy and peroxy groups have been obtained.

Keywords: Epoxide, Peroxide, Polymer cross-linking, Gel-fraction, Film hardness

Aims and background

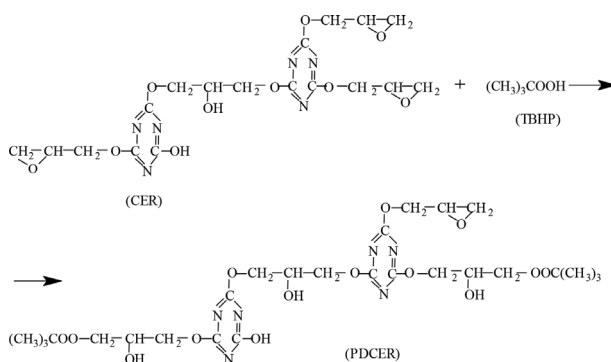
Combinations of polymers provide typically better properties than single polymers.¹ Sufficient interactions between the components are needed.² One good option here is the formation of polymeric networks.^{3,4}

Epoxy resins are widely used *per se* as well for modification of properties of other polymers; applications include protective coatings, glues, and more.⁵⁻⁹ The range of applications may be extended by modification of epoxy resins by hydroperoxides.^{10,11}

To preserve the reactivity of the modified epoxy resins, the reaction between resin and hydroperoxides must proceed in such a way that epoxy groups are only partially exchanged for peroxy fragments.¹⁰ For this purpose, potassium hydroxide,¹¹ quaternary ammonium salts¹² or Crown-ethers¹³ are used as catalysts. Crown ethers are cyclic compounds that include each a ring containing several ether groups. Typically crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e., -CH₂CH₂O-. Oligomers with labile -O-O- bonds and residual epoxy groups synthesised on the basis of dianic epoxy groups are widely used in manufacturing because the mixtures may be formed by both radical and condensation mechanisms.¹³

In this work, we have studied creation of reactive oligomers based on cyanuric epoxy resin (PDCER). The oligomers containing peroxy, epoxy and hydroxy groups may be used as components of polymeric mixtures containing epoxies.

The PDCER may be synthesised according to the following scheme



Experimental

Materials

The product used as initial cyanuric epoxy resin (CER) was synthesised on the basis of cyanuric acid and epichlorohydrine according to the procedure described in Ref. 14. Cyanuric epoxy resin has the number-average molecular mass, $M_n = 540 \text{ g mol}^{-1}$; the epoxy groups content that is the epoxy number, e.n. = 14%.

Tert-butylhydroperoxide (TBHP) was synthesised according to the procedure described in Ref. 15. After vacuum distillation at 308–310K/13–14hPa, TBHP had the following characteristics: $n_D^{20} = 1.4006$; $d_4^{20} = 0.8961$; in Ref. 15, we find 310K/13hPa, $d_4^{20} = 0.8960$, $n_D^{20} = 1.40065$; thus, values are quite close to ours.

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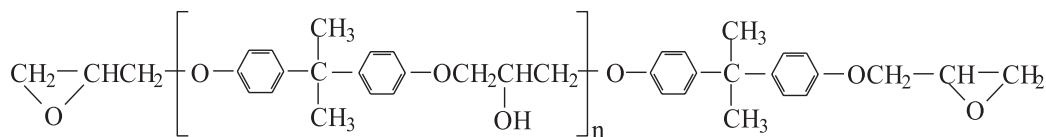
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The system 18-Crown-6 + ZnCl₂ with the molar ratio of 1 : 3 was the catalyst of the reaction between the CER and the TBHP. The amount of the catalyst was 6.7 mol% with respect to 1 g-eq of CER epoxy groups.

