Epoxy Resin Modified by Aliphatic Cyclic Carbonates

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Synopsis

Bidentate and tridentate cyclic carbonates obtained from the reaction of aliphatic epoxy compounds with carbon dioxide were used for the modification of an epoxy resin. The compositions obtained exhibited low viscosity, short gel time, and low exothermic effect accompanying the crosslinking. On the basis of model reactions, a mutually accelerating effect of epoxy and cyclic carbonate groups on the crosslinking of the studied systems by triethylenetetramine was found (synergistic effect). The cured epoxide–cyclic carbonate compositions exhibited considerably higher impact resistance and tensile strength in comparison with epoxy resins.

INTRODUCTION

Commercial epoxy resins crosslinked by standard amine curing agents are materials characterized by many valuable mechanical and electric properties. However, the comparatively small elasticity and impact resistance of epoxy resins are one of their main disadvantages. Therefore, modifications are carried out in order to improve their elasticity and other mechanical properties.

The improvement in the flexibility of epoxy resins by means of polyurethanes is one such modification method. The reactions of isocyanates with hydroxyl groups present in the epoxy resin, as well as curing of the mixture of low molecular weight epoxy resins and isocyanates with polyamines, are also employed for this purpose.[1,2]

The presence of urethane linkages in the cured products can also be obtained from the reaction of compounds having 1,3-dioxolan-2-one rings with amines,[3,4] thereby avoiding the use of expensive and toxic isocyanates [see eq. (1)].

As was shown earlier,[5] the substitution of part of the oxirane rings in epoxy resins by cyclic carbonate groups leads to an increase in strength of the resins. A considerable increase in the viscosity of the epoxy resin, with an increase in the content of cyclic carbonate groups, however, was an important disadvantage of this method. This worsened the processing features and considerably limited the application of resins, especially those with a higher concentration of cyclic carbonate groups.

In this work, the results of our own studies on the reaction of aliphatic and cycloaliphatic poly(epoxy compounds) with carbon dioxide are presented. The products thus obtained, containing one or more 1,3-dioxolan-2-one rings per molecule, were applied as active thinners of epoxy resins. These products will be referred to as cyclic carbonate compounds.

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EXPERIMENTAL

Materials

Commercial epoxy resin Epidian 6 with an epoxide content of 0.52 eq/100 g (Chemical Works "Organika-Sarzyna," Poland), triethylene glycol diglycidyl ether (TGDE) (Institute of Industrial Chemistry, Poland), vinylcyclohexene dioxide (VCDO) (cycloaliphatic epoxy resin ERL-4206—Union Carbide Co., USA), epoxidized rape oil of an epoxide content of 0.33 eq/100 g (Erogplast ER—Chemical Works "Boryszew," Poland), phenyl glycidyl ether (Koch-Light Lab. Ltd., UK), and triethylenetetraamine (TETA) (Loba Chemie, Austria) were used without additional purification. 18-Crown-6-ether (1,4,7,10,13,16-hexaoxacyclooctadecane) was obtained by the method given by Gokel.[6]

Synthesis of Cyclic Carbonates

To a 60-cm^3 stainless steel pressure cylinder were added 0.1–0.2 mol of the aliphatic epoxy compound, 0.9 mmol of 18-crown-6, and 2 mmol of potassium iodide. Carbon dioxide was then introduced to the system under a pressure of ca. 30 atm. The pressure cylinder was then closed and placed for 48 h in a thermostated oil bath at 120 ± 5°C. The cylinder was then cooled to 60°C and the excess of CO_2 was liberated. The product obtained was characterized by means of the carbonate number (number of cyclic carbonate group equivalents per 100 g of product) calculated on the basis of changes of the epoxide content prior to and after reaction with CO_2.

Model Reactions of 3,3′-(Oxytriethylenoxy)-Di-1,2-Propanediol Dicarbonate (TGDEC) with TETA

To a thermostated 250-cm^3 flask, 25 g of TGDEC and 25 g of 1,4-dioxane were introduced. Then 4 g of TETA (stoichiometric amount with respect to TGDEC) was added. The reaction was carried out at 20 ± 1°C, and 0.5-g samples were collected from the system into a 25-cm^3 measuring flask, dissolved in chloroform, and monitored by IR spectroscopy. Changes of the cyclic carbonate content of the studied system within time were determined by means of the previously prepared analytical curve. A similar procedure was applied for the other systems studied.

