

*Michael Bratychak¹, Bogdana Bashta¹, Piotr Bruzdziak², Olena Astakhova¹
and Olena Shyshchak¹*

CROSS-LINKING OF EPOXY-OLIGOESTERIC MIXTURES IN THE PRESENCE OF CARBOXY-CONTAINING DERIVATIVE OF ED-24 EPOXY RESIN

¹Lviv Polytechnic National University,

12, St. Bandera str., 79013 Lviv, Ukraine; mbratych@polynet.lviv.ua

²Gdansk University of Technology, 11/12 Gabriela Narutowicza str.,
PL 80-952, Gdansk, Poland; piotr.bruzdziak@pg.gda.pl

Received: September 19, 2012 / Revised: October 16, 2012 / Accepted: November 23, 2012

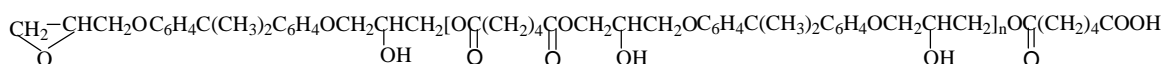
© Bratychak M., Bashta B., Bruzdziak P., Astakhova O., Shyshchak O., 2013

Abstract. Cross-linking of epoxy-oligomeric mixtures has been studied at room temperature and at heating to 383, 403 and 423 K for 15, 30, 45, 60 and 75 min in the presence of polyethylenepolyamine. The mixtures consist of industrial ED-20 epoxy resin, oligoesteracrylate TGM-3 and carboxy-containing derivative of ED-24 epoxy resin. The effect of mixture composition, temperature and process time on the gel-fraction content and hardness of polymeric films has been examined. Using IR-spectroscopy the chemism of network formation has been determined.

Keywords: epoxy resin, oligoesteracrylate, carboxy group, IR-spectroscopy, acid number, cross-linking, gel-fraction, film hardness.

1. Introduction

Epoxy resins are mixed with other oligomers to reduce the price of wares based on epoxies on the one hand, and to improve the operational characteristics of the



where $n = 2-3$

Polyethylenepolyamine (PEPA) was the hardener.

2. Experimental

2.1. Materials

The used industrial ED-20 dianic epoxy resin had a molecular mass (M_n) of 390 g/mol and epoxy number ($e.n.$) of 20.0 %. Its formula is given in [4].

materials on their basis – on the other [1]. Among all epoxy-oligomeric mixtures the mixtures containing dianic epoxy resin, as well as oligomers with unsaturated double bonds are of special attention [2]. In most cases the unsaturated oligomers are plasticizers of epoxy mixtures and are not chemically bound with polymeric network of cross-linked epoxy resin [3]. Such plasticization allows to decrease the wares brittleness but does not improve the operational properties. That is why earlier it was suggested to introduce the peroxy derivative of ED-20 epoxy resin, (3-aminopropyl)triepoxysilane [2] or fluorine-containing derivatives of epoxy resins [4, 5] to the mixture to improve the products quality. On the other hand it is known [6] that films adhesion properties are improved due to the introduction of compounds with carboxy and esteric groups.

This work deals with the investigations of epoxy-oligomeric mixtures cross-linking based on industrial ED-20 dianic epoxy resin and TGM-3 oligoesteracrylate in the presence of carboxy-containing derivative of ED-24 epoxy resin (CDER) of the general formula:

Oligoesteracrylate TGM-3 was used as received without additional purification. Its M_n 280 g/mol, formula is given in [4].

CDER was synthesized by the procedure described in [7]. It was found: M_n 1880 g/mol, $e.n.$ 4.1 % and carboxy groups content 3.5 %.

PEPA was used as received without additional purification.

2.2. Experimental Procedure

2.2.1. Cross-linking of epoxy-oligomeric mixtures

Epoxy-oligomeric mixtures, the composition of which is given in Table 1, were prepared as follows: all components (except PEPA) were mixed at room temperature till the homogeneous mass was obtained. Then PEPA was added under stirring. The mixture was vacuumized till bubbles disappeared. The obtained product was poured over degreased glass plate of standard size. Cross-linking of polymeric mixtures was carried out stepwise: first at room temperature for 24 h and then at heating to 383, 403 and 423 K for 15, 30, 45, 60 and 75 min. The structural changes were controlled by the determination of gel-fraction content and films hardness. Gel-fraction was determined using extracting of grinded samples by acetone in a Soxhlet apparatus for 12 h at heating and hardness – using M-3 pendulum device at room temperature.