To prepare the epoxy + polymer mixtures, we have used:

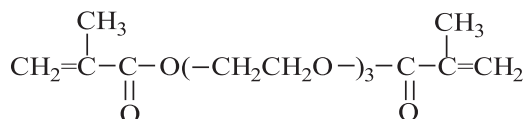
- (a) commercial dianic epoxy resin (ED-20) with the formula



with $M_n = 390 \text{ g mol}^{-1}$ and e.n. 20.4%;

- (b) a petroleum resin with epoxy groups (PREG), a product of C⁹ fraction co-oligomerisation. The C⁹ fraction is the waste product of hydrocarbons pyrolysis to ethylene. The co-oligomerisation takes place in the presence of an oligomeric initiator according to the procedure described in Ref. 16. The following was found for PREG: $M_n = 5050 \text{ g mol}^{-1}$, e.n. = 0.5%, bromine number = 14.0 g Br₂/100 g product;

- (c) oligoesteracrylate (TGM-3) with the formula



with $M_n = 280 \text{ g mol}^{-1}$;

- (d) polyethylenepolyamine (PEPA), a hardener used without additional purification.

Analytical methods

The active oxygen content ($[O]_{act}$) in PDCER was determined using the iodometric method.¹⁷ It is a redox titration method in which the appearance or disappearance of elementary iodine indicates the end point.

The epoxy number was determined using a method described in Ref. 18. It is the number of gram-equivalents of epoxy groups per 100 g of a given polymer. The molecular mass was determined by means of cryometry in dioxane. IR-spectra were recorded using a Specord M-80 spectrophotometer within the absorption range of 400–4000 cm⁻¹. The gel-fraction content (G, %) in cross-linked samples was determined using extraction of grinded polymeric films by acetone in a Soxhlet apparatus for 14 h. The polymeric film hardness (H, relative units) was determined using a Persoz type pendulum device at room temperature. There is a pendulum swinging on two balls resting on a coated test panel. The amplitude of pendulum's oscillations decreases more rapidly on softer surfaces. Therefore, the measure of the material hardness is the number of oscillations made by the pendulum within the specified limits of amplitude determined by accurately positioned photo sensors.

CER+TBHP reaction

The reaction was studied in a three-necked reactor equipped with a mechanical stirrer, a backflow condenser

and a thermometer. The reactor loaded with CER and TBHP was heated to 313, 323 or 328 K. Then the catalyst was added as 25% aq. solution of 18-Crown-6 and 20% aq. solution of ZnCl₂. The synthesis was carried out for 30, 60, 90, 180, or 240 min. Toluene was added to separate the catalytic mixture. The organic layer was washed by water. The solvent was distilled under vacuum at

the temperatures not higher than 328 K. The product so obtained was dried at the temperature of 323 K and the residual pressure of 1–2 hPa until the mass became constant. The epoxy groups content, active oxygen content and molecular mass of the synthesised product were determined.

PDCER synthesis

The synthesis was carried out in a three-necked reactor. One-hundred gram of CER and 300 mL of acetone were loaded. The mixture was heated to 323 K. Then 98.9 g of TBHP, 5.7 g of 18-Crown-6 as 25% aq. solution and 8.9 g of ZnCl₂ as 20% aq. solution were added under continuous stirring. The process time was 9 h. The catalytic system was separated and the oligomer was dried under vacuum. We obtained 133 g of PDCER.

Crosslinking

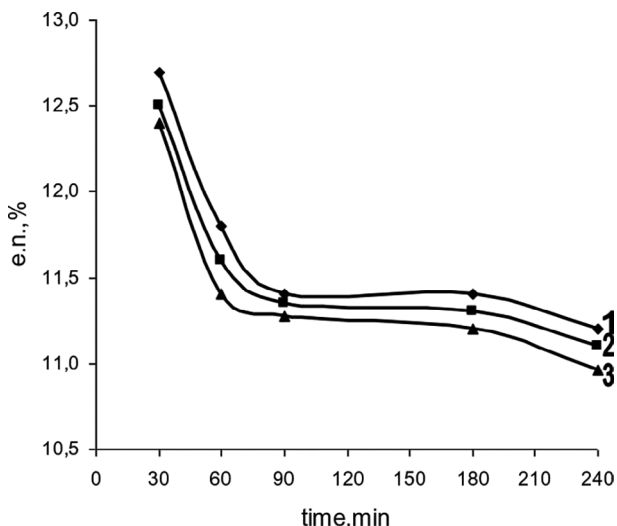
A mixture was created from the components by mixing until a homogeneous mass was obtained. Then PEPA was added, the mixture was mixed again and applied over glass plates of standard size. Crosslinking was carried out stepwise: first at room temperature for 24 h, then by maintaining at 383, 403 or 423 K for 15, 30, 45, and 60 min. The process was controlled by the determination of gel-fraction content and hardness of the films so obtained.

