

Synthesis and properties of carboxy derivative of Epidian 6 monomethacrylate

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DOI: [dx.doi.org/10.14314/polimery.2016.766](https://doi.org/10.14314/polimery.2016.766)

Abstract: We present the synthesis of an oligomer with carboxy and methacrylic groups based on Epidian 6. The effect of the catalyst nature and amount, solvent nature and process temperature on the rate of the reaction between Epidian 6 monomethacrylate and adipic acid was examined at 313, 323 and 333 K in the presence of 4-dimethylaminopyridine, 1,4-diazobicyclo[2.2.2]octane, and benzyltrimmonium chloride. The synthesized oligomer was characterized using chemical and IR-spectroscopic analyses. We suggest the use of the synthesized product as an active additive to epoxy-oligoesteric blends based on Epidian 5. The chemistry of the film forming process has been determined using IR-spectroscopy.

Keywords: epoxy resin, adipic acid, carboxy group, methacrylic group, crosslinking, gel-fraction, infra red spectroscopy.

Synteza i właściwości karboksylowej pochodnej monometakrylanu Epidianu 6

Streszczenie: Na bazie żywicy epoksydowej Epidian 6 w temp. 313, 323 oraz 333 K w obecności 4-dimetyloamino-pirydyny, 1,4-diazobicyklo[2.2.2]oktanu oraz chlorku benzylotriamoniowego otrzymywano oligomery zawierające grupy karboksylowe i metakrylowe. Zbadano wpływ ilości i rodzaju użytego katalizatora, rozpuszczalnika oraz temperatury procesu na szybkość reakcji monometakrylanu Epidianu 6 z kwasem adypinowym. Zsyntetyzowany oligomer charakteryzowano metodami chemicznymi i na podstawie analizy FT-IR. Przebieg procesu formowania cienkich warstw (błon) badano za pomocą spektroskopii w podczerwieni. Uzyskany produkt może być wykorzystany jako aktywny dodatek do mieszanin epoksydowo-oligoestrowych wytwarzanych z żywicy Epidian 5.

Słowa kluczowe: żywica epoksydowa, kwas adypinowy, grupa karboksylowa, grupa metakrylowa, sieciowanie, frakcja żelowa, spektroskopia IR.

Oligomers (polymers) with different reactive groups are widely used as the binders between polymeric components in the blend [1–3] allowing the combination of polymeric compounds obtained *via* both condensation and polymerization reactions into a single, three-dimensional network. Epoxy resins may be used to obtain oligomers with different reactive groups due to the fact that epoxy resin molecules contain epoxy groups that are capable of conversion into other, functional groups [4, 5].

In the last decade, epoxy oligomer based compounds with unsaturated acrylate groups, as well as epoxy or peroxy groups, were synthesized [6–8]. At the same time, epoxy derivatives with carboxy and epoxy or peroxy groups were obtained [9]. Oligomers based on epoxy

resins with unsaturated acrylate and carboxy groups are not described in the literature.

In this work we obtain an oligomer based on Epidian 6 with carboxy and methacrylic groups in its structure. Epidian 6 is a diglycidyl ether of bisphenol A. The synthesis of the carboxy derivative of Epidian 6 monomethacrylate (CDEMMA) is represented by Scheme A.

