Cross-linked epoxy-isocyanate blends containing Epidian-6 modified by glycols

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Abstract: Polymeric films of cross-linked structure may be formed using epoxy-isocyanate blends composed of Epidian-5 epoxy resin, 4,4′-diphenylmethanediisocyanate (MDI), Z-1 polyamine hardener and Epidian-6 epoxy resin modified by glycols. The effect of the component natures and ratio, process temperature and time on the gel-fraction content, as well as film hardness, was examined. The chemistry of the film forming process was determined using infrared-spectroscopy (IR).

Keywords: epoxy-isocyanate blends, polyamine hardener, epoxide, diisocyanate, 1,4-butanediol, cross-linking, gel-fraction, infrared-spectroscopy.

Usieciowane mieszaniny epoksydowo-izocyjanianowe zawierające żywicę Epidian-6 modyfikowaną glikolami

Streszczenie: Z mieszaniny epoksydowo-izocyjanianowej, otrzymanej z żywicy epoksydowej Epidian-5, utwardzacza Z-1 i diizocyjanianu 4,4′-metylenodifenylu (MDI), oraz żywicy epoksydowej Epidian-6 zmodyfikowanej glikolami wytwarzano folie polimerowe o usieciowanej strukturze chemicznej. Oceniano wpływ składu jakościowego i ilościowego mieszaniny, temperatury oraz czasu reakcji na zawartość frakcji żelowej gotowych folii polimerowych i ich twardość. Przebieg procesu formowania folii badano metodą spektroskopii w podczerwieni (IR).

Słowa kluczowe: mieszanina epoksydowo-izocyjanianowa, utwardzacz poliamidowy, żywica epoksydowa, diizocyjanian, 1,4-butanodiol, sieciowanie, frakcja żelowa, spektroskopia w podczerwieni.

Materials based on epoxy resins have a number of positive properties but are also characterized by an insufficient abrasion resistance and adhesive strength relative to aluminum and other non-ferrous metals [1]. On the other hand, materials based on polyurethanes have low resistances to corrosive media, insufficient hardness and strength [2]. By combining the epoxy resin fragments and polyurethanes, we may avoid the above-mentioned drawbacks and obtain materials with sufficiently high operational characteristics [3–5]. Therefore, these mixtures are used for the production of top-quality protective coatings, polymer-concrete compositions, building mastics, etc. [6–9].

Many researchers have studied epoxy-isocyanates blends [3–10]. All of them point to the interaction between the secondary hydroxyl groups of epoxy resin and isocyanate groups that occurs in the blends at high temperatures (333 K or more) without the catalyst and results in urethane group formation [2, 3]. It is also known that epoxy resins are usually cross-linked with aliphatic amines [4, 11]. This hampers the use of compounds with free isocyanate groups due to their capability of fast reactions with the amine groups of the hardener leading to the formation of non-uniform coatings due to fast cross-linking [2].

To avoid the above-mentioned drawback, the researchers [3, 10, 12] suggested the use of blocked isocyanates while forming materials based on epoxy-isocyanate blends, *i.e.* products of interaction between isocyanates and certain compounds containing mobile hydrogen atoms.

The forming temperature of products based on epoxy resins, blocked-isocyanates and epoxy resin hardener varies over a wide range of 373–423 K and depends on the temperature of isocyanate deblocking, which depends, in turn, on the nature of the blocking agent. Moreover, an additional factor is that epoxy resins contain secondary hydroxy groups in their structure that react with isocyanate groups at elevated temperatures [2, 3].

This work deals with investigations concerning the formation of polymeric films based on Epidian-5 epoxy resin, diisocyanate and polyamine in the presence of

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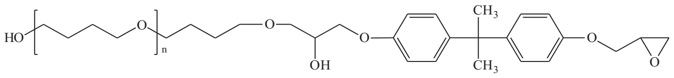
Epidian-6 epoxy resin modified by glycols (HDER). The formula of the latter compound is shown in Scheme A:



where: n = 0 (HDER-I) or n = 26–28 (HDER-II)

Scheme A

Unlike Epidian-5, modified compounds based on Epidian-6 contain free primary hydroxyl groups apart from their epoxy and secondary hydroxyl groups. This fact should influence the film forming temperature and the process of three-dimensional structure formation as well.