Analytical and Testing Methods

The content of epoxy groups in the resin was determined by the hydrogen chloride in dioxane method.[7] IR spectra were recorded on a Specord IR 71 (GDR) spectrophotometer, in the form of a film or $CHCl_3$ solution in 0.26-mm absorption cells. Dynamic viscosity measurements were conducted by means of a rotational viscometer—Rheotest RV (GDR). The gel time of the modified resin was measured for 10-g samples using TETA as curing agent.

Exotherm profiles were monitored for samples of 50 g of the epoxy resin and TETA composition in glass tubes of 2.5 cm diameter. The tested composition was thermostated at 50°C, and the rise of temperature of the thermosetting composition vs. time was measured.

The deflection temperature was measured on a Martens apparatus. The hardness of cured resins was measured on a Brinell apparatus type HP 250. Impact resistance of cured resins was measured on a pendulum tester with a simple-beam Charpy impact specimen.

Mechanical properties were determined on a Instron 1115 testing machine at a rate of crosshead movement $v = 1$ mm/min for static tension test, $v = 2$ mm/min for static compression test, $v = 5$ mm/min for lapshear strength test, and $v = 30$ mm/min for T-peel strength test. The lapshear strength was tested with 100 × 25 × 1.8 mm aluminum plates with 1.5-cm overlap on 2-cm-wide specimens. The T-peel test was performed for 100 × 30 × 0.5 mm plates bent along the shorter symmetry axis and glued in a T-shape.

Chemical resistance studies toward the action of aggressive media were carried out by determining mass changes of disc samples of 40 mm diameter and 2 mm thickness immersed in the appropriate medium.

RESULTS AND DISCUSSION

Three aliphatic and cycloaliphatic epoxy compounds were chosen for the reaction with carbon dioxide: triethylene glycol diglycidyl ether (TGDE), vinylcyclohexene dioxide (VCDO), and epoxidized rape oil (ERO). The products obtained were of a higher viscosity with respect to that of the initial resin. In the IR spectrum, absorption bands at 1800 and 1070 cm^{-1} were present, corresponding to the C=O stretching vibrations in the 1,3-dioxolan-2-one ring and vibrations of the ring, respectively (Fig. 1). Cyclic carbonate groups content in the resin varied from 0.14 eq/100 g in the case of the carbonate obtained from ERO (EROC), 0.3 eq/100 g for the carbonate from TGDE (TGDEC) to

Fig. 1. IR spectrum of 3,3′-(oxytriethylenoxy)-di-1,2-propanediol dicarbonate (TGDEC).

0.70 eq/100 g for the carbonate from VCDO (VCDOC). The effect of temperature on the dynamic viscosity of the initial resins and carbonates obtained from them is presented in Figure 2. In all cases the viscosities of the obtained carbonates were higher than those of the initial resins; the viscosities of TGDEC and EROC were, however, much lower than that of the epoxy resin alone. It is believed that the increase in viscosities of the studied resins was caused mainly by an increase in the polarity resulting from the formation of polar carbonyl groups in the 1,3-dioxolan-2-one rings. A relatively small increase in viscosity, observed for TGDEC in comparison with the epoxy resin modified with CO_2,[5] is probably connected with the presence of flexible aliphatic polyether units.

The effect of temperature on the dynamic viscosity of the epoxide–cyclic carbonate compositions is presented in Figure 3 for various contents of cyclic carbonate groups. In all cases, the viscosity of the compositions was lower than that of the epoxy resin alone. The reactivity of epoxide–cyclic carbonate compositions was studied by measuring their gel time with TETA. A considerable shortening of the gel time with an increase in concentration of cyclic carbonate groups in the compositions was observed for systems with TGDEC and VCDOC (Table I). However, in the case of the composition containing EROC–epoxy resin, contrary to other systems, a prolongation of the gel times with an increase