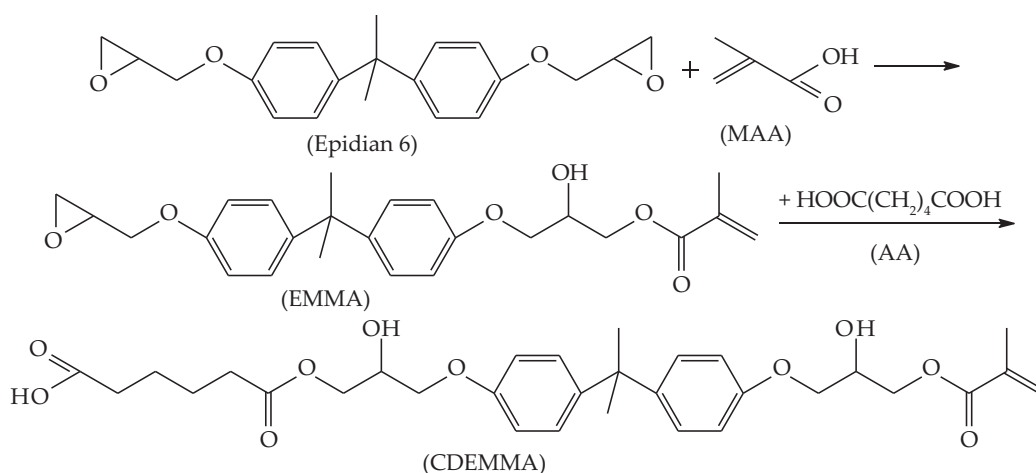
One can see from Scheme A that CDEMMA may be obtained in two stages. At the first stage an oligomer with free epoxy and methacrylic groups (EMMA) is formed due to the reaction between Epidian 6 and methacrylic acid (MAA). The procedure of EMMA synthesis was developed earlier [8]. EMMA was used as an initial compound to obtain an oligomer with carboxy and methacrylic groups (CDEMMA).

The aim of present work is to develop the CDEMMA synthesis procedure and establish the possibility of its practical application. The synthesized product may be used as an active additive for the production of polymer films based on Epidian 5 industrial resin, the crosslinking of which takes place in the presence of polyamine curing agents.

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Scheme A

EXPERIMENTAL PART

Materials

– Epidian 6 was supplied by Ciech (Poland). Methacrylic acid (MMA) was purchased from Merck (Germany) and was used as received.

– EMMA was synthesized using Epidian 6 and MMA according to the procedure described in [8]. It was characterized by a molecular mass (M_n) of 420 g/mol, content of epoxy groups of 10.8 and bromine number of 36.3 g Br₂/100 g product.

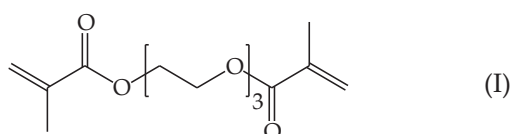
– Adipic acid (AA) was supplied by DuPont (Monsanto, USA).

– Benzyltriethylammonium chloride (BTEAC), 4-dimethylaminopyridine (4-D), 1,4-diazobicyclo[2.2.2]octane (DABCO), 2-propanol, and 1,4-dioxane were used as received without additional purification (Sigma-Aldrich, Germany).

– Petroleum ether was a fraction 313–343 K. Density $d_4^{20} = 0.650 \text{ g/cm}^3$.

– Epidian 5 (Ciech, Poland) was used as an initial epoxy resin to obtain epoxy-oligoesteric mixtures. Its molecular mass (M_n) was 390 g/mol and content of epoxy groups = 20.0 %.

– Oligoesteracrylate (TGM-3, Ukraine) is an esterification product of methacrylic acid and triethyleneglycol in the solvent medium in the system excluding the contact between the reaction medium and metal surface. Its molecular mass is 286 g/mol [Formula (I)]:



– Polyethylenepolyamine (PEPA), (KTM Krym, Ukraine) and tetraethylenetetramine (TETA), (Z-1, Cedar, Poland) were the curing agents and were used as received without additional purification.

Procedure for studying the reaction kinetics

The reaction between EMMA and AA was studied in a three-necked reactor equipped with a mechanical stirrer, reflux condenser, and thermometer. EMMA, solvent, and AA were placed into the reactor and heated to a predetermined temperature with an accuracy of $\pm 1 \text{ K}$. Then, the catalyst was added. After defined periods of time, samples of 0.5 cm^3 were withdrawn and the acid concentration [C_a (mol/dm³)] was determined.