Optimisation of PDCER synthesis

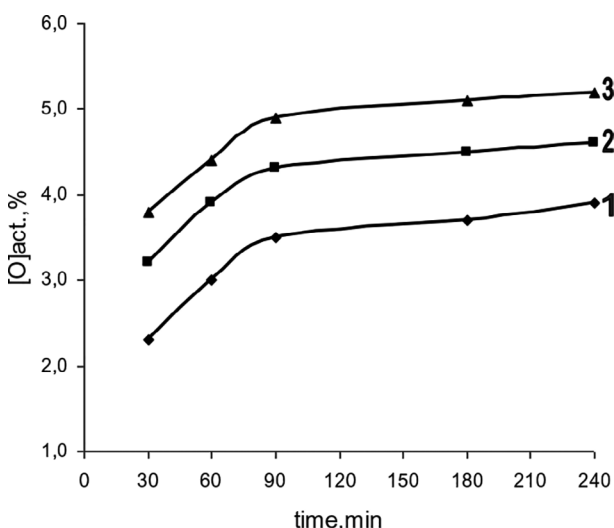
Taking into account our previous results,¹³ we established that the reaction between epoxy groups of the resin and hydroperoxide successfully proceeds using 18-Crown-6 + ZnCl₂ catalytic system with the molar ratio of 1 : 3. That is why this system was used for the synthesis of reactive oligomers based on CER and TBHP.

The experimental results showing the effect of temperature and process time on the characteristics of obtained PDCER are displayed in Figs. 1–3.

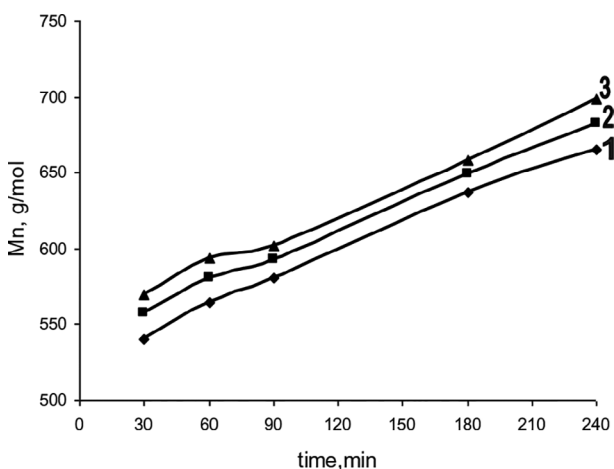
When processing time increases (Fig. 1), the epoxy groups content decreases. The largest decrease is observed in the first 90 min. Further increase of the process time practically does not affect the amount of epoxy groups in PDCER so synthesised. The temperature does not have a significant effect on the amount of epoxy groups, but at 333 K the mixture becomes dark. This fact indicates the presence of side reactions. Therefore, the temperature of 323 K is selected as optimum temperature. The content of peroxy groups at 323 K for 90 min is 4.3% (Fig. 2).