Table 1

Composition of epoxy-oligomeric mixtures

Component	Component content, mass parts				
	I	II	III	IV	V
ED-20	82	73	55	91	60
CDER	9	18	36	–	40
TGM-3	9	9	9	9	–
PEPA	13	9	9	14	9

2.2.2. Determination of acid number in cross-linked samples

25 ml of KOH solution (0.1 N) in the mixture of 2-propanol+dioxane (ratio 1:1) were added to 0.5-0.6 g of the extracted, dried and grinded product. The obtained mixture was sustained at room temperature for 48 h without stirring. Then it was titrated by 0.05 N solution of hydrochloric acid in the presence of phenolphthalein.

The acid number (*a.n.*, mg KOH/g) is calculated in accordance with the formula:

$$a.n. = \frac{(V_1 - V_2) \cdot 2.8k}{a}$$

where V_1 is a volume of 0.05 N solution of HCl spent for the blank test titration, ml; V_2 is a volume of 0.05 N solution of HCl spent for the sample titration, ml; k is a correction factor of 0.05 N solution of HCl; a is a sample weight, g.

2.2.3. IR-spectroscopic investigations (FT-IR)

IR-spectroscopic investigations were carried out using Thermo Electron Corporation-Nicolet 8700 device in the spectroscopic laboratory of Gdansk Technical University (Poland). The device is equipped with an adapter Specac Golden Gate with ATR diamond crystal.

The epoxy-oligomeric mixtures prepared by the procedure described above are applied by a thin layer over the plate with KBr. The film is pressed by other plate with KBr using mechanical instrument and IR-spectrum is recorded. The plates with the films are placed in a desiccator and sustained at room temperature for 24 h. Then the following spectrum is recorded. After heating at 423 K IR-spectra are recorded every 30 min.

3. Results and Discussion

3.1. Cross-linking of Epoxy-Oligomeric Mixtures

The results represented in Table 2 (mixtures I, II and III) reveal that gel-fraction content in the samples and films hardness depend upon the mixture composition, temperature and cross-linking time. The increase of CDER amount in the mixtures from 9 to 36 mass parts decreases gel-fraction content and films hardness at the cross-linking at room temperature. It means that at room temperature the cross-linked products are formed only in the presence of ED-20 resin due to the interaction between epoxy groups of the resin and PEPA molecules. During cross-linking CDER with an epoxy group at one end only grafts to the matrix based on ED-20 resin. At room temperature TGM-3 molecules do not participate in the formation of three-dimensional network based on ED-20 molecules. The further heating of cross-linked at room temperature films to 383, 403 and 423 K increases both gel-fraction content and films hardness (*vide* Table 2). To our mind, it means that at heating the reactions proceed leading to the additional formation of cross-linked structures. First of all, it is the reaction between ED-20 and CDER epoxy groups and secondary aminogroups of PEPA.

Not only cross-linking temperature but cross-linking time affect the gel-fraction content and films hardness as well. Moreover, the increase of both temperature and time increase the above-mentioned values. Hence, not only the reaction between epoxy groups and secondary amines but other reactions take place during cross-linking. We refer three-dimensional cooligomerization of oligoesteracrylate molecules and CDER carboxy group interaction with hydroxy groups of ED-20 resin to those other reactions increasing gel-fraction content of the samples and films hardness, as well as with hydroxy groups formed due to the interaction between epoxy group of ED-20 with PEPA at the initial stages of cross-linked structures formation. The literature data [6] indicate the possibility of interaction between carboxy and hydroxy groups. Moreover, the higher temperature the higher rate of the mentioned reaction. The above-mentioned assumption is confirmed by the data

presented in Table 2. The higher cross-linking temperature and greater amount of CDER in the initial mixture (mixture III) lead to the greater amount of formed insoluble products due to the interaction between hydroxy and CDER carboxy groups and three-dimensional cooligomerization of TGM-3 molecules. Thus, for the mixture III at room temperature only 44.0 % of insoluble products are formed, the films hardness does not exceed 0.16 rel. units. At the heating to 423 K for 30 min the gel-fraction content is 91.0 %, film hardness is 0.97 rel. units. The results of the mixture IV (without CDER) cross-linking reveal the possibility of the reaction proceeding

between epoxy group and secondary amine groups, as well as three-dimensional cooligomerization of TGM-3 molecules (Table 2). On the other hand the results obtained at cross-linking of the mixture V reveal the possibility of the reaction proceeding in the presence of CDER carboxy group.

