Curing of epoxy oligomers by isocyanates

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The curing of epoxy oligomers by isocyanates, as a function of structure and ratio of components, as well as of synthesizing conditions, has been studied. It was found that differences exist in reactions occurring during epoxy–isocyanate formation in bulk and in thin layer on substrate. The aspects studied were the effect of the structure of epoxy oligomers and isocyanates on relative reactivity of oligomers and on polymer formation and their structural changes depending on synthesizing temperature. Epoxy oligomers and isocyanates of various chemical structures were investigated by i.r. spectrography, differential thermal analysis, chemical analysis, electrical relaxation and electron microscopy. It is shown that the interaction between epoxy oligomers and isocyanates comprises two consecutive stages: formation of urethanes and 2-oxazolidones. The presence of tertiary nitrogen atoms in the structure of epoxy oligomer or isocyanate causes additional trimerization of isocyanate and formation of isocyanurate cycles. The structure of epoxy oligomer and isocyanate essentially influences their relative reactivity in the formation of oxazolidones and determines the temperature ranges in which these reactions take place. It is also shown that the conditions of formation and the ratio of components have a considerable effect on the chemistry of interaction in the epoxy–isocyanate oligomeric system. The interaction temperature in the epoxy–isocyanate system is the cause of varied degree of cross-linking, topological and supermolecular structure of polymers.

(**Keywords: epoxy oligomer; isocyanate; oxazolidone; isocyanurate; urethane; activation energy; rate constant; structure; morphology**)

INTRODUCTION

Increasing attention has recently been paid to epoxy oligomer- and isocyanate-based polymers, due to their application as coatings, adhesives and filling compounds of high heat resistance and chemical stability to various aggressive agents[1–3].

In the curing of epoxies by isocyanates the reaction between oxirane cycle and isocyanate (NCO) groups is of great importance, in addition to urethane formation due to the interaction between the secondary hydroxyl groups of epoxy oligomers and isocyanate groups. The process of urethane formation in various systems has been sufficiently well studied[4–6], whilst the interaction between epoxies and isocyanates has been mostly concerned with monomeric components of catalysed synthesis. It is shown that the reaction of α-oxide cycles with monoisocyanates occurs at temperatures of the order of 160–200°C resulting in formation of oxazolidones[7,8]. Mechanisms of oxazolidone cycle formation are proposed[9–11], based on a different method of isocyanate group break-up (either in the N=C or C=O double bond). In this reaction various catalysts are used: amines, quaternary ammonium compounds, pyridine, Lewis acids, etc.[12,13]. Some investigators have found that, in the presence of catalysts in a monomeric epoxy–isocyanate mixture, the reaction of oxazolidone formation might be supplemented by trimerization of NCO groups, resulting in the emergence of isocyanurate cycles[13,14].

It has also been reported[15] that, in addition to the reaction between the secondary hydroxyl (OH) groups of epoxy oligomers and isocyanates in epoxy–isocyanate systems, formation of carbodiimides, ureas, isocyanurates and oxazolidones is possible.

As a result of the ambiguity of published information on chemical reactions dependent on synthesizing conditions, the absence of data concerning the effect of epoxy oligomer and isocyanate structures on their relative reactivity in the interaction reactions, scanty information about the effect of the component ratio, and that of the synthesizing temperature on the interaction chemistry, properties and structure of epoxy–isocyanate polymers, we were prompted to carry out a series of investigations aimed at clarifying these problems. The results are reported in this paper.

EXPERIMENTAL

Epoxy oligomers and isocyanates of various chemical structures were studied. Their characteristics are given in *Tables 1* and *2*. Epoxy oligomers were purified by reprecipitation with petroleum ether from a solution in toluene, dried *in vacuo* to constant weight, and the content of functional groups (epoxy and hydroxyl) determined chemically[16,17]. Molecular weight was found by the ebullioscopic method. Isocyanates diphenylmethane diisocyanate (4,4′-DPMDI) and isophorone diisocyanate (IP) were purified by vacuum distillation at $P_{res} = 0.2$ mmHg. The content of NCO groups in isocyanates was determined according to the technique described by Stagg[18].