SYNTHESIS OF CDEMMA

CDEMMA was synthesized in a three-necked reactor in the medium of inert gas. 100 g of EMMA, 32.7 g of adipic acid (AA) dissolved in 350 cm^3 of 2-propanol and 15.3 g of benzyltriethylammonium chloride (BTEAC) as a 60 % aqueous solution were loaded into a reactor, heated to 353 K and stirred for 5 hrs. Then, the mixture was cooled to room temperature and placed into a separating funnel. 350 cm^3 of toluene was added, the catalyst was washed out and the mixture was reduced under vacuum at 313 K until 1/3 of the initial volume remained. The residue was poured into petroleum ether. The obtained viscous product (CDEMMA) was dried first in air and then in a vacuum drier at 303 K until the mixture weight became constant. We obtained 115.5 g of CDEMMA (yield of 87 %), which is soluble in the majority of organic solvents and does not contain epoxy groups. The product characteristics are: molecular mass 570 g/mol, carboxy groups content 7.16 %, bromine number 25.1 g Br₂/100 g product.

The investigation procedure of epoxy-oligoesteric mixtures crosslinking

The mixtures were prepared by pouring the epoxy-oligoesteric mixture over glass plates of 75 x 35 mm. The mixture components were blended with PEPA or TETA curing agent. The crosslinking reaction was carried out stepwise: at first – at room temperature for 24 hrs and

then at 383, 403, or 423 K for 15, 30, 45, 60, or 75 min. The process was controlled by measuring the gel-fraction content (G) in a Soxhlet apparatus after extraction by acetone for 12 hrs and the hardness (H , relative units) using a M-3 pendulum device at room temperature (ISO 1522).

Methods of testing

IR-spectroscopic investigations of CDEMMA

IR-spectroscopic investigations of CDEMMA were carried out using a Specord M40 spectrophotometer (Bruker, Germany). The samples were prepared as the films formed from CDEMMA solution in acetone, which were applied over the plates with KBr (layer thickness was 0.03 mm). The spectra were recorded in the range of 4000–400 cm^{-1} with an integration time of 1 s.

IR-spectroscopic studies of epoxy-oligomeric mixtures

IR-spectra of epoxy-oligomeric mixtures were recorded using Thermo an Electron Corporation-Niclet 8700 instrument in the laboratory of Gdansk University of Technology. The instrument is equipped with a Specac Golden Gate device with ATR diamond crystal. The epoxy-oligomeric mixture prepared according to the procedure described previously was applied as a thin layer over KBr plates and the IR-spectrum was recorded. The plate with the film was placed into a dessicator, left for 24 hrs at room temperature and the spectrum was recorded. Then, the sample was heated to 383 K for 30 min followed by spectrum recording and, finally, to 403 K (30 min) and 423 K (30 min).

RESULTS AND DISCUSSION

Kinetic regularities of CDEMMA synthesis

To determine the conditions for the reaction between EMMA and AA, we studied the effect of the catalyst nature and amount, solvent nature, process temperature and time on the reaction rate. The results are presented in Fig. 1 and Fig. 2, as well as in Table 1.

The reaction between AA and EMMA is a second order reaction (Fig. 1). At the same time, this reaction has almost an equal reaction rate in the presence of BTEAC and 4-D catalysts. While using DABCO, the reaction rate decreases (Fig. 1, Table 1). Taking into account the availability of BTEAC, it was chosen as the reaction catalyst. The decrease in reaction temperature and catalyst amount decreases the effective rate constant (Table 1). The nature of the reaction medium has a slight effect on the reaction rate (Table 1). The effect of reaction time on the epoxy group concentration C_{ep} is represented in Fig. 2. After 4–5 hrs, the epoxy group concentration is less than 0.02 mol/dm^3 , *i.e.*, less than the inaccuracy of measurements. The obtained results were used to de-

velop the procedure of CDEMMA synthesis, described earlier.