EXPERIMENTAL PART

Materials

Epidian®-5 (Sarzyna-Ciech) was used as an initial epoxy resin. Its molecular weight (M_n) is 390 g/mol and content of epoxy groups (*CEG*) is 20.0 %.

4,4'-Diphenylmethanediisocyanate (MDI, Suprasec 1306, Huntsman) was used as the isocyanate.

Triethylenetetramine (Z-1, CEDAR) was used as a hardener.

The modified HDER-I was synthesized according to the procedure described in [12], using Epidian®-6 (Sarzyna-Ciech) and 1,4-butandiol (BD, Merck KGaA, Germany) as the starting components. It has a M_n 420 g/mol, *CEG* 11.2 % and hydroxyl number (*HN*) 277 mg KOH/g. The starting compounds for HDER-II were Epidian-6 and polyTHF-200 oligoether (BASF, Canada Inc.) with M_n 1950 g/mol, *HN* 54.7 mg KOH/g and acid number (*AN*) ≤ 0.05 mg KOH/g. The HDER-II characteristics are: M_n 2040 g/mol, *CEG* 3.3 % and *HN* 53 mg KOH/g.

Cross-linking of epoxy-isocyanate blends

Epoxy-isocyanate blends, the compositions of which are given in Table 1, were prepared in two stages. In the first stage, HDER or BD was blended with MDI at room temperature for 10–15 min. Then, Epidian-5 was added with stirring until a homogeneous mixture was obtained. In the second stage, Z-1 hardener was added and the mixture was poured over previously degreased glass plates.

Methods of testing

Film formation was studied under the following conditions: first the compositions were cured at room temperature for 24 h and then at 383, 403 or 423 K for 15, 30, 60 or 90 min. The structural changes were controlled by gel-fraction content (*G*, %) of the ground samples in a Soxhlet apparatus during their extraction by chloroform for 10 h and film hardness (*H*, relative units) determined with a M-3 pendulum device at room temperature (ISO 1522).

Table 1. Composition of epoxy-isocyanate blends

Component	Component content in the blend, wt %				
	I	II	III	IV	V
Epidian-5	85.0	92.5	85.0	85.0	70.0
HDER-1	-	5.0	10.0	-	20.0
HDER-2	-	-	-	10.0	-
BD	10.0	-	-	-	-
MDI	5.0	2.5	5.0	5.0	10.0
Z-1	11.8	12.1	12.0	11.9	11.8

IR-spectra of epoxy-isocyanate blends were recorded using a Thermo Electron Corporation-Nicolet 8700 instrument at the spectroscopic laboratory of Gdansk University of Technology. The instrument is equipped with a Specac Golden Gate adapter and diamond crystal ATR. The epoxy-isocyanate blends were applied in a thin layer over KBr plates and IR-spectra were recorded. Then, the plates were placed in a desiccator, held for 24 h at room temperature before more IR-spectra were recorded. Then, the blends were heated at 383 K (30 min), 403 K (30 min) and 423 K (30 min). IR-spectra were recorded after every heating step.

RESULTS AND DISCUSSION

Cross-linking of epoxy-isocyanate blends

To follow the formation of polymeric films based on epoxy-isocyanate blends (Table 1), it was necessary to determine the effect of the process temperature and time, HDER character and amount, as well as MDI amount, on the gel-fraction content and film hardness. The blend with BD instead of MDI (blend I, Table 1) was examined for comparison (Tables 2, 3).

Already, at room temperature, epoxy-isocyanate blends with HDER form films for which the values of the gel-fraction content and hardness are higher than those of the blend without HDER (blend I). This means that HDER at room temperature participates in the formation of the polymeric film due to the presence of a free epoxy group in the HDER molecule. The compositions with HDER (blends II–V) and with BD (blend I) heated to 383 K or higher temperatures resulted in the formation of three-dimensional networks. Thus, we may assume that the reactions resulting in the formation of cross-linked structures proceed at elevated temperatures.