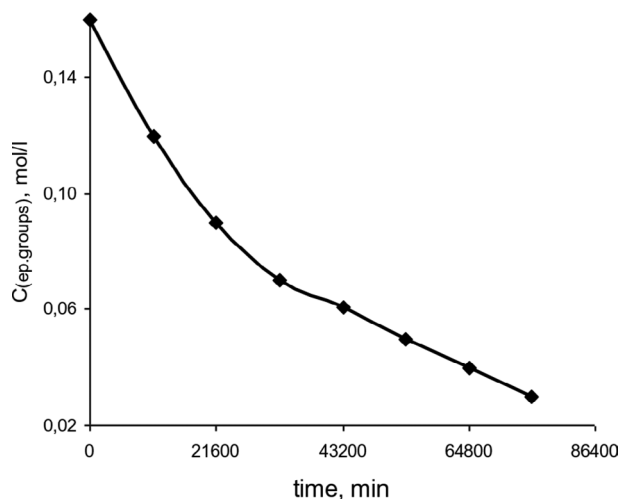
1 Dependence of epoxy number on the temperature and process time: 313K (1); 323K (2) and 333K (3)



2 Dependence of active oxygen content on the temperature and process time: 313K (1); 323K (2) and 333K (3)



3 Dependence of molecular mass on the temperature and process time: 313K (1); 323K (2) and 333K (3)



4 Dependence of epoxy groups concentration on the process time at 323K

The molecular mass of synthesised PDCER practically does not depend on the temperature whereas the reaction time has a significant effect (Fig. 3). Therefore, in order to determine the process time during which only a half of epoxy groups in the initial CER may be substituted for peroxy fragments, we studied the change of the epoxy groups concentration (Fig. 4).

We found that a sufficient decrease of the epoxy groups concentration is achieved after 9h. The results so obtained were taken into consideration during the development of PDCER synthesis procedure given in PDCER synthesis subsection. Our PDCER is characterised by $M_n = 1210 \text{ g mol}^{-1}$, $[\text{O}]_{\text{act}} = 5.3\%$ and $\text{e.n.} = 6.9\%$. The product is soluble in acetone, 1,4-dioxane and other organic solvents. It is stable during storage under normal conditions without significant change of the active oxygen content.

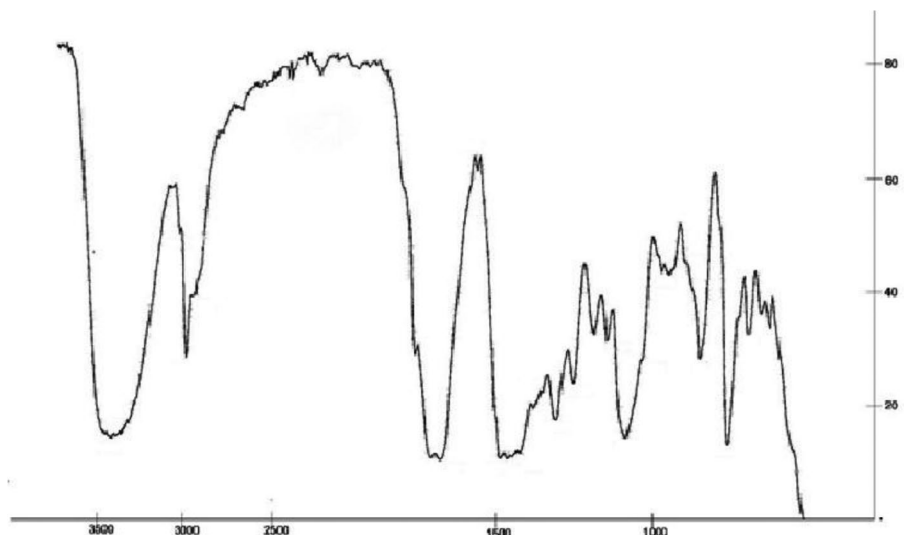
Spectroscopy results for PDCER

To confirm the structure of the synthesised PDCER, we have recorded its IR-spectrum (Fig. 5).

PDCER cross-linking

The possibility of using synthesised PDCER for cross-linking of mixtures based on the commercial dianic epoxy resin ED-20 has been studied by the procedure described in Crosslinking subsection. The mixture II was taken as an example. Its composition is represented in Table 1. The mixture I was taken for the comparison (it contained no PDCER). The obtained results are presented in Table 2.