In order to establish the role of CDER carboxy group in the cross-linking of epoxy-oligomeric mixtures the investigations concerning the determination of acid number (*a.n.*) in the samples were carried out using the procedure described in Subsection 2.2. The obtained results are represented in Table 3.

Table 2

Dependence of gel-fraction content and films hardness upon the temperature and cross-linking time

Symbol	T, K	Mixture in accordance with Table 1	Symbol values at cross-linking time, min					
			24 h under ambient conditions	15	30	45	60	75
G	383	I	82.0	85.1	88.6	89.0	89.4	90.0
		II	77.7	80.2	82.0	83.0	85.2	86.0
		III	44.0	51.3	75.4	79.4	80.4	82.3
	403	I	82.0	89.6	88.8	89.1	90.0	90.3
		II	77.7	82.1	84.0	85.0	86.0	87.5
		III	44.0	53.2	77.7	85.2	87.2	87.2
	423	I	82.0	89.7	90.0	90.4	91.6	92.2
		II	77.7	83.5	84.0	85.0	85.7	88.0
		III	44.4	83.0	91.0	93.2	93.9	94.0
		IV	80.7	91.5	92.8	92.9	94.0	94.2
		V	71.7	79.1	86.6	87.6	92.1	92.1
	H	383	I	0.55	0.75	0.82	0.83	0.85
II			0.44	0.66	0.71	0.78	0.81	0.83
III			0.16	0.21	0.68	0.74	0.77	0.87
403		I	0.55	0.82	0.83	0.87	0.89	0.92
		II	0.44	0.77	0.90	0.93	0.95	0.95
		III	0.16	0.30	0.77	0.94	0.97	0.98
423		I	0.55	0.88	0.89	0.94	0.95	0.95
		II	0.44	0.91	0.91	0.93	0.94	0.95
		III	0.16	0.93	0.97	0.99	0.99	0.99
		IV	0.45	0.82	0.84	0.88	0.88	0.91
		V	0.26	0.71	0.82	0.87	0.87	0.87

Notes: G – gel-fraction content, %; H – films hardness, rel. units

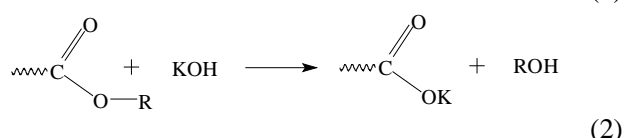
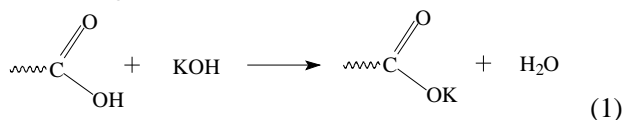
Table 3

Dependence of *a.n.* upon the temperature and cross-linking time

T, K	Mixture in accordance with Table 1	<i>A.n.</i> values for cross-linking time, min					
		24 h under ambient conditions	15	30	45	60	75
383	II	24.9	25.2	26.1	27.4	28.3	29.0
	III	34.5	36.2	37.5	40.6	41.4	42.2
403	II	24.9	26.6	27.0	28.3	29.1	29.5
	III	34.5	42.1	46.1	48.0	48.3	53.3
423	II	24.9	29.2	36.0	36.5	37.0	41.0
	III	34.5	47.3	48.6	51.5	52.1	56.0
	IV	12.2	12.6	12.9	13.5	13.8	14.0
	V	34.2	34.2	34.3	34.1	34.1	34.6

One can see from Table 3 that the samples are characterized by *a.n.* at the cross-linking at room temperature as well as at heating. At the same time the heating to 383, 403 and 423 K for 15–75 min increases *a.n.* values.