In the first stage, HDER and MDI react quickly at room temperature as the free primary hydroxyl group of HDER and isocyanate group of MDI react readily with each other. The same situation is found with blend I. With the molar excess of primary hydroxyl groups in the initial compounds, the complete reaction between the isocyanate groups of MDI and hydroxyl groups of HDER or BD occurs resulting in the formation of linear compounds with free epoxy groups (blends II–V) or a hy-

T a b l e 2. Dependence of gel-fraction content on the blend composition, cross-linking time and temperature

Blend (according to Table 1)	Content of gel-fractions of the blend composition, %					
	Cross-linking time, min					
	24 h, room temperature	*T*, K	15	30	60	90
I	69.4	383	74.7	80.2	84.7	85.4
		403	76.7	83.1	84.8	85.7
		423	80.4	84.8	85.4	85.9
II	72.9	383	77.3	82.1	85.6	87.2
		403	83.3	88.7	91.1	94.9
		423	86.6	93.3	94.8	95.5
III	74.1	383	78.9	84.6	90.8	92.6
		403	83.3	89.5	93.2	95.4
		423	90.6	94.7	97.1	97.3
IV	72.6	383	81.3	85.7	88.1	90.2
		403	85.2	89.8	94.3	95.9
		423	88.7	95.4	96.2	96.5
V	74.3	383	78.8	85.4	91.7	92.9
		403	87.8	91.4	95.5	96.4
		423	89.1	95.8	96.7	97.1

droxyl group (blend I). After addition of Epidian-5 and hardener Z-1 to the resulting blends, the cross-linking occurs at room temperature within 24 h. In the case of blend I, only molecules of Epidian-5 and Z-1 participate in the process. For blends II–V the compounds formed in the first stage in the reaction between HDER and MDI additionally participate in the cross-linking. This leads to an increase in the gel-fraction content and film hardness (Tables 2 and 3). The samples heated to 383 K or higher temperatures have increased gel-fraction content and hardness because of the reaction between residual epoxy groups with secondary and primary hydroxyl groups of the blend components (blends II–V). In blend I, the reaction between primary hydroxyl groups of BD and residual epoxy groups of Epidian-5 is also possible. The fact that the gel-fraction content remains practically constant even after heating at 423 K for 90 min (Table 2) confirms this conclusion. For blends II–V the increase in temperature has a positive effect on the content of insoluble products.

T a b l e 3. Dependence of films hardness on the blend composition, cross-linking time and temperature

Blend (according to Table 1)	Hardness of films of the blend composition, relative units					
	Cross-linking time, min					
	24 h, room temperature	*T*, K	15	30	60	90
I	0.44	383	0.69	0.71	0.71	0.71
		403	0.75	0.76	0.76	0.77
		423	0.79	0.80	0.80	0.80
II	0.62	383	0.72	0.81	0.81	0.81
		403	0.74	0.81	0.81	0.81
		423	0.80	0.81	0.81	0.81
III	0.65	383	0.77	0.81	0.88	0.88
		403	0.79	0.83	0.88	0.88
		423	0.81	0.88	0.88	0.89
IV	0.51	383	0.67	0.71	0.79	0.86
		403	0.70	0.77	0.84	0.86
		423	0.73	0.80	0.86	0.87
V	0.66	383	0.78	0.81	0.88	0.89
		403	0.79	0.85	0.88	0.89
		423	0.83	0.86	0.89	0.89