The interaction of oligomers was studied by i.r. spectroscopy (Spectrometer UR-20, Carl Zeiss, Jena, Germany), differential thermal analysis (d.t.a.; Paulik–Paulik–Erdei derivatograph, MOM, Hungary. Rate of temperature elevation 0.03 ± 0.002°C s^{-1}, weighed charge 0.3×10^{-3} kg) and chemical analysis. Kinetic

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Table 1 Characteristics of epoxy oligomers

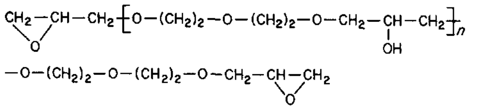
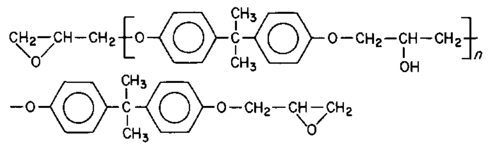
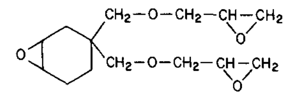
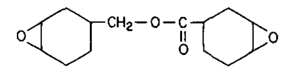
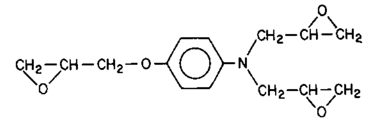
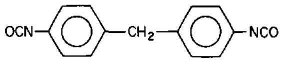
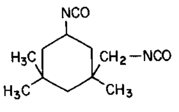
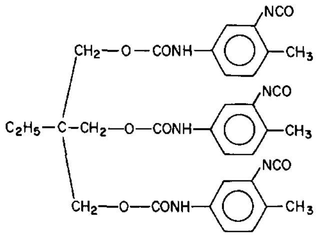
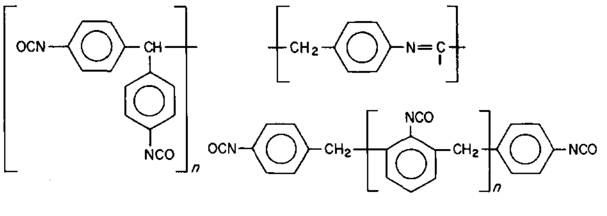
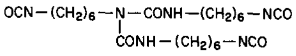
No.	Epoxy oligomer	Designation	Ideal formula	Content (%)		M_n
				Epoxy groups	OH groups	
1	Epichlorohydrin and diethylene glycol condensation product	DEG-1		26.8	4.77	290
2	Diphenylol propane and epichlorohydrin condensation product	ED-20		17.8	2.17	500
3	1,1-Di(oxymethyl)-3,4-epoxycyclohexane diglycidyl ether	UP-650T		35.0	2.0	309
4	(3,4-Epoxy cyclohexyl methylene)-3,4-epoxy cyclohexyl carbonate	UP-632		30.5	absent	220
5	n-(N,N'-diglycidyl amino)phenol glycidyl ether	UP-610		40.1	absent	360

Table 2 Characteristics of isocyanates

No.	Isocyanate	Designation	Ideal formula	NCO group content (%)	M_n
1	4,4'-diphenylmethane diisocyanate	4,4'-DPMDI		33.6	250
2	Isophorone diisocyanate	IP		37.8	275
3	Trimethylolpropane and toluylene diisocyanate adduct	TDI-TMP adduct		13.5	1000
4	Polyisocyanate, a product of diphenylmethane diisocyanate polymerization	PIC		29.1	440
5	Polyisocyanate biuret	PB	 $\mathrm{OCN{-}(CH_2)_6{-}\underset{CONH-(CH_2)_6-NCO}{N}{-}CONH{-}(CH_2)_6{-}NCO}$	20.5	410

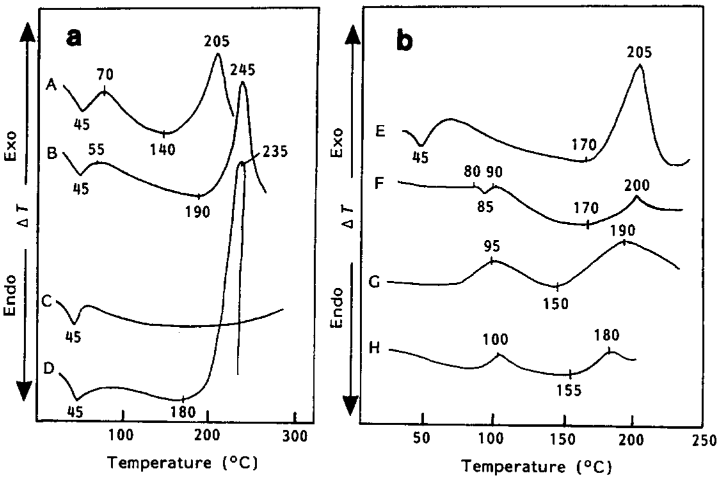


Figure 1 D.t.a. thermograms of epoxy–isocyanate systems (NCO, OH and epoxy group ratio 2:1:1 eq.). (a) Based on 4,4'-DPMDI and epoxy oligomers: A, DEG-1; B, ED-20; C, UP-632; D, UP-650T; (b) based on DEG-1 and isocyanates: E, 4,4'-DPMDI; F, TDI-TMP adduct; G, IP; H, PB

reaction parameters of epoxy and isocyanate groups were calculated according to refs 19 and 20.