As expected, we find that the gel-fraction content and film hardness depend upon cross-linking conditions and composition of epoxy-oligomeric mixtures. At room temperature, cross-linking of the mixture I (without PDCER) takes place only owing to the interaction of epoxy groups of the ED-20 resin and PREG with primary amino groups of PEPA hardener. During heating, additional cross-linking occurs owing to the reaction between unreacted epoxy groups with secondary amino groups of PEPA molecules or between epoxy groups and the secondary hydroxyl groups of the resin. At and above 383K, the homopolymerization of TGM-3 molecules is also



5 IR-spectrum of PDCER

Table 1 Composition of epoxy-oligomeric mixtures

Component	Components content (mass particles)	
	I	II
Dianic epoxy resin ED-20	95	70
PDCER	–	25
Petroleum resin with epoxy groups (PREG)	5	5
TGM-3	10	10
Polyethylenepolyamine (PEPA)	14	14

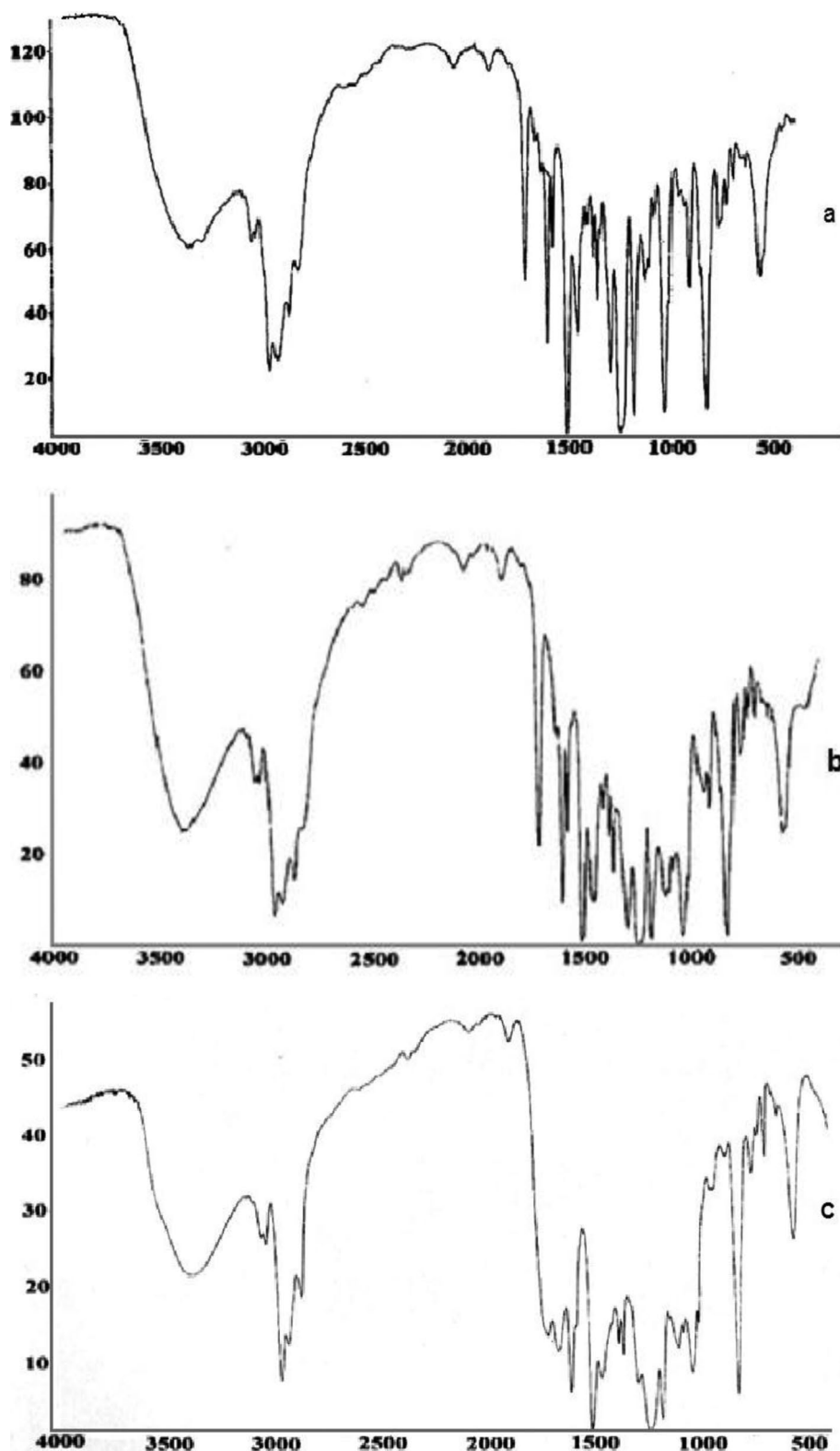
possible in the presence of air oxygen. Moreover, an increase of temperature to 403 or 423K affects only little the increase of gel-fraction content. We see that compositions in the Series I (without PDCER) have hardness after 60min practically the same after curing at 383 or 403K; the hardness after curing at 423K is higher. In Series II, the hardness goes symbatically with the curing temperature.