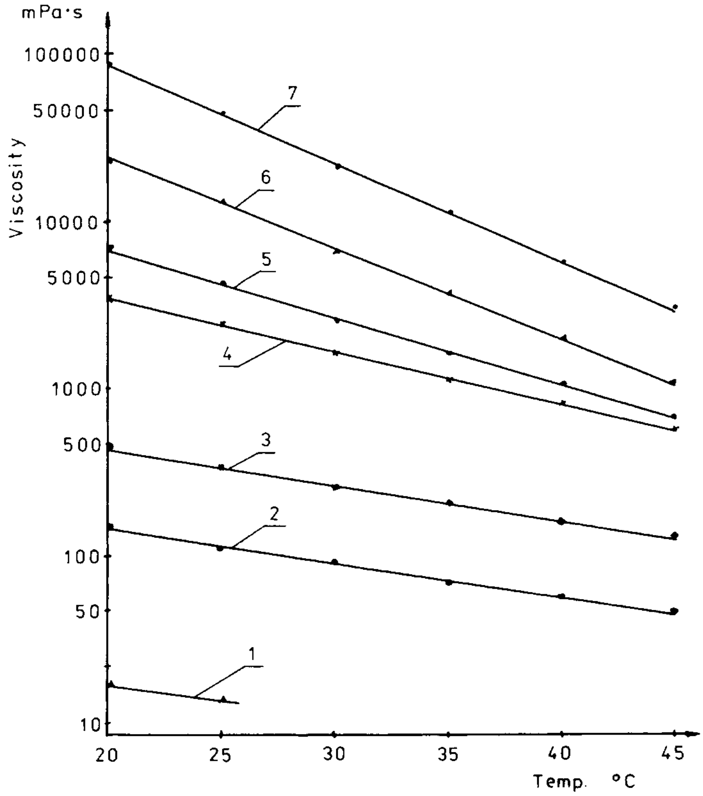


Fig. 2. Dependence of the dynamic viscosity on temperature of epoxy resins and carbonates obtained from them: (1) VCDO, (2) TGDE, (3) ERO, (4) EROC, (5) TGDEC, (6) Epidian 6, (7) VCDOC.

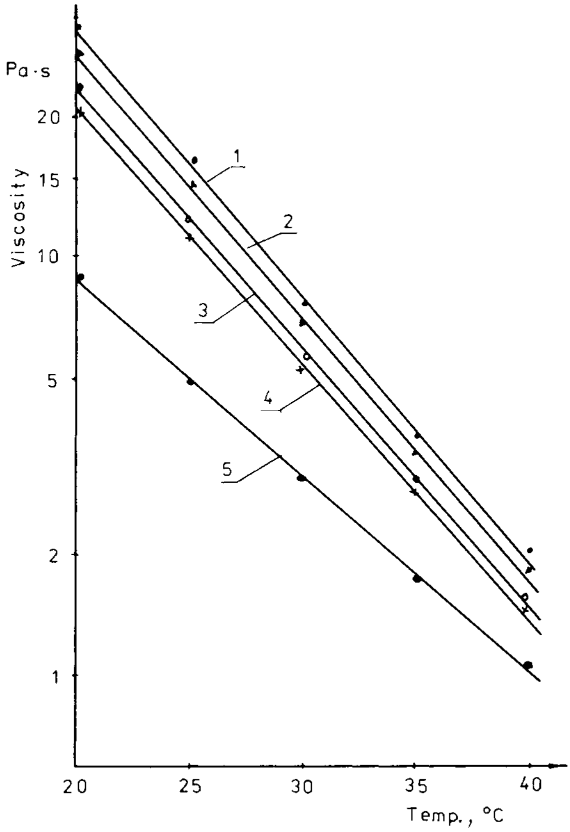


Fig. 3. Dependence of the dynamic viscosity on temperature for Epidian 6—TGDEC compositions of various cyclic carbonate content: (1) Epidian 6, (2) 9%, (3) 17 g, (4) 35% of cyclic carbonate groups, (5) TGDEC.

in the modifier content was observed. The hindered approach of the amine groups to the 1,3-dioxolan-2-one rings present inside the EROC molecules may be the reason for the somewhat longer gel time of that system.