The obtained results indicate that the acid number determined for the cross-linked samples corresponds to the following reactions:

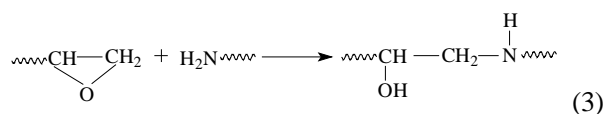


Thus, potassium hydroxide is used for the determination of *a.n.* for the reaction with CDER free carboxy groups (reaction 1) and for esteric groups hydrolysis (reaction 2). It is difficult to determine from Table 3 which part of one or other reactions takes place in this case. If we assume that at room temperature CDER carboxy groups do not react with hydroxy groups of ED-20 resin cross-linked in the presence of PEPA and TGM-3 molecules are not cooligomerized, the *a.n.* determined for 24 h (ambient conditions) should correspond to CDER amount in the polymeric mixture. At the same time the results obtained for the mixture IV (without CDER) show that at room temperature a partial cooligomerization of TGM-3 molecules takes part because *a.n.* in such a case is 12.2 mg KOH/g. The possibility of partial cooligomerization is explained as follows: in spite of cross-linking proceeding at room temperature, the reaction between PEPA primary aminogroups and ED-20 epoxy groups is an exothermal one [6] resulting in films heating and partial cooligomerization of TGM-3 molecules. Therefore the value of *a.n.* at room temperature calculated for the mixture IV corresponds to the reaction (2). The following heating for 15–75 min to 423 K increases *a.n.* It means the further cooligomerization of TGM-3 molecules. Besides ED-20 resin the mixture V contains only CDER molecules. Therefore the calculated value of *a.n.* at room temperature corresponds to the content of carboxy groups in the mixture. Moreover, the further heating does not practically change *a.n.* If we assume the interaction between CDER carboxy groups and ED-20 hydroxy groups, then *a.n.* determination is carried out accordingly to the reaction (1).

To confirm the assumption about the chemism of cross-linked structures formation based on epoxy-oligoesteric mixtures in the presence of carboxy-containing derivative of ED-24 epoxy resin the IR-spectroscopic investigations were carried out by the procedure described in Subsection 2.2.3.

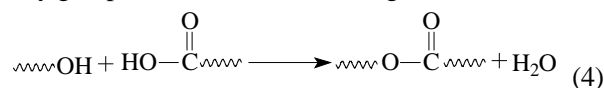
We chose the mixture III (Table 1) for investigations. The structural changes were controlled by absorption bands: 918 cm^{-1} (typical of epoxy ring stretching vibrations); 3440 cm^{-1} (hydroxy groups); 1717 cm^{-1} (carbonyl group in acids) and 1731 cm^{-1} (carbonyl group in esters). It was determined that IR-spectra of the mixture IV recorded after mixture preparation, after its keeping up at room temperature for 24 h and after heating at 423 K for 30, 60 and 90 min are non-identical.

The sufficiently intensive absorption band was found at 918 cm^{-1} typical of epoxy ring stretching vibrations in ED-20 resin and CDER (Figs. 1 and 2). The sustenance of polymeric mixture at room temperature for 24 h leads to the decrease of band intensity but it does not disappear. It indicates that under adduced conditions epoxy groups of ED-20 resin and CDER interact with PEPA molecules in accordance with the reaction:



The proceeding of the reaction (3) is illustrated in Fig. 3. The sharp increase of the absorption band characterizing hydroxy group stretching vibrations at cross-linking for 24 h at room temperature is observed.

The further heating of the polymeric mixture to 423 K leads to the complete depletion of epoxy groups (Figs. 1 and 2) and the decrease of intensity of absorption band at 3440 cm^{-1} (Fig. 3). The latter fact indicates that hydroxy groups react at 423 K according to the reaction (4):



We may assert that the additional cross-linking of the mixture components takes place while heating due to the interaction between CDER carboxy groups and hydroxy groups of the structure cross-linked according to the reaction (3). This additional cross-linking is confirmed by the data of Table 2. On the other hand, the possibility of the reaction (4) proceeding is confirmed by IR-studies represented in Figs. 4 and 5.