The introduction of PDCER into the polymeric mixture (mixture II) decreases the gel-fraction content during cross-linking at room temperature on one hand and increases this value during heating on the other hand (Table 2).

Moreover, we observe a considerable increase of the amount of insoluble products at 403K and higher temperatures. This means that PDCER molecules with labile –O–O– groups participate in the formation of insoluble products at elevated temperatures. At room temperature, cross-linking in the mixture II takes place owing to the interaction between PEPA primary aminogroups and epoxy groups of ED-20 resin and PRE, as well as PDCER oligomer. Since the total amount of epoxy groups in the mixture II is less than in the mixture I, the amount of insoluble products in the mixture II cross-linked at room temperature is less in comparison with the mixture I. PDCER molecules participate in the formation of three-dimensional structures owing to the reaction of epoxy groups with PEPA and preservation of peroxy groups. Heating of the mixture II decomposes –O–O– bonds, with the formation of free radicals capable of starting polymerisation involving double bonds of both TGM-3 oligoesteracrylate and partially cross-linked PREG. The higher the temperature, the higher is the rate of peroxy groups decomposition and the higher the content of insoluble products in the mixture (Table 2). While in the case of the mixture I, at 383K and higher temperatures, TGM-3 molecules may be homopolymerized and not bonded with the molecules of cross-linked ED-20 and PREG; in the case of the mixture II, we have TGM-3 molecules chemically bonded with the molecules of the main matrix. To confirm this assumption, we studied the mixture II by

Table 2 Dependence of gel-fraction content (G) and films hardness (H) on the cross-linking temperature and time, and mixture composition