It was found that the dilution of the system with cyclic carbonates causes a decrease in the exothermic effect of the accompanying crosslinking. The series of exotherm profiles of the epoxide–cyclic carbonate compositions cured with TETA are presented in Figures 4 and 5. They illustrate the influence of carbonate group concentration on the maximum temperature reached during crosslinking. The lower peak exotherms were observed for higher concentration of cyclic carbonate groups. The smaller internal stress in the five-membered 1,3-dioxolan-2-one ring compared to the three-membered ring, and the lower crosslinking density (smaller concentration of the reactive groups) in comparison to that of the epoxy resin are additional factors producing the smaller thermal effect of curing in the epoxide–cyclic carbonate compositions.

Studies on a model reaction of cyclic carbonate with amine in the presence of oxirane rings were carried out in order to explain the acceleration of the gel effect of the epoxide–cyclic carbonate compositions. The extent of conversion of the cyclic carbonate groups for the system TGDEC–TETA is presented in

TABLE I
Effect of Composition and Temperature on Gel Time of Modified Resins

Composition	Cyclic carbonate content[a] (%)	Modifier[b] content (wt %)	Gel time (min)			
			25°C	30°C	40°C	50°C
Epidian 6	0	0	260	105	60	30
TGDE + Epidian 6	0	5	170	70	60	30
	0	10	200	135	80	35
	0	20	240	165	85	35
	0	40	300	215	95	40
TGDEC + Epidian 6	4	5	130	85	40	15
	9	10	130	85	40	15
	17	20	105	75	40	10
	35	40	80	70	30	10
VCDOC + Epidian 6	6.5	5	115	85	40	12
	13	10	85	65	25	8
	24	20	70	50	20	5
	42	40	50	35	15	5
EROC + Epidian 6	1.5	5	150	115	68	28
	3	10	160	120	72	30
	6	20	170	130	80	35
	14	40	160	135	90	45

[a] Calculated as $\frac{\text{carbonate content}}{\text{carbonate content} + \text{epoxide content}} \times 100\%$.

[b] TGDE: triethylene glycol diglycidyl ether; TGDEC: TGDE carbonate; VDOC: vinylcyclohexene dioxide carbonate; EROC: epoxidized rape oil carbonate.

Figure 6. Curve 2 was determined for the system containing substrates in a stoichiometric amount, curve 4 for the system consisting also of phenyl glycidyl ether (PGE) in an amount equal to that of TGDEC (maintaining the same

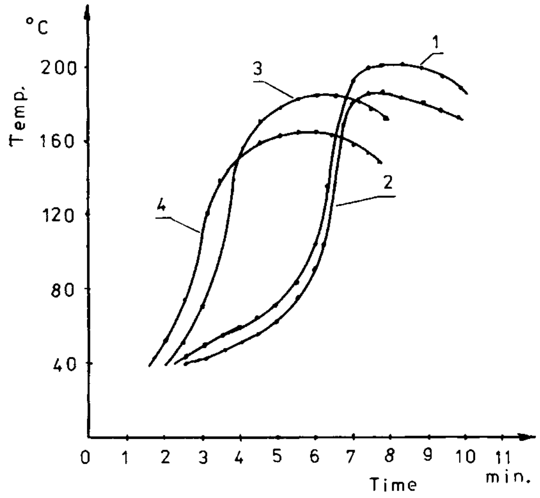


Fig. 4. Exotherm profiles of the epoxide–cyclic carbonate compositions (Epidian 6 + TGDEC): (1) Epidian 6, (2) 4%, (3) 17%, (4) 35% of cyclic carbonate groups.

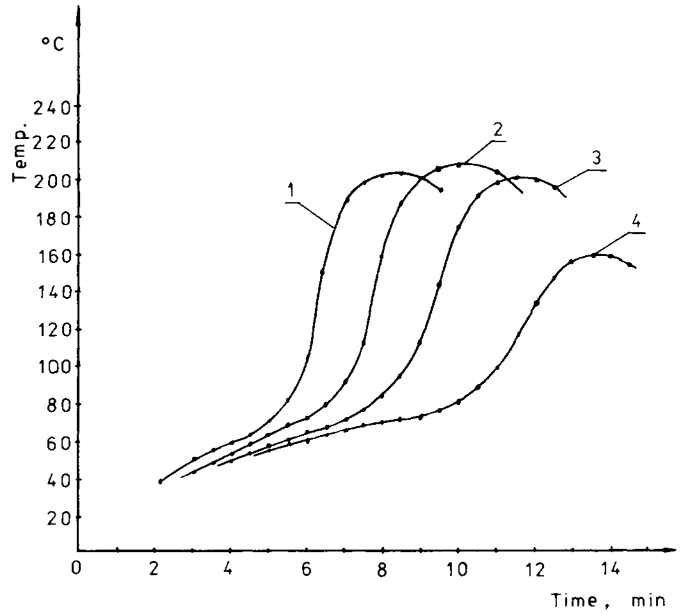


Fig. 5. Exotherm profiles of the epoxide–cyclic carbonate compositions (Epidian 6 + EROC): (1) Epidian 6, (2) 3%, (3) 6%, (4) 14% of cyclic carbonate groups.