The dynamics of structural changes in epoxy–isocyanate polymers were estimated by electrical relaxation[21] and electron microscopy. Electrical relaxation studies were conducted by a.c. bridge R5079 (Tochelectropribor, Kiev, Ukraine) in the temperature range of 0–200°C at 1 kHz working frequency. Microphotographs were obtained by electron microscope (JEM-100C, Jeol, Japan). Carbon replicas[22] from the surface of cured polymers were prepared by oxygen etching[23]. Photographs were taken at accelerating voltage of 80 kV and 20 000-fold magnification.

RESULTS AND DISCUSSION

Figure 1 shows d.t.a. thermograms indicating the interaction between epoxy oligomers of various chemical structures and 4,4'-DPMDI (*Figure 1a*) and between aliphatic epoxy oligomer DEG-1 and various isocyanates (*Figure 1b*). As can be seen from the thermograms, in the curing of epoxy oligomers by isocyanates at steady temperature elevation (non-isothermal conditions) there occur successive reactions forming urethane groups in the presence of hydroxyl groups in epoxy oligomers and formation of 2-oxazolidones due to the interaction of epoxy and isocyanate groups. These reactions are separated by a large temperature interval. The reaction of urethane formation is observed on d.t.a. thermograms in the range 40–90°C and that of oxazolidone formation at 140–260°C (*Figure 1a*). The exothermal peaks of these reactions were confirmed by i.r. spectroscopy. Thus, when the epoxy–isocyanate mixtures are heated to 70°C, i.r. spectra exhibit an absorption band at 1730 cm^{-1}, which corresponds to urethane groups. I.r. spectra of mixtures heated to 240°C exhibit, in addition to the 1730 cm^{-1} absorption band, a shoulder of 1760 cm^{-1} of carbonyl group valence oscillation in 2-oxazolidones[24]. At the same time the NCO group absorption band disappears at 2280 cm^{-1} and the epoxy group absorption band at 920 cm^{-1}, the latter remaining unchanged up to 100°C.

Our investigations have revealed[25] that the presence of tertiary nitrogen atom in the structure of one of the mixture components (epoxy oligomers or aromatic isocyanate) causes, along with urethane formation, trimerization of isocyanate. In the case of isocyanate PIC interaction with epoxy oligomers of various chemical structure, it is shown that the heat release in these reactions is observed on d.t.a. thermograms in the range 80–130°C, the maximum being within 90–115°C (*Figure 2*). A typical isocyanate trimerization peak is also observed in the interaction between 4,4'-DPMDI and epoxy oligomer UP-610 containing a tertiary nitrogen atom in its structure (*Figure 2*, curve A). Formation of isocyanurate cycles was confirmed by i.r. spectroscopy. I.r. spectra of samples cured at 100°C exhibited absorption bands of 1710 and 1420 cm^{-1} typical of isocyanate trimers[26]. The presence of a tertiary nitrogen atom in the structure of aliphatic isocyanates does not cause the formation of isocyanurate cycles, as evidenced by the curing of epoxy oligomer DEG-1 by polyisocyanate of biuret structure (*Figure 1*, curve H). (The exothermal peak at 100°C on the d.t.a. curve is attributed to

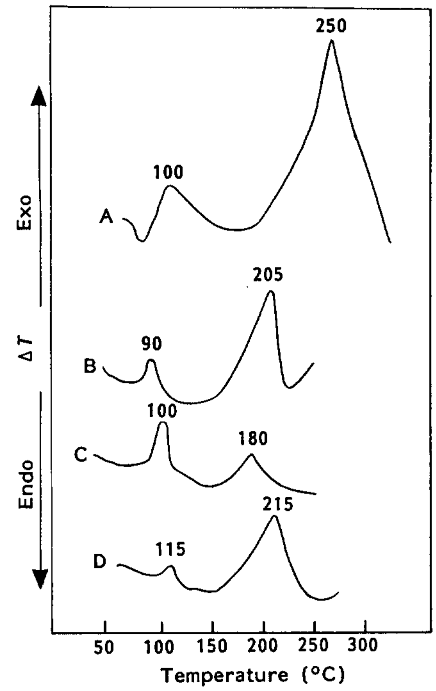


Figure 2 D.t.a. thermograms of epoxy–isocyanate systems: A, UP-610 + 4,4'-DPMDI; B, UP-650T + PIC; C, DEG-1 + PIC; D, ED-20 + PIC