IR-spectroscopic investigations of the structure

The structure of the synthesized product was confirmed by IR spectroscopy (Fig. 3). The absorption band at 912 cm^{-1} is absent in the synthesized oligomer, indicating the absence of free epoxy groups that were substituted for carboxy fragments according to Scheme A. The presence of the methacrylate fragment is proved by the absorption band at 1636 cm^{-1} , corresponding to the double bond conjugated with a carbonyl group $>\text{C}=\text{O}$. The presence of a free carbonyl group is confirmed by the stretching vibrations at 1720 cm^{-1} . In the initial EMMA, the carbonyl group of the ester bond is proved by the band at 1728 cm^{-1} . The so called ester band ($-\text{C}-\text{O}-\text{C}-$)

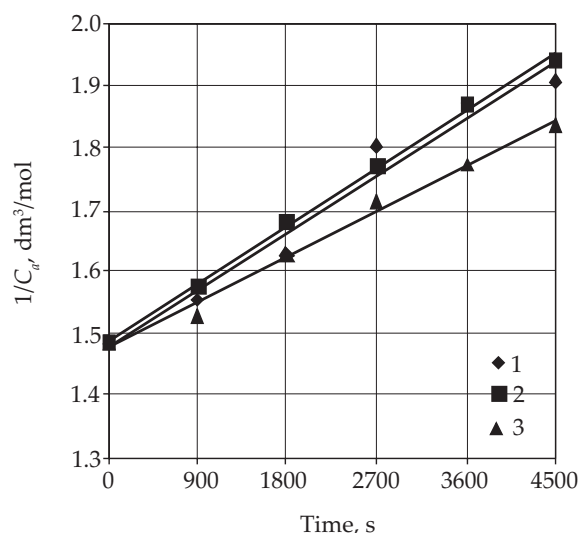


Fig. 1. Kinetic anamorphoses in $1/C_a - t$ coordinates for the reaction between EMMA and AA at 353 K in 2-propanol solvent using different catalysts: 1 – BTEAC, 2 – 4-dimethylaminopyridine, 3 – DABCO, at 30 mol % relative to AA; the AA amount is 1 mole per 1 g-eq. of EMMA epoxy group

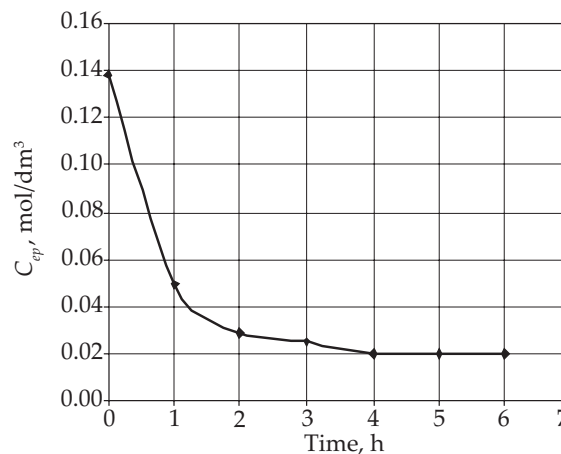


Fig. 2. Epoxy group concentration (C_{ep}) vs. the reaction time (t) between EMMA and AA at 353 K in 2-propanol solvent; catalyst – BTEAC at 30 mol % relative to AA, the AA amount is 1 mole per 1 g-eq. of EMMA epoxy group

Table 1. Effective rate constants for the reaction between AA and EMMA

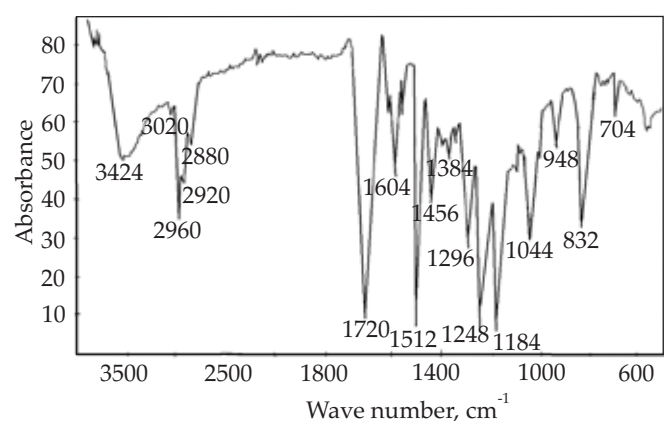
Catalyst and its amount relative to AA ¹⁾ , mol %	Solvent	Reaction temperature, K	$K_f \cdot 10^3$, dm ³ /(mol · s)
BTEAC; 30.0	2-propanol	353	10.71 ± 0.16
4-Dimethylaminopyridine; 30.0	2-propanol	353	11.45 ± 0.34
DABCO; 30.0	2-propanol	353	7.96 ± 0.21
BTEAC; 5.0	2-propanol	343	1.25 ± 0.13
BTEAC; 10.0	2-propanol	343	2.5 ± 0.20
BTEAC; 20.0	2-propanol	343	3.6 ± 0.18
BTEAC; 30.0	2-propanol	343	4.58 ± 0.26
BTEAC; 40.0	2-propanol	343	7.22 ± 0.35
BTEAC; 30.0	2-propanol	333	3.44 ± 0.19
BTEAC; 30.0	1,4-dioxane	353	12.56 ± 0.21