At room temperature the intensity of the carbonyl group absorption band in acid (Figs. 4 and 5) does not change. It means that the reaction (4) does not proceed under mentioned conditions. The heating leads to the disappearance of band at 1717 cm^{-1} and appearance of absorption band at 1731 cm^{-1} indicating the proceeding of the reaction (4). On the other hand, in spite of the constant intensity of the carbonyl group absorption band in the acid at room temperature, the intensity of the absorption band at 1731 cm^{-1} typical of carbonyl groups in esters increases. The latter fact confirms the partial three-dimensional cooligomerization of TGM-3 molecules at the cross-linking at room temperature.

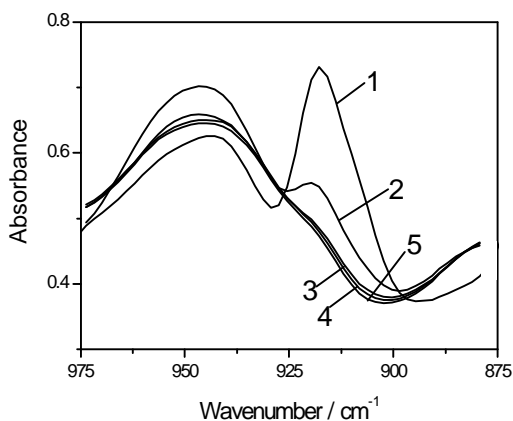


Fig. 1. Intensity of absorption band at 918 cm^{-1} in the mixture III after preparation (1); after keeping up at room temperature for 24 h (2); at heating to 423 K for 30 (3), 60 (4) and 90 (5) min

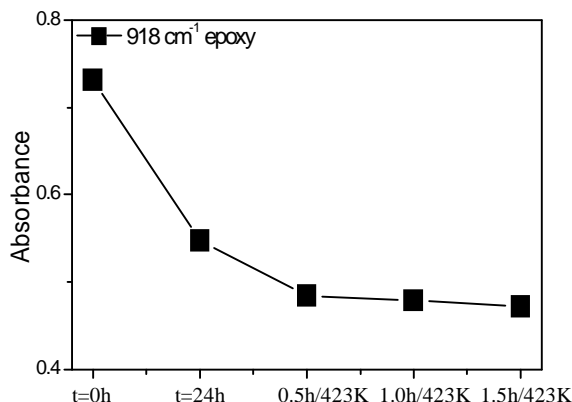


Fig. 2. The change of intensity of absorption band at 918 cm^{-1} in the mixture III during cross-linking

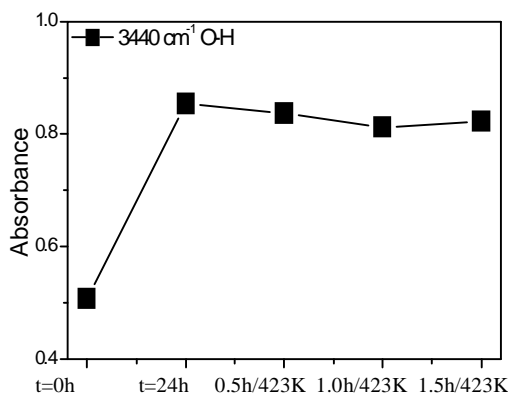


Fig. 3. The change of intensity of absorption band at 3440 cm^{-1} in the mixture III during cross-linking

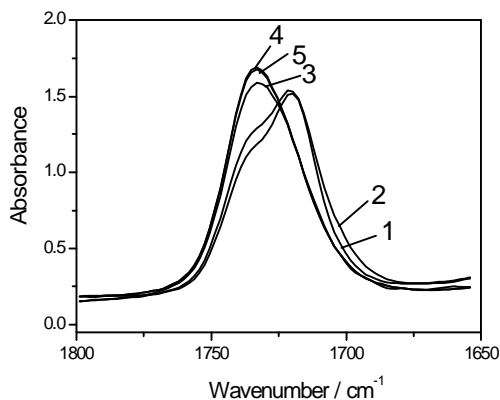


Fig. 4. Intensity of absorption band at 1717 cm^{-1} (1, 2) and 1731 cm^{-1} (3, 4 and 5) in the mixture III after preparation (1); after keeping up at room temperature for 24 h (2); at heating to 423 K for 30 (3), 60 (4) and 90 (5) min