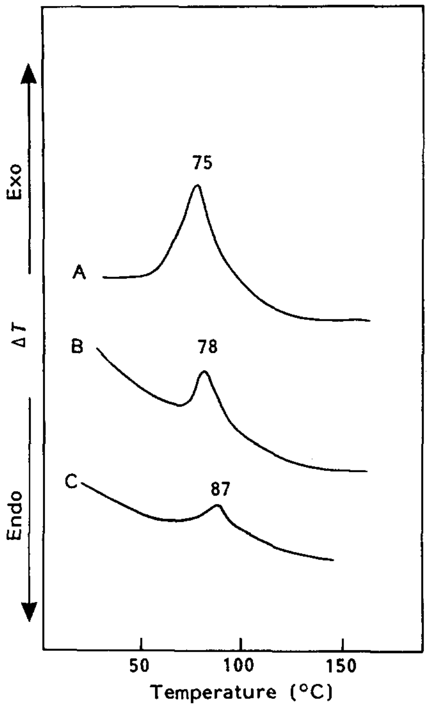


Figure 3 D.t.a. thermograms of systems based on PIC and epoxy oligomers (NCO and OH groups ratio 1:1 eq.): A, DEG-1; B, ED-20; C, UP-650T

urethane formation which follows from the i.r. spectra exhibiting a peak at 1730 cm^{-1} but lacking the bands typical of isocyanurates.)

The structure of components in the epoxy–isocyanate system determines the reactivity of functional oligomer groups in the formation of both the urethane and oxazolidone groups. The reaction of urethane formation in isocyanate PIC-based systems can occur with mixed components and will not therefore be shown on d.t.a. thermograms (*Figure 2*), since the content of secondary OH groups per eq. of the epoxy group is negligible and the reaction has a low thermal effect. The exothermal peaks in the reaction of urethane formation in this event can be observed when the concentration of secondary OH groups in the system is increased and the reaction takes place at equivalent ratios of NCO and OH groups (i.e. ratio of 1:1 eq.). *Figure 3* shows the process of urethane formation in epoxy–isocyanate compositions at equivalent ratio of NCO and OH groups in the system. As can be seen, peak maxima are observed within 75–87°C, characterizing various chemical structures. Studies of kinetic reaction behaviour in isothermal urethane formation confirm the relative reactivity dependence (ascertained by d.t.a.) of secondary OH groups in epoxy oligomers in the reaction with isocyanate hardener (*Figure 3*). The kinetic curves for urethane formation in the epoxy–isocyanate oligomeric systems are expressed by the relationship $x/[a(a-x)] \rightarrow f(\tau)$, where a is the initial concentration of the functional groups, x is the current concentration of NCO groups and τ is time. Analysis of these curves shows that this reaction is subject to the equation of the second order reaction and has no specific peculiarities to compare with the urethane formation reaction, which involves oligoesters or oligoethers and isocyanates[5,27]. Effective reaction rate constants in urethane formation due to the interaction between the secondary OH groups of oligoepoxides UP-650T, DEG-1 and ED-20 and isocyanate PIC comprise: 0.13 × 10^{-2}; 1.72 × 10^{-2} and 0.18 × 10^{-2} eq. NCO/1000 g min^{-1}, respectively.

The epoxy oligomer of aliphatic structure proved to be of the highest reactivity. Inclusion of cyclic fragments into the epoxy oligomer structure reduces the activity of OH groups in epoxy oligomers in the reaction of urethane formation[28]. The studies of relative reactivity of epoxy groups belonging to epoxy oligomers of various structures have shown a series of activities of epoxy oligomers in reactions with isocyanates in the formation of oxazolidone cycles. This series differs from the activity series for epoxy oligomers in systems cured by amines or anhydrides[29]. It has been found that the epoxy cycles of the aliphatic epoxies are the most active in the reaction of oxazolidone formation. The presence of aromatic and alicyclic rings in the epoxy oligomer molecule considerably reduces the reactivity of the epoxy group, whereas the oxyrane group of the alicyclic epoxy oligomer is altogether non-reactive with NCO groups of polyisocyanates under these conditions (*Figure 1*, curve C).