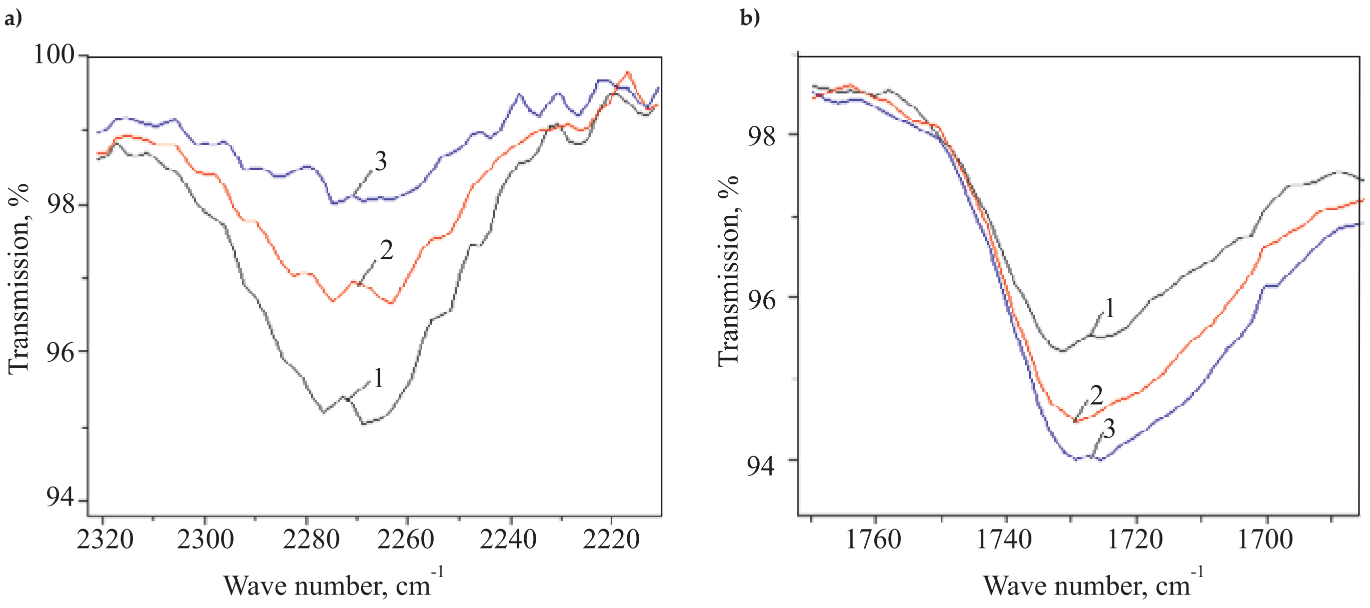


Fig. 1. The intensity of absorption bands of: a) isocyanate group in MDI, b) carbonyl groups in urethanes, after reaction between HDER-I and MDI carried out for: 1 – 30 s, 2 – 90 s, 3 – 150 s

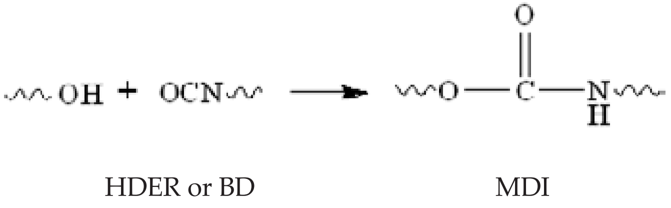
When comparing the blends with HDER and those with BD, one observes the positive effect of HDER on the formation of polymeric films with high values of gel-fraction content and hardness. The increase in the amount of HDER increases the above-mentioned properties. The type of HDER does not influence the content of insoluble products.

The increase in temperature and curing time enhances both gel-fraction content and film hardness. This means that, under these conditions, the reactions proceed without involving the Z-1 amine groups.

IR-spectroscopic investigations

To establish the chemistry of film formation, we carried out IR-spectroscopic investigations. Blends III and IV (Table 1) were chosen for these experiments.

According to the procedure, in the first stage, HDER or BD was blended with MDI until a homogeneous mixture was obtained. At this time, a sharp decrease in the intensity of the absorption band at 2263–2275 cm^{-1} was observed (Fig. 1), corresponding to the stretching vibrations of the isocyanate group. At the same time, the intensity of the band at 1730 cm^{-1} increased, indicating the formation of urethane groups. The results demonstrate that the reaction between HDER or BD and MDI proceeds according to Scheme B:



$$\sim\sim OH + OCN\sim\sim \longrightarrow \sim\sim O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{H}{N}\sim\sim$$

Scheme B

The reaction (Scheme B) leads to the complete consumption of isocyanate groups allowing the use of the resulting product for further reactions with epoxy resin Epidian-5 and amine hardener Z-1.