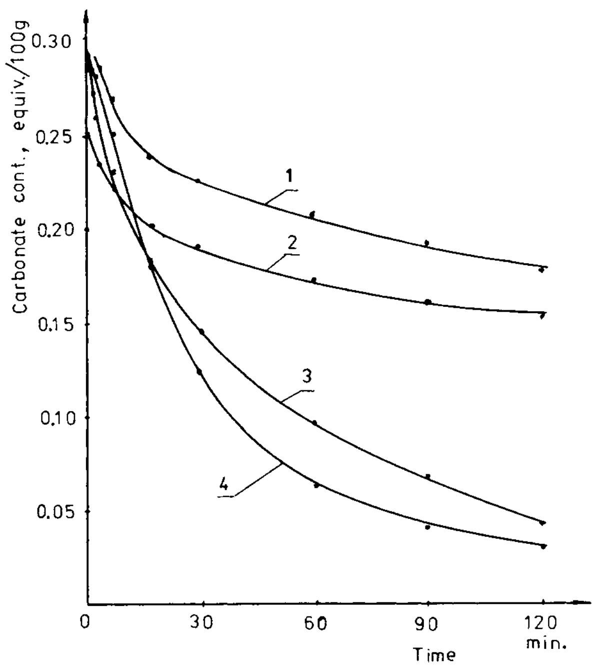


Fig. 6. Carbonate content changes within time for model reactions of TGDEC with TETA: (1) stoichiometric amount of TGDEC and TETA in the presence of the reaction products of phenyl glycidyl ether with TETA in 1,4-dioxane, (2) stoichiometric amount of TGDEC and TETA in 1,4-dioxane, (3) twofold excess of TETA with respect to the stoichiometric amount of TGDEC in dioxane, (4) stoichiometric amount of TETA with respect to TGDEC and phenyl glycidyl ether.

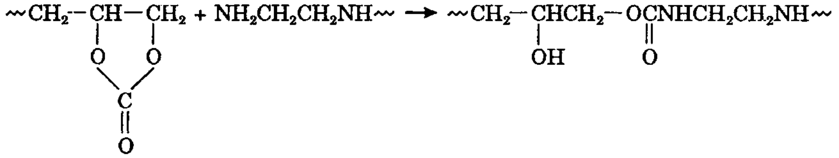
concentration of cyclic carbonates in the system) and for TETA used in a stoichiometric amount with respect to both substrates. (PGE was used as a monofunctional substituent of the epoxy resin.) Curve 3 was determined for the system consisting of 1,4-dioxane instead of PGE (in an amount to maintain the same concentration of cyclic carbonate and amine groups as in system 4). Curve 1, however, illustrates the decrease in cyclic carbonate content for the system containing additionally the product of the PGE and TETA reaction.

The curves show that, in systems containing an epoxy compound (curve 4), the cyclic carbonate groups react fastest with the amine, i.e., faster than for the system containing an excess of TETA, or for the system containing β-hydroxyamine linkages (product of the PGE and TETA reaction).

On the basis of these model reactions, the effect of the presence of oxirane rings on the reaction rate of cyclic carbonates with amines is evident. On the other hand, the reaction rate of epoxy groups with the amine determines the overall gel time in the studied epoxide–cyclic carbonate compositions (the content of epoxide groups is within 58–98.5%, while of cyclic carbonate ones 1.5–42%). Since a clear effect of the presence of cyclic carbonates on the gel time was observed (Table I), a synergistic effect occurs here (mutually accelerating effect of epoxy and cyclic carbonate groups on the crosslinking).

The effect of addition of cyclic carbonates on the physicomechanical properties of an epoxy resin was determined using standard tests (results are presented in Tables II–V).