¹⁾ AA content – 1 mole per 1 g-eq. of EMMA epoxy group; BTEAC was used as 60 % aqueous solution.

is also present at 1044 and 1296 cm⁻¹. The increase in intensity of the absorption band at 3424 cm⁻¹ (compared to that in EMMA spectrum), corresponding to the stretching vibrations of the secondary OH-group, indicates the AA molecules bonding with EMMA due to the opening of the epoxy ring.

Crosslinking in the presence of CDEMMA

The crosslinking properties of the synthesized CDEMMA were investigated according to the procedure described earlier. PEPA or TETA were used as curing agents.

**Fig. 3.** IR spectrum of CDEMMA**Table 2.** Composition of epoxy-oligoesteric mixtures

Component	Component content, weight part					
	I	II	III	IV	V	VI
Epidian 5	90	90	95	80	70	90
CDEMMA	–	10	5	20	30	10
TGM-3	10	–	–	–	–	–
PEPA ¹⁾	12.6	12.6	13.3	11.2	9.8	–
TETA	–	–	–	–	–	12.6

¹⁾ The amount of amine curing agent was calculated, taking into account the content of epoxy groups in the mixture, *i.e.*, 14 g of amine curing agent is necessary for 20 g of epoxy groups.

The composition of the mixtures used to prepare epoxy-oligoesters are presented in Table 2. The results are given in Table 3.

The gel-fraction content and hardness of the obtained films depend on mixture composition, crosslinking time, and temperature.

While comparing mixtures I and II (Table 2), one can see that both hardness and gel-fraction content are considerably higher for mixture II (with CDEMMA), regardless of crosslinking conditions. In the initial stages of Epidian 6 crosslinking in the presence of PEPA, a great amount of heat is released followed by a mixture of heating and polymerization of double bonds in CDEMMA molecules. Thus, the resulting films have the hardness of 0.64 rel. units and content of insoluble products of 81.3 % at room temperature after 24 hrs. Then, we studied the effect of CDEMMA on the crosslinking of epoxy-oligomeric mixtures (Table 3). An increase in CDEMMA amount from 5 to 30 weight parts (mixtures II–V) decreases the gel-fraction content but increases the film hardness both at room and elevated temperatures. The reason is that the share of crosslinked molecules formed due to Epidian 6 crosslinking increases with higher CDEMMA amounts.

While studying the effect of temperature on the content of insoluble products and hardness, the temperature of 403 K was found to be optimal.

Table 3. Dependence of gel-fraction content and film hardness on temperature, crosslinking time, and mixture composition