The origin of isocyanates affects the process of oxazolidone formation in a considerably lower degree than the structure of epoxy oligomers (*Figure 1b*). Studies were conducted with aliphatic oligoepoxide DEG-1 and polyisocyanates of various structure: aliphatic PB, alicyclic IP and aromatic 4,4′-DPMDI and adduct TDI-TMP. The spread of temperatures on d.t.a. curves at the initial stages of oxazolidone formation, depending on the structure of isocyanates, is considerably less than in the event when epoxy oligomers of various structures are used in oxazolidone formation, being within the range of 140–160°C. In the isocyanates considered here, the sequence of activity remains the same, depending on the structure, as the sequence observed in epoxy oligomers, i.e. aliphatic > alicyclic > aromatic[25].

By calculating the d.t.a. curves according to Borchardt–Daniels[20] and Kissinger[19] the first order reaction of oxazolidone formation was determined and the rate constants and activation energies E_{eff} of oxazolidone formation were found (*Table 3*). The reaction of oxazolidone formation is distinguished by high values of E_{eff} of the order of 129.2–193.9 kJ mol^{-1}, dependent on the structure of epoxy oligomer taking part in the reaction. As can be seen from *Table 3*, the aliphatic epoxy oligomer has the lowest E_{eff} and its rate constant at 200°C is higher by one order than in the aromatic ones[25]. It can be assumed that steric hindrances and lower kinetic mobility of oligomers having cyclic groups (epoxy oligomers and isocyanates) are the determining factors in the reactivity of epoxy and isocyanate groups in the formation of cyclic structures of oxazolidones. These factors are much more important than the electron structure of oligomer molecules, if the viewpoint of

Table 3 Kinetic reaction parameters in oxazolidone formation during interaction between 4,4′-DPMDI and epoxy oligomers of various chemical structure

Epoxy oligomer	Reaction rate constant ($K \times 10^2$ s^{-1}) at different temperature 200°C	205°C	Effective activation energy, E_{eff} (kJ mol^{-1})
DEG-1	8.32	16.50	129.2
UP-650T	0.67	1.15	188.1
ED-20	0.30	0.48	193.9

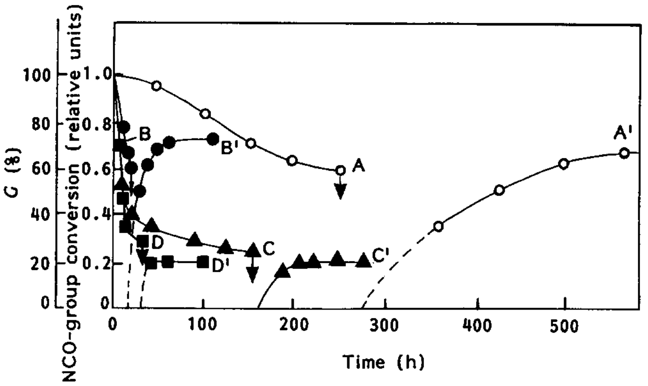


Figure 4 NCO group conversion and yield of cross-linked polymer (G) of epoxy–isocyanate composition 2 (curve A,A′–B,B′) and composition 1 (curve C,C′–D,D′) at curing temperature 25°C. Curves A,A′, C,C′, in bulk; curves B,B′, D,D′, in thin layer on substrate

Gulbins and Hamann[10,30] be followed that the formation of oxazolidone cycles runs through a stage of dioxalane cycle formation with subsequent regrouping into oxazolidone cycle. The above data on chemical transformation in epoxy–isocyanate systems were obtained during continuous temperature elevation. It was therefore of interest to analyse the influence of the time factor on the curing process of compositions under isothermal conditions at room temperature, especially as regards systems in which one of the components contains in its molecule a tertiary nitrogen atom. For this purpose the curing of epoxy oligomer UP-650T by isocyanate PIC at 25°C was studied and the effects on this of the component ratio in the system and of synthesizing conditions, in bulk or thin layer on substrate, were analysed.

Functional group compositions were chosen as follows: NCO to OH group ratio 1:1 (composition 1); NCO to epoxy to OH group ratio 2:1:1 (composition 2). Composition 2 can be considered as a system with a large excess of NCO groups (NCO/OH = 7 eq.), since at low temperatures the epoxy groups do not react with isocyanates.