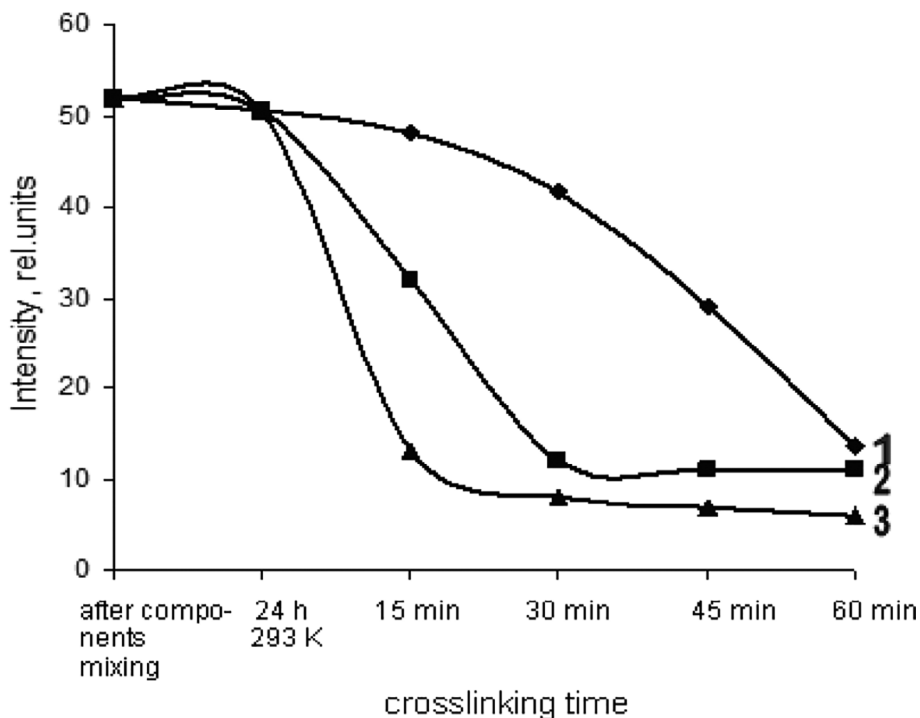
Mixture in accordance with Table 1	T, K	Index	Index value for the cross-linking time, min				
			24h, room temperature	15	30	45	60
I	383	G	75.8	84.5	84.9	85.2	85.7
		H	0.10	0.49	0.61	0.66	0.70
	403	G	75.8	84.6	84.8	85.0	85.3
		H	0.10	0.50	0.62	0.67	0.69
	423	G	75.8	84.7	84.9	85.2	85.3
		H	0.10	0.51	0.62	0.70	0.78
II	383	G	70.1	71.0	72.4	78.1	81.2
		H	0.14	0.38	0.47	0.51	0.58
	403	G	70.1	73.8	77.8	81.9	89.6
		H	0.14	0.40	0.62	0.71	0.76
	423	G	70.1	77.5	83.1	87.7	94.3
		H	0.14	0.46	0.68	0.76	0.80



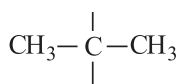
6 IR-spectra of the mixture II before cross-linking *a*, after cross-linking at room temperature for 24h *b*, and after maintaining at 403K for 45min *c*

IR-spectroscopy. With the aim of identification of functional groups in the mixture, we separately recorded the spectra of ED-20 resin, PDCER oligomer, TGM-3 oligoesteracrylate, PREG, and PEPA. The absorption band at 915cm^{-1} typical of the stretching vibrations of the epoxy rings is observed in the spectra of ED-20 resin. The presence of hydroxy groups is confirmed by the absorption band at 3504cm^{-1} . The presence of epoxy groups in PDCER is confirmed by the absorption

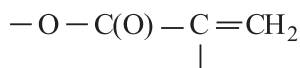
band at 1250cm^{-1} and the presence of hydroxy groups by the absorption band at 3440cm^{-1} . Moreover, the latter band is more intensive compared with that in ED-20, a manifestation of higher concentration of hydroxy groups in PDCER. The presence of peroxy groups in PDCER is confirmed by the doublet of hem-dimethyl deformation vibrations at 1380 and 1360cm^{-1} typical of $(\text{CH}_3)_3\text{C}$ groups. This band coincides with the band of



7 The change of intensity of epoxy groups absorption bands at 915cm⁻¹ during cross-linking of the mixture II at the temperatures of 383 (1), 403 (2) and 423 (3) K



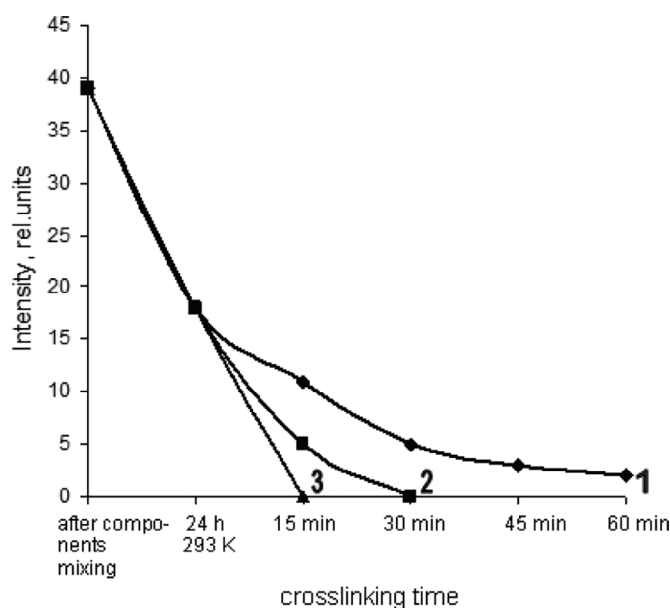
groups, which was found in the spectrum of ED-20 resin but is more intensive in this case. The double bonds in TGM-3 are identified by the absorption band at 1720cm⁻¹ typical of the stretching vibrations of carbonyl group in esteric bond located near the double bond.