Temperature K	Mixture number according to Table 2	Index ¹⁾	Index value during crosslinking time, min					
			24 hrs under normal conditions	15	30	45	60	75
383	II	G	81.3	86.9	88.7	92.4	93.9	94.6
		H	0.64	0.76	0.82	0.83	0.84	0.87
403	I	G	71.7	80.1	85.5	87.6	88.6	89.4
		H	0.29	0.50	0.63	0.77	0.79	0.80
	II	G	81.3	87.8	89.6	92.3	94.5	95.3
		H	0.64	0.76	0.80	0.83	0.85	0.88
	III	G	79.9	87.5	87.9	92.0	93.0	94.0
		H	0.50	0.75	0.79	0.81	0.82	0.85
	IV	G	77.5	86.4	88.4	92.1	92.3	92.6
		H	0.66	0.77	0.79	0.85	0.85	0.88
	V	G	75.6	85.9	88.1	91.6	91.7	92.0
		H	0.67	0.77	0.82	0.86	0.88	0.90
	VI	G	79.9	85.8	86.6	90.1	92.5	93.3
		H	0.61	0.80	0.84	0.86	0.88	0.88
423	II	G	81.3	90.1	92.9	94.3	95.4	96.3
		H	0.64	0.85	0.87	0.89	0.90	0.90

¹⁾ G – gel-fraction content, %; H – film hardness determined by M-3 pendulum device, rel. units.

The values of the gel-fraction and hardness do not depend on the kind of curing agent (mixtures II and VI, Table 3). Only at room temperature are these values slightly higher for mixture II (PEPA as a curing agent).

To confirm the above-mentioned chemistry of the polymeric network formation, we carried out IR spectroscopic investigations according to the procedure described earlier. For this purpose, mixture VI with CDEMMA (Table 2) was taken.

The structural changes were controlled by absorption bands at 918 cm^{-1} , corresponding to the asymmetric stretching vibrations of the epoxy ring; at 3440 cm^{-1} – the hydroxy group; at 1610 cm^{-1} – double bond and 1720 cm^{-1} – carbonyl group.

The spectra recorded after mixture preparation, after exposure at room temperature for 24 hrs and after heating, are different (Fig. 4). The intense absorption band at 918 cm^{-1} in the starting mixture corresponds to the epoxy ring in Epidian 6. Mixture exposure for 24 hrs at room temperature and further heating results in the disappearance of this group. This means that the epoxy groups react with TETA molecules followed by epoxy ring opening and hydroxy group formation (Fig. 5).

The most intense formation of hydroxy groups is observed at 383 K. Further heating decreases their number, indicating the possibility of their chemical reaction with the carboxy group of CDEMMA.

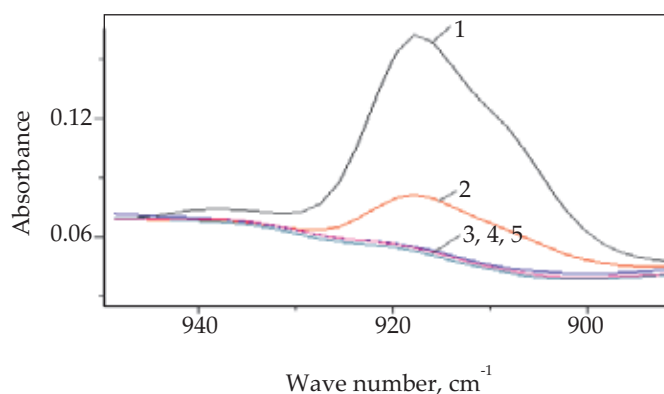
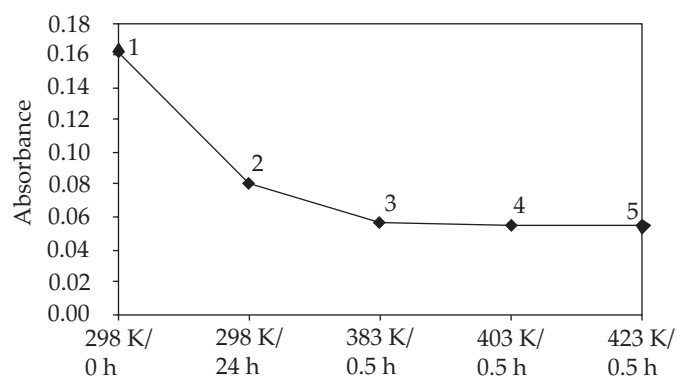