Curves indicating gel fraction accumulation and yield of cross-linked polymer in the process of interactions in compositions 1 and 2 are shown in *Figure 4*. It is evident that, with equivalent ratio of isocyanate and hydroxyl groups of epoxy oligomers the main reaction in composition 1 is the reaction of urethane formation (*Figure 4*, curves C, D). I.r. spectra exhibit an intensive band of urethane group absorption in the region of 1730 cm^{-1} with a drop of NCO group absorption at 2280 cm^{-1}. The epoxy group absorption band at 920 cm^{-1} remains unchanged. With the excess of isocyanate (composition 2; *Figure 4*, curves A, B) and polymer formation at room temperature, in addition to urethane formation, comprising only 3.16% of the contribution to these systems, the main reaction is the isocyanate trimerization. This reaction runs at a rate three orders lower than the urethane formation[28].

Fragments of i.r. spectra of epoxy–isocyanate composition 2, shown in *Figure 5*, confirm that the bulk urethane formation in the system runs very rapidly, and the bands in the region of 1730 cm^{-1} appear at the early stages of the process. During the interaction the valence oscillation band of carbonyl group in isocyanurate cycle increases at a great pace, reaching a maximum at 1710 cm^{-1}, so that at the final stage of polymer formation there actually occurs a reconstruction of the absorption band of valence oscillations in polymer carbonyl groups: the peak becomes more intense at 1710 cm^{-1}, the band being rearranged into a sort of shoulder at 1730 cm^{-1} (*Figure 5a*). Apart from this, the intensity of the second characteristic band of isocyanurate absorption in the region 1420 cm^{-1} also increases. Typical of composition 2 is a greater drop of critical degree of reaction completion at the point of gel formation from 0.75 (for composition 1) to 0.40 (for composition 2). This fact confirms intensive reaction of polyisocyanate trimerization. The appearance of additional branch points caused by the formation of isocyanurate cycles determines gel formation in the system at low degrees of reaction completion as a result of mean functionality increase. The yield of cross-linked polymer increases to 70% instead of 20%, due also to the formation of additional cross-linking points, i.e. isocyanurate cycles.

Polymer formation in a thin layer on substrate results in a considerably rapid conversion of isocyanate groups, as compared to bulk polymer formation, due to the increased rate of isocyanate trimerization on the substrate (*Figure 4*, curves A, B). In our view it is associated with the catalytic effect of traces of air humidity acting as a proton donor in the system epoxy–tertiary nitrogen atom present in the structure of isocyanate PIC[31]. As is well known, similar systems act as catalysts in trimerization reactions[32]. The absence of such a proton donor in the bulk composition leads to a considerable drop of

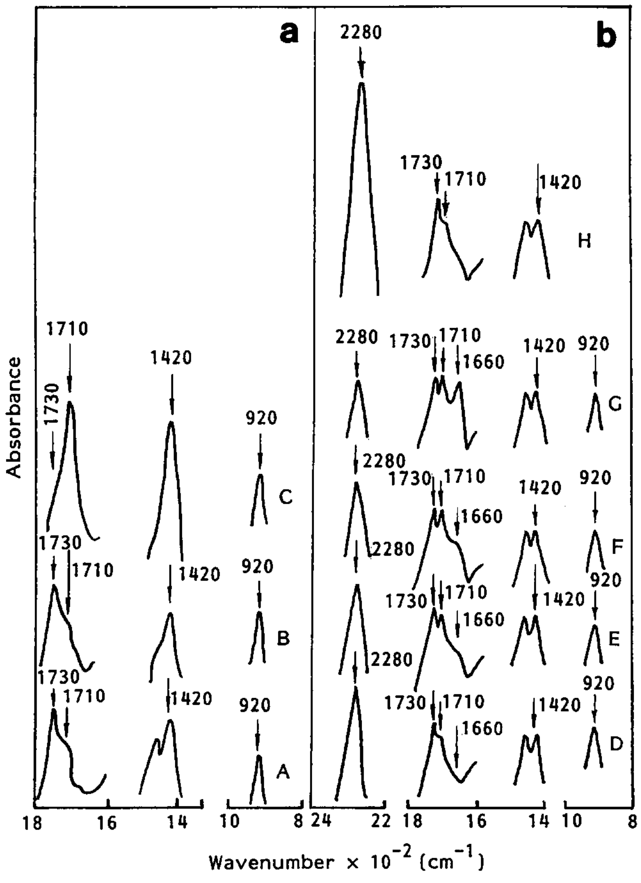


Figure 5 Fragments of i.r. spectra of individual PIC (H) and composition 2 cured (a) in bulk and (b) in thin layer on substrate. A,D, Initial composition; B,E, after 40 h; C, after 200 h; F, after 90 h; G, after 170 h