The presence of epoxy groups in PREG is confirmed by the absorption band at 914cm⁻¹ and the presence of double bonds at 1601cm⁻¹.

The spectra of the mixture II before cross-linking (Fig. 6a), after cross-linking at room temperature for 24h (Fig. 6b) and at heating to 403K for 45min. (Fig. 6c) are not the same. Before cross-linking, we find the absorption band at 915cm⁻¹ typical of epoxy groups, deformation vibrations doublet at 1384 and 1362cm⁻¹ characterising a fragment of peroxy groups, the absorption band at 1715cm⁻¹ typical of stretching vibrations of unsaturated compound carbonyl group, as well as the absorption band at 1607cm⁻¹ corresponding to the double bond in PREG (Fig. 6a).

After the film cross-linking at room temperature for 24h, the epoxy groups concentration (Fig. 6b) decreases. Moreover, this value tends to zero after heating to 403K and maintaining that temperature for 45min (Figs. 6c and 7). Also, we can see



8 The change of intensity of the absorption band of bond at 1607cm⁻¹ during cross-linking of the mixture II at the temperatures of 383 (1), 403 (2) and 423 (3) K

from Fig. 7 that at 423K the epoxy groups disappear from the mixture after 15min, at 403K – after 30min and at 383K – after more than 1h. The decrease of epoxy groups concentration is accompanied by the intensity increase of absorption band at 3383cm^{-1} (Fig. 6b).

All the above-mentioned results confirm that, at room temperature as well as above it, cross-linking between ED-20, PREG and PDCER takes place owing to the interactions between epoxy groups of the oligomers with PEPA followed by the hydroxy groups formation.

The participation of peroxy groups of PDCER, double bonds of TGM-3 and PREG in cross-linking is confirmed by the decrease of intensity of absorption bands at 1384 and 1362cm^{-1} corresponding to the $(\text{CH}_3)_3\text{C}$ -fragment, and the absorption bands at 1715 and 1607cm^{-1} (Fig. 8) corresponding to the unsaturated fragment in TGM-3 and PREG, respectively.

Thus, our IR-spectroscopy results confirm the participation of synthesised PDCER in the formation of a three-dimensional structure.

A survey of results

Reactive oligomers with labile $-\text{O}-\text{O}-$ bonds, epoxy and hydroxy groups have been synthesised via a modification of cyanuric epoxy resin by tert-butylhydroperoxide in the presence of the catalytic system 18-Crown-6 + ZnCl_2 (molar ratio 1:3). The reaction time considerably affects the oligomer molecular mass and the amount of peroxy and epoxy groups in it.

The presence of above-mentioned groups is confirmed by the chemical analyses and IR-spectroscopy. The presence of peroxy fragments is confirmed by the absorption band at 880cm^{-1} and deformation vibrations doublet at 1380 and 1360cm^{-1} .

Three-dimensional structures of the polymeric films consisting of ED-20 dianic epoxy resin (e.n.=20%), petroleum resin, TGM-3 oligoesteracrylate and reactive oligomer are formed in the presence of both epoxy and peroxy groups.

Partial exchange of the commercial epoxy resin ED-20 for PDCER allows increasing the amount of insoluble products and polymeric films hardness as compared to the mixture without PDCER.

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