Fig. 4. Absorbance of the band at 918 cm^{-1} and its change: 1 – after preparation of the polymeric mixture, 2 – exposure at room temperature for 24 hrs, 3 – heating for 30 min at 383 K, 4 – heating for 30 min at 403 K, 5 – heating for 30 min at 423 K

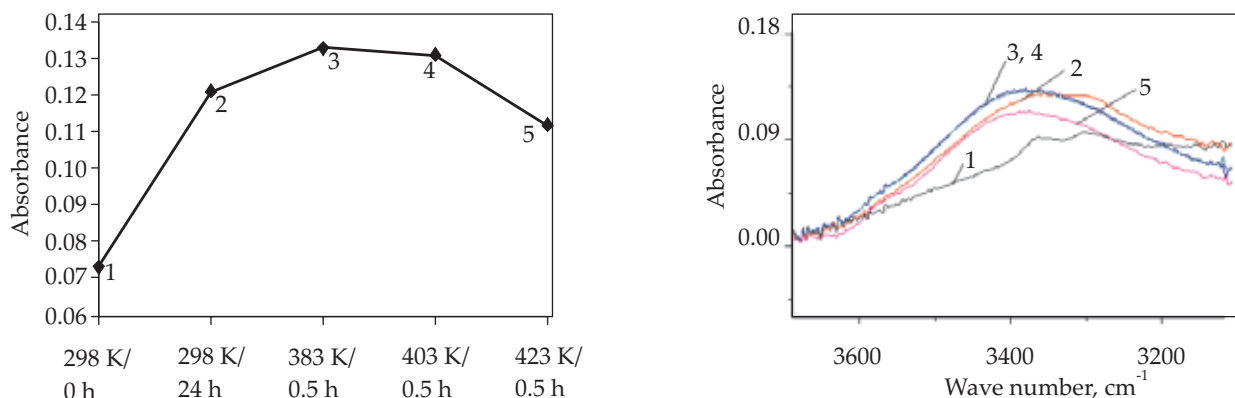


Fig. 5. Absorbance of the band at 3440 cm^{-1} and its change: 1 – after preparation of the polymeric mixture, 2 – exposure at room temperature for 24 hrs, 3 – heating for 30 min at 383 K, 4 – heating for 30 min at 403 K, 5 – heating for 30 min at 423 K

The results represented in Figs. 6 and 7 show the participation of CDEMMA carboxy and methacrylic fragments in the formation of the three-dimensional structure. Due to heat release accompanied by the reaction of the epoxy group with PEPA, partial polymerization occurs at room temperature relative to double bonds. The decrease in intensity of the absorption bands at 1720 cm^{-1} ,

corresponding to the vibrations of the carboxy group in esters of unsaturated acids (Fig. 6), and 1610 cm^{-1} , corresponding to double bonds (Fig. 7) indicates the above-stated inference. Further heating favors the processes due to which the amount of bonds characterizing the

$=\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}-$ group is decreased.