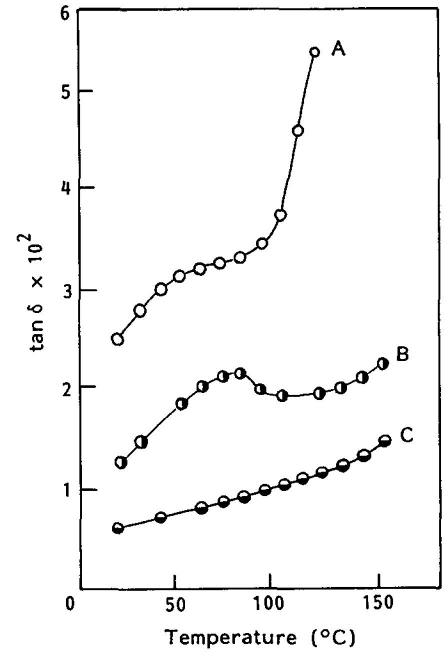


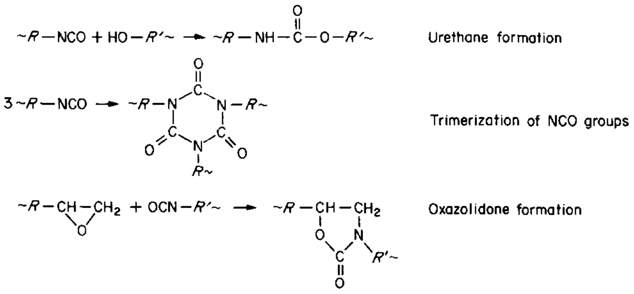
Figure 6 Dependence of dielectric loss tangent on temperature of epoxy–isocyanate polymer cured at: A, 25°C; B, 100°C; C, 160°C

isocyanate trimerization rate constant in the given component ratio.

Analysis of i.r. spectra of a polymer forming on substrate (*Figure 5b*) indicates that in the interaction of oligomers, as well as the intensity growth of band 1710 cm^{-1}, a band appears in the region of 1660 cm^{-1} characteristic of carbonyl group oscillations in urea groups. I.r. spectra of a polymer following 170 h of curing have triplet oscillations with maxima of 1660, 1710 and 1730 cm^{-1}, indicating the presence of urea, isocyanurate and urethane fragments, respectively, in the cured polymer (*Figure 5*, curve G).

The influence of curing temperature on the dynamics of structural changes in polymers was estimated by electric relaxation and electron microscopy. Investigations were conducted on samples of a system of epoxy oligomer UP-650T and isocyanate PIC cured at various temperatures (25, 100 and 160°C) under isothermal conditions in a thin layer on substrate. The ratio of functional groups of NCO, OH and epoxy groups was 2:1:1 eq.

Changes in polymer structure at molecular level depended on various chemical reactions occurring at various temperatures:



Changes in molecular organization of epoxy–isocyanate polymers, depending on the synthesizing temperature, result in changes of topological and supermolecular structure, thus influencing the properties of epoxy–isocyanate polymers[33].

Figure 6 shows dipole-segmental polymer mobility depending on the temperature of synthesis. Studies of molecular mobility have shown that polymers obtained at room temperature are distinguished by the absence of the maximum and anomalous growth of tan δ values with the rise of measurement temperature, attributable to the presence of a large amount of non-reacting functional groups and low-molecular fragments. Structural morphology of this polymer is distinguished by low heterogeneity and globular surface formation due to polymer matrix, formed mainly from urethane and urea fragments (*Figure 7a*).