Table II illustrates the dependence of deflection temperatures, hardness, and impact resistance on the cyclic carbonate concentrations (content of modifier) in the system with an epoxy resin. No clear decrease in the deflection temperature was obtained for the studied systems (up to 10 wt % of the modifier content), in some cases (VCDOC) higher values were obtained. It is known that the deflection temperature of chemically cured resins depends to a great extent on the crosslinking density.[8] The actual crosslinking degree decreases with an increase in the content of carbonate groups in the system. The 1,3-dioxolan-2-one ring can react with, at most, four protons of TETA (the urethane linkage proton does not take part in further crosslinking).



$$\sim CH_2-\underset{\underset{\displaystyle\diagdown\underset{\underset{\displaystyle O}{\|}}{C}\diagup}{O\quad O}}{CH-CH_2} + NH_2CH_2CH_2NH\sim \longrightarrow \sim CH_2-\underset{OH}{\underset{|}{C}}HCH_2-O\underset{O}{\underset{\|}{C}}NHCH_2CH_2NH\sim \qquad (1)$$

However, the presence of polar groups, such as carbonyl (occurring in 1,3-dioxolan-2-one rings and urethane linkages) and hydroxyl groups, enables the formation of hydrogen bonds, i.e., between the unreacted cyclic carbonate groups and the urethane groups with the hydroxyl and urethane protons. These bonds cause an increase in the apparent degree of crosslinking of the epoxide–cyclic carbonate composition, which compensates, to a great extent, the decrease in the actual degree of crosslinking.

Similarly to the case of the deflection temperature, also the hardness of the studied compositions does not change appreciably with a change of the cyclic carbonate modifiers content (Table II). In systems containing VCDOC an increase in hardness was even observed.

TABLE II
Effect of the Composition of Modified Resins on the Deflection Temperature (DT), Hardness and Impact Resistance

Composition	Cyclic carbonate content[a] (%)	Modifier[b] content (wt %)	DT (°C) Upon curing at 25°C	DT (°C) Upon postcuring at 90°C	Hardness (MPa) Upon curing at 25°C	Hardness (MPa) Upon postcuring at 90°C for 2 h	Impact resistance (kJ/m^2) Upon curing at 25°C	Impact resistance (kJ/m^2) Upon postcuring at 90°C
Epidian 6	0	0	59	90	168	183	5.8	5.9
Epidian 6 + TGDE	0	5	65	82	177	188	9.0	19.7
	0	10	58	78	171	178	12.5	15.4
	0	20	58	71	163	168	12.4	18.6
	0	40	41	58	142	154	14.7	10.3
Epidian 6 + TGDEC	4	5	59	91	175	175	6.7	16.5
	9	10	58	85	165	181	7.4	11.9
	17	20	59	71	166	182	9.4	21.3
	35	40	47	56	147	185	37.1	35.6
Epidian 6 + VCDOC	6.5	5	57	94	185	185	3.8	11.7
	13	10	54	88	185	194	4.8	13.2
	24	20	42	75	185	200	—	—
	42	40	43	70	217	213	—	—
Epidian 6 + EROC	1.5	5	67	86	166	173	0.9	7.4
	3	10	61	85	162	169	1.5	8.0
	6	20	60	71	147	149	3.4	13.3
	14	40	56	54	89	132	8.0	17.0

[a] See Table I, footnote a.
[b] See Table I, footnote b.

TABLE III

Effect of the Composition of Modified Resins on Mechanical Properties

Composition	Cyclic carbonate content[a] (%)	Modifier[b] content (wt %)	Tensile strength (MPa)	Yield strength (MPa)	Elongation at break (%)	Compressive strength (MPa)	Yield point (MPa)	Compressive strain (%)	Plastic strain (%)
Epidian 6	0	0	37	12	4.0	260	110	50	11.0
Epidian 6 + TGDE	0	5	54	14	6.5	250	108	50	10.7
	0	10	53	13	6.6	260	107	50	11.3
	0	20	55	15	7.3	255	99	50	9.9
	0	40	53	13	8.6	250	88	50	7.0
Epidian 6 + TGDEC	4	5	47	15	5.4	275	121	50	13.3
	9	10	57	14	6.4	275	118	45	11.3
	17	20	69	13	8.0	245	124	50	9.8
	35	40	54	14	6.5	235	128	55	8.0
Epidian 6 + VCDOC	6.5	5	28	14	2.7	285	122	45	13.7
	13	10	33	14	3.0	275	118	50	11.3
	24	20	35	13	3.4	255	131	50	9.8
	42	40	41	13	3.7	235	157	60	8.0
Epidian 6 + EROC	1.5	5	42	14	4.3	255	107	50	11.7
	3	10	50	12	6.8	255	105	50	12.4
	6	20	41	13	6.0	235	86	50	10.4
	14	40	35	9	8.0	—	—	—	—