IR-spectra of blend III are presented in Fig. 2. Obviously, the spectrum of the blend after mixing all components (spectrum 1) differs from that (spectrum 2) of the blend after heating.

An intensive absorption band is observed at 918 cm^{-1} (Fig. 3) corresponding to the stretching vibrations of the epoxy ring in Epidian-5 and in the product obtained from HDER-I and MDI. This band is practically missing from the blend kept at room temperature for 24 h and

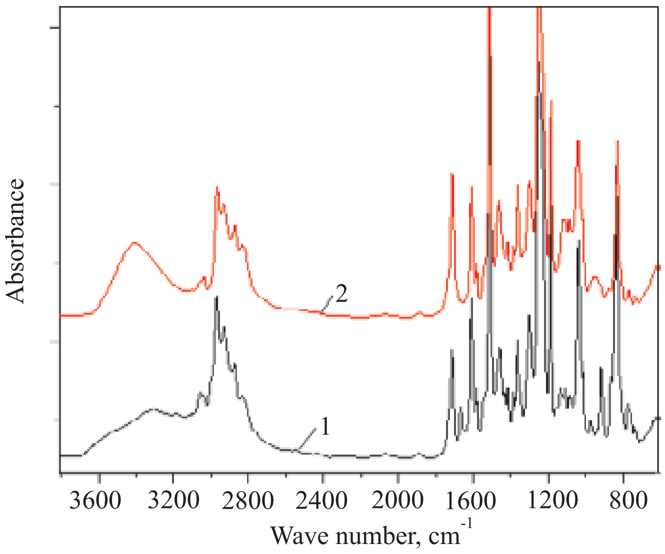


Fig. 2. IR-spectra of blend III: 1 – after mixing all components, 2 – after curing for 24 h at room temperature with further gradual heating at 383 (0.5 h), 403 (0.5 h) and 423 K (0.5 h)

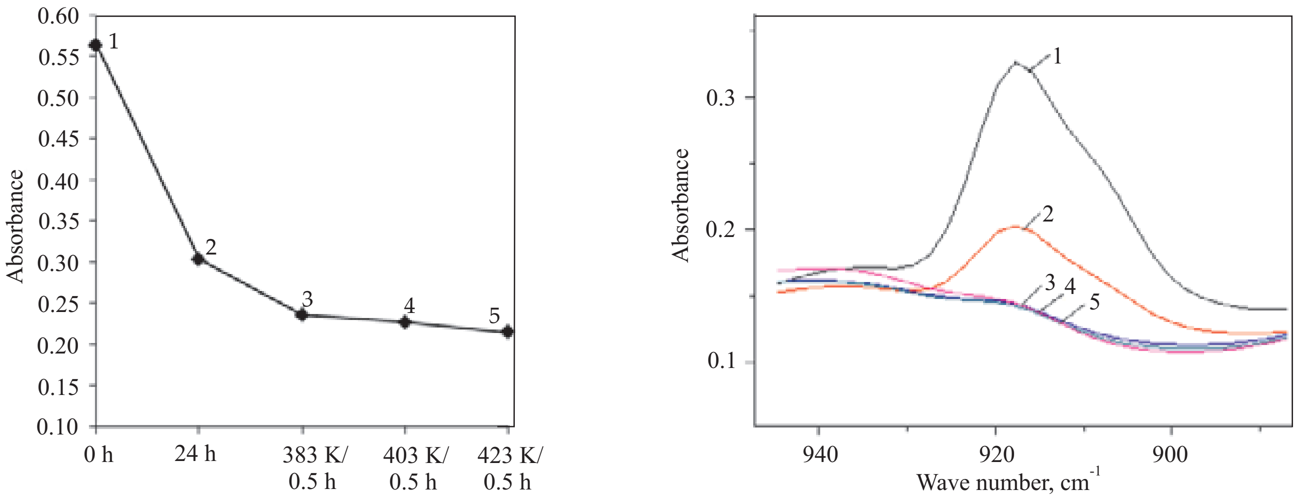


Fig. 3. The change in intensity of the absorption band at 918 cm^{-1} during cross-linking of: 1 – after mixing the components of blend III, 2 – after curing at room temperature for 24 h, 3 – after heating at 383 K (0.5 h), 4 – after heating at 403 K (0.5 h), 5 – after heating at 423 K (0.5 h)