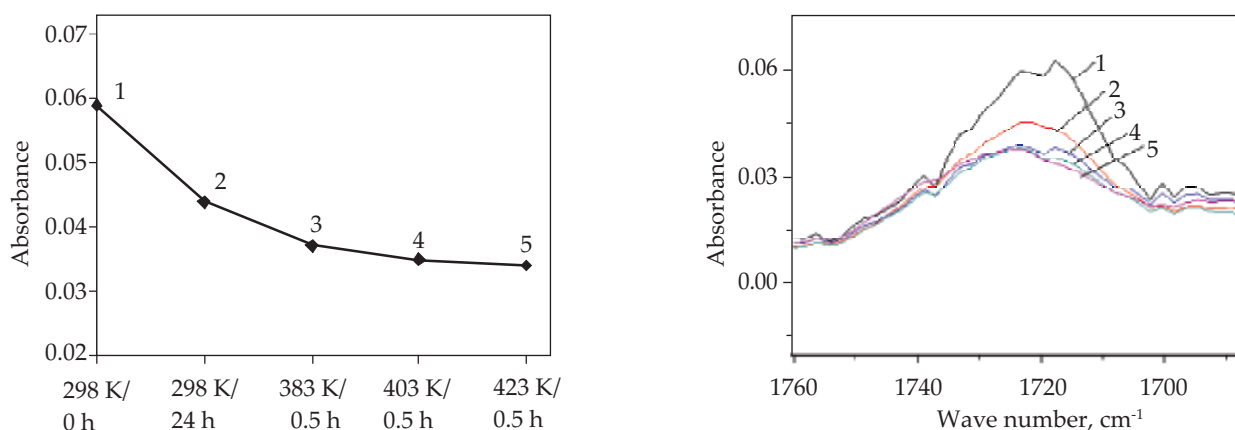


Fig. 6. Absorbance of the band at 1720 cm^{-1} and its change: 1 – after preparation of the polymeric mixture, 2 – exposure at room temperature for 24 hrs, 3 – heating for 30 min at 383 K, 4 – heating for 30 min at 403 K, 5 – heating for 30 min at 423 K

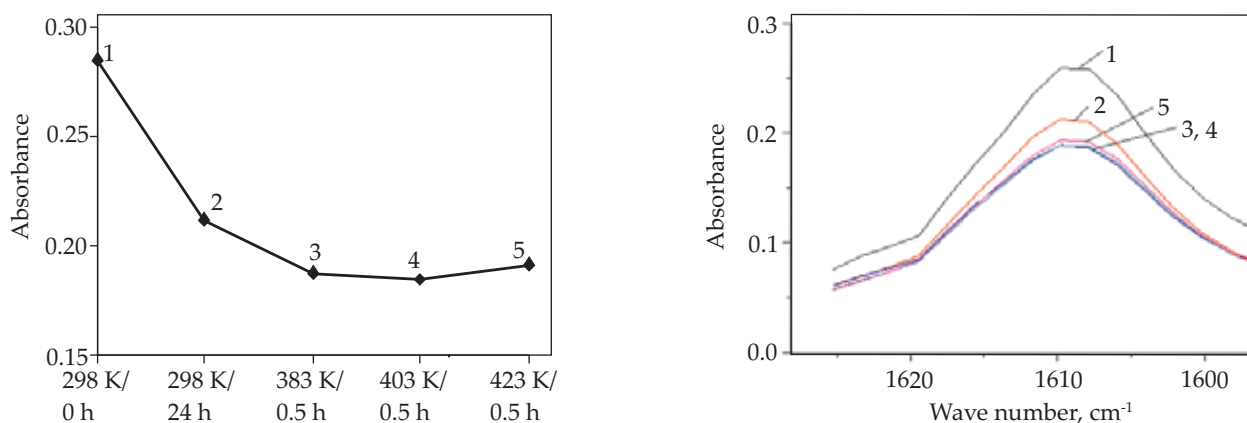


Fig. 7. Absorbance of the band at 1610 cm^{-1} and its change: 1 – after preparation of the polymeric mixture, 2 – exposure at room temperature for 24 hrs, 3 – heating for 30 min at 383 K, 4 – heating for 30 min at 403 K, 5 – heating for 30 min at 423 K

The obtained results show that, in mixture VI (Table 2), all components participate in film formation. At room temperature, the initial Epidian 5 and CDEMMA form a structure in the presence of TETA. In this structure, CDEMMA molecules are grafted to the main matrix based on Epidian 5. Moreover, free methacrylic fragments of CDEMMA are partially copolymerized by double bonds and form insoluble products. The increase in temperature leads to the reaction between unreacted epoxy groups with the secondary amine groups of TETA and hydroxy groups which were formed at the first stage. After further heating, copolymerization of CDEMMA fragments takes place due to oxygen in the air and, as a result, the amount of insoluble products is increased (Table 3).

CONCLUSIONS

We synthesized a new oligomeric product based on Epidian 6. Methacrylic end fragments, free carboxy, and hydroxy groups are present in its structure. The presence of different functional groups in the synthesized product allows its use as a binder in complex polymer mixtures consisting of unsaturated and polycondensation polymers.

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Received 26 X 2015.