[a] See Table I, footnote a.

[b] See Table I, footnote b.

TABLE IV
Effect of the Modified Resins Composition on Lapshear Strength and T-Peel Strength of an Adhesive Joint

Composition	Cyclic carbonate content[a] (%)	Modifier[b] content (wt %)	Lapshear strength (MPa)	Peel strength (kN/m)
Epidian 6	0	0	4.12	107
Epidian 6 + TGDE	0	10	3.53	98
	0	20	5.00	186
Epidian 6 + TGDEC	9	10	5.68	127
	17	20	5.10	108
Epidian 6 + VCDOC	13	10	5.68	78
	24	20	6.57	157
Epidian 6 + EROC	3	10	3.14	59
	6	20	6.86	108

[a] See Table I, footnote a.

[b] See Table I, footnote b.

The influence of cyclic carbonates on the impact resistance of the studied compositions appeared to be substantial. The compositions with TGDEC and TGDE exhibited high impact resistance. The structure of TGDEC and TGDE molecules, composed of flexible polyether units, as well as the lower crosslinking density (in the case of TGDEC) result in a more than twofold increase in impact resistance in comparison to that of the epoxy resin. The presence of the other modifiers also had a similar effect. Especially interesting results were

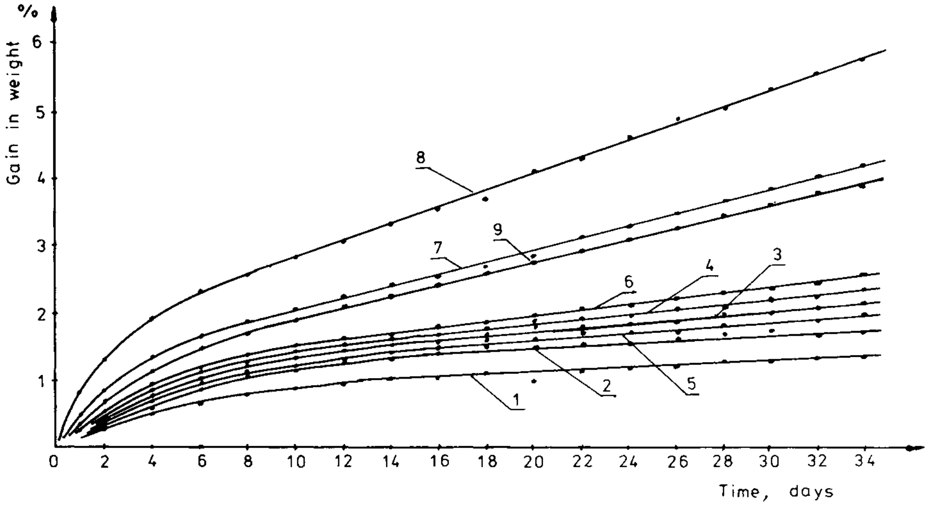


Fig. 7. Gain in weight of modified resins cured with TETA depending on the dwell time in water at 20°C: (1) Epidian 6, (2) EROC, 10 wt %, (3) EROC, 20 wt %, (4) TGDEC, 10 wt %, (5) TGDE, 10 wt %, (6) VCDO, 10 wt %, (7) TGDEC, 20 wt %, (8) VCDOC, 20 wt %, (9) TGDE, 20 wt %.