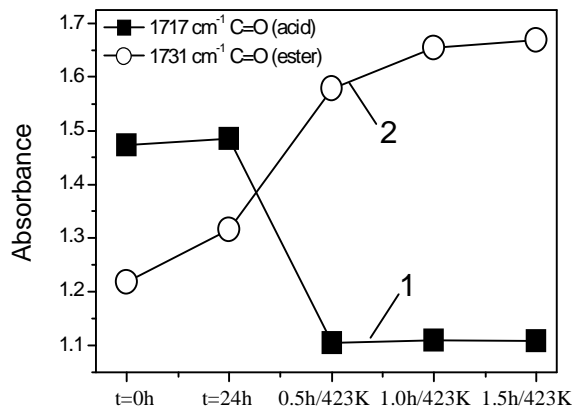


Fig. 5. The change of intensity of absorption band at 1717 cm^{-1} (1) and 1731 cm^{-1} (2) in the mixture III during cross-linking

Thus we may ascertain that at room temperature the cross-linking of epoxy-oligoesteric mixtures takes place due to the interaction between ED-20 and CDER molecules with PEPA. The process proceeds according to the reaction (3). Under mentioned conditions the partial cooligomerization of TGM-3 molecules takes place as well. The mixtures heating leads to the further formation of three-dimensional molecules due to the interaction between free carboxy groups of CDER molecule which is a part of the main matrix with hydroxy groups formed in accordance with the reaction (3). Such additional cross-linking takes place according to the reaction (4). Moreover, at heating three-dimensional cooligomerization of TGM-3 molecules takes place.

4. Conclusions

While cross-linking of epoxy-oligomeric mixtures based on industrial ED-20 dianic epoxy resin, oligo-esteracrylate TGM-3, carboxy-containing derivative of ED-24 resin and polyethylenepolyamine at room temperature and heating to 383, 403 and 423 K it has been established that extent of cross-linked structures formation depends upon the mixture composition and cross-linking conditions. The introduction of carboxy-containing oligomer into the mixture increases gel-fraction content of the samples and films hardness. Using IR-spectroscopy the chemism of cross-linked structures formation has been examined.

References

- [1] Zhyiltsova S., Myhhalchuk V., Platonova O. and Biloshenko V.: Chem. & Chem. Techn., 2011, **5**, 49.
- [2] Bratychak M., Shyshchak O., Nosova N. et. al.: Ukr. Khim. Zh., 2007, **73**, 121.
- [3] Bratychak M., Chervinsky T., Gagin M. et. al.: Ukr. Khim. Zh., 2006, **72**, 58.
- [4] Bratychak M., Kochubei V., Shust O. et. al.: Chem. & Chem. Techn., 2011, **5**, 41.
- [5] Bratychak M., Shust O., Astakhova O. et. al.: Ukr. Khim. Zh., 2010, **76**, 116.
- [6] Ellis B.: Chemistry and Technology of Epoxy Resins. Blackie Academic and Professional, London 1993.
- [7] Bratychak M., Astakhova O., Mykhailiv O. et. al.: Chem. & Chem. Techn., 2012, **6**, 51.

СТРУКТУРУВАННЯ ЕПОКСИ-ОЛІГОЕСТЕРНИХ СУМІШЕЙ В ПРИСУТНОСТІ КАРБОКСИЛВІСНОЇ ЕПОКСИДНОЇ ПОХІДНОЇ СМОЛИ ЕД-24

Анотація. Вивчено структурування за кімнатної температури і при нагріванні до 383, 403 або 423 К впродовж 15, 30, 45, 60 і 75 хв. епоксидно-олігоестерних сумішей, що складаються з промислової епоксидної смоли ЕД-20, олігоестеракрилату ТГМ-3 і карбоксилвмісної похідної епоксидної смоли ЕД-24 (КПЕС) в присутності поліетиленполіаміну. Встановлено вплив складу суміші, температури і тривалості структурування на вміст гель-фракції в зразках та твердість полімерних плівок. З використанням ІЧ спектроскопії встановлено хімізм утворення просторовозитих структур.

Ключові слова: епоксидна смола, олігоестеракрилат, карбоксильна група, кислотне число, структурування, ІЧ спектроскопія, гель-фракція, твердість плівок.