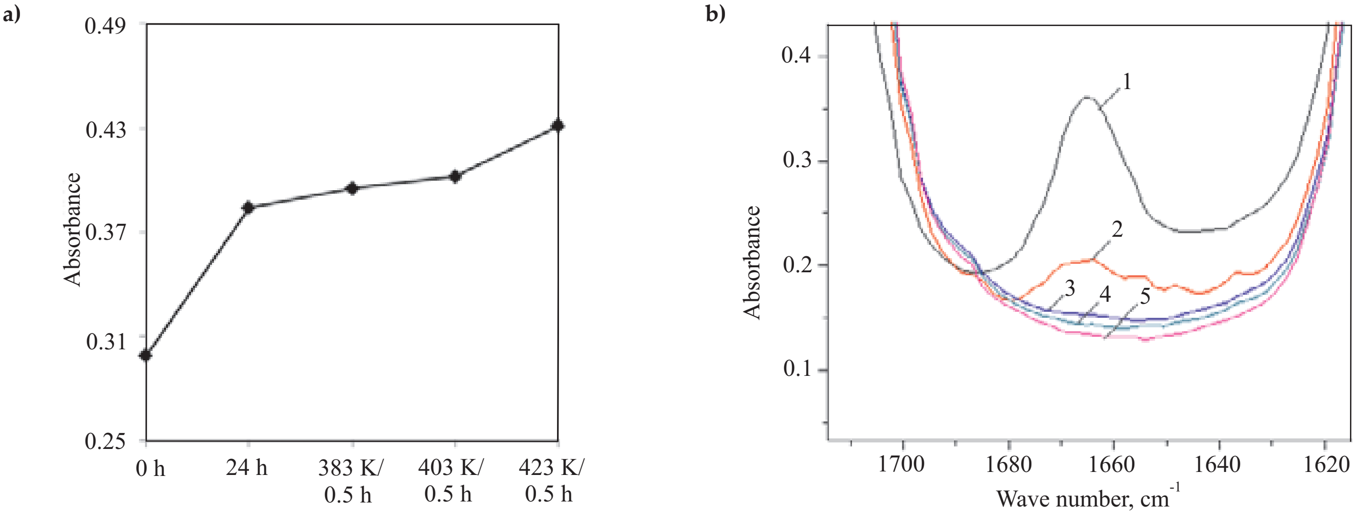


Fig. 4. The change in intensity of the absorption band: a) at 3400 cm^{-1} corresponding to the stretching vibrations of hydroxyl groups, b) at 1660 cm^{-1} corresponding to the deformation vibrations of primary amine groups in Z-1 hardener during cross-linking; 1 – blend III, 2 – after curing at room temperature for 24 h, 3 – after heating at 383 K (0.5 h), 4 – after heating at 403 K (0.5 h), 5 – after heating at 423 K (0.5 h)

then heated. This means that the epoxy groups of Epidian-5 and the product obtained during the first stage reacts with hardener molecules to form hydroxyl groups. The results given in Figs. 1 and 4 confirm this.

The same results were obtained while studying blend IV. The increase in temperature and reaction time (Fig. 4a) increases the amount of hydroxyl groups in the blend, providing the possibility of further chemical reactions that leads, as a result, to the increase in the gel-fraction content (Table 2) and film hardness (Table 3).

CONCLUSIONS

Following the results of our investigation, we propose a new approach to the formation of films based on epoxy resins and diisocyanate in the presence of Epidian-6 modified by glycols. The films are formed stepwise. In the first stage, compounds without free isocyanate groups, but with urethane fragments and free epoxy groups, are formed in the reaction between HDER and MDI. This allows the formation of polymeric films during the second stage in the presence of amine hardener Z-1. The film contains fragments of Epidian-5 epoxy resin and MDI. The role of HDER is to bond Epidian-5 and MDI molecules into a unified three-dimensional network containing 97.1 % of insoluble products.

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