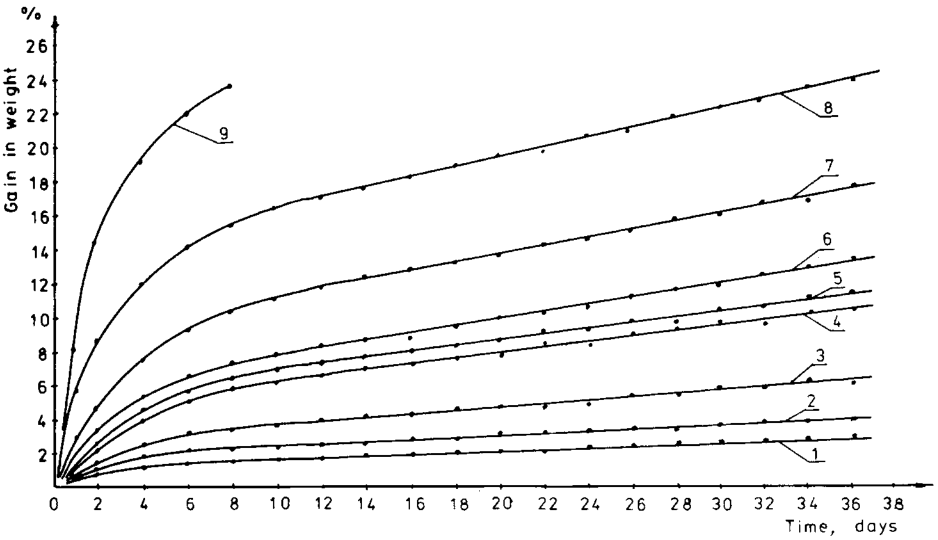


Fig. 8. Gain in weight of the modified resins cured with TETA depending on the dwell time in 10% H_2SO_4 at 20°C: (1) Epidian 6, (2) EROC, 10 wt %, (3) EROC, 20 wt %, (4) TGDEC, 10 wt %, (5) TGDE, 10 wt %, (6) VCDO, 10 wt %, (7) TGDEC, 20 wt %, (8) VCDOC, 20 wt %, (9) TGDE, 20 wt %.

obtained for samples subjected to static tensile strength and static compressive strength tests (Table III). The presence of polar β-hydroxyurethane and cyclic carbonate linkages in the systems studied apparently causes an increase in the cohesion forces occurring in them, which in turn results in an increase of strength features. The tensile strength of samples with TGDEC increases, in comparison to that of the epoxy resin, by ca. 60% for samples postcured at 90°C. A similar increase in tensile strength was observed for other epoxide–cyclic carbonate compositions. The introduction of cyclic carbonates to the epoxy resin increases its flexibility. This is indicated by a rise in ultimate elongation of the modified compositions in comparison to that of the epoxy resin. The greatest values were observed for the compositions with TGDEC and EROC—the elongation increased by 100–400% in comparison to that for the epoxy resin.

Adhesion studies were also carried out on the lapshear strength and T-peel strength of adhesive joints containing epoxide–cyclic carbonate resins. Additional polar groups (C=O) introduced to the adhesives upon modification form hydrogen and covalent bonds and therefore cause an increase in the resin adhesion to the aluminum surface. The higher flexibility of the composition also affects the strength features: a 20–65% increase in shear strength is obtained over that of adhesive joints produced from the unmodified epoxy resin (Table IV).

Studies of the chemical resistance (mass changes within immersion time in different aggressive media) are presented in the form of diagrams in Figures 7 and 8. An analysis of the results for the epoxide–cyclic carbonate compositions studied shows that they have a worse chemical resistance with respect to that of samples made from the unmodified epoxy resin. This is connected with the smaller crosslinking density and presence of hydrophilic groups, which facilitates the penetration of aggressive media. However, when comparing the systems: TGDEC–epoxy resin and TGDE–epoxy resin, it can be noticed that the compositions containing the cyclic carbonate resin exhibit a greater resistance toward dilute acids (especially for greater content of the modifier), despite their smaller crosslinking density.

In conclusion, the results of our studies on epoxide–cyclic carbonate compositions show a similar increase in reactivity and lowering of the exothermic effect as previously found for epoxy resins modified with CO_2.[5] An increase of strength features and flexibility was also obtained while maintaining the thermal resistance. Moreover, in the epoxide–cyclic carbonate compositions the viscosity of the system was lower than that of either the epoxy resin modified by CO_2 and an unmodified one. Thus, aliphatic cyclic carbonates may be used as active thinners of epoxy resins.

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