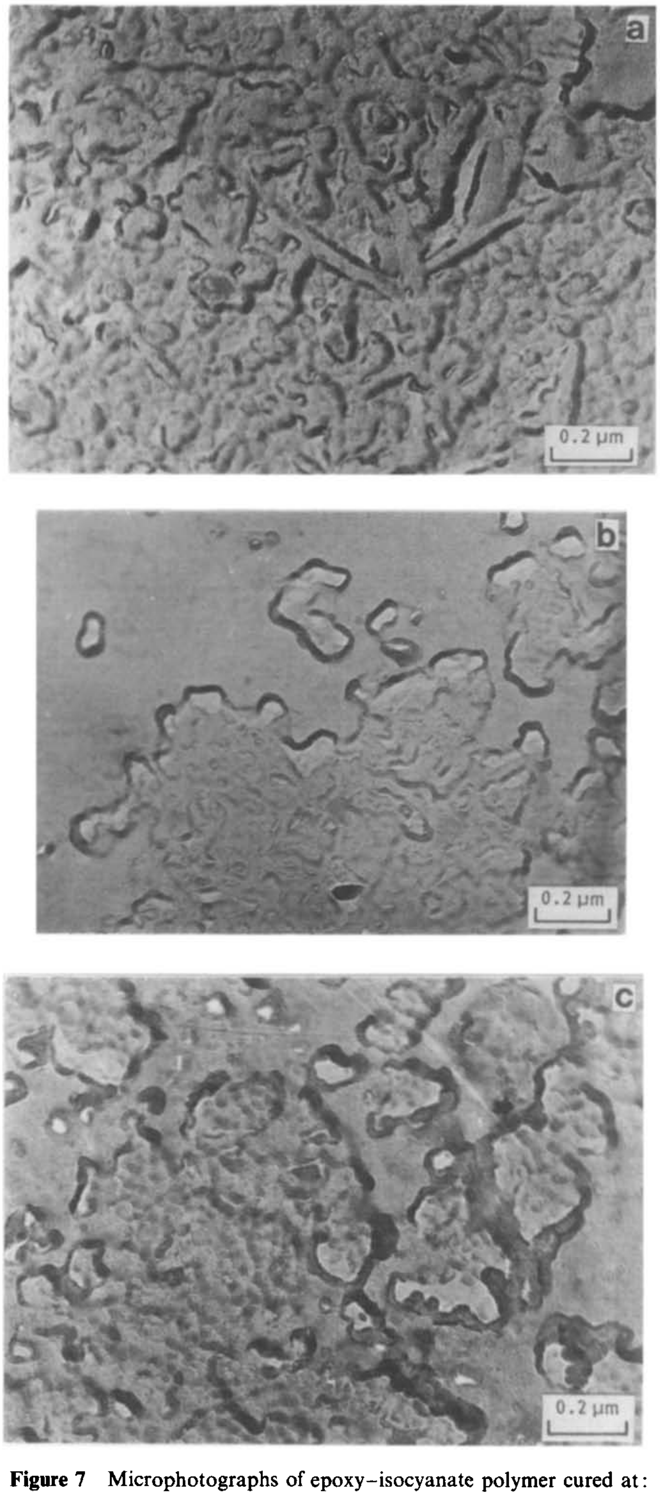


Figure 7 Microphotographs of epoxy–isocyanate polymer cured at: (a) 25°C; (b) 100°C; (c) 160°C

The elevation of synthesizing temperature to 100°C results in greater yield of cross-linked polymer and restricts molecular mobility. The curve of tan δ exhibits a distinct maximum at 78°C and reduction of absolute tan δ values in comparison to a low temperature sample as a result of a large contribution by the reaction of isocyanate trimerization into the polymer structure. Microphotographs of a sample cured at 100°C exhibit a distinct phase separation which leads to the appearance of a new microphase, this being associated with the formation of rigid cyclic structures of isocyanate trimers along with urethane fragments (*Figure 7b*).

Polymer synthesis at 160°C, when the entire complex of chemical interactions is being accomplished in the system (urethane formation, trimerization of isocyanate groups and formation of oxazolidones), leads to even greater changes in the morphology of epoxy–isocyanate polymer surface at a general increase of the phase boundary, to incomplete phase separation, but to a more homogeneous distribution of phases (*Figure 7c*). The incompleteness of phase separation is attributable to the fact that during high temperature curing there occurs, in the early stages of the process, a sharp drop of macromolecular mobility due to growing lattice density[33]. Absence of the maximum on the dielectric loss tangent *versus* temperature curve and an even greater drop of its absolute values in epoxy–isocyanate polymers synthesized at 160°C points to the completion of spatial structure formation and to the absence of mobile fragments (*Figure 6*, curve C).

CONCLUSIONS

The studies of chemical interaction in non-catalysed oligomeric epoxy–isocyanate compositions have shown that two main reactions occur in these systems, separated by a considerable temperature interval: the formation of urethanes and oxazolidones. The presence of tertiary nitrogen atoms in any of the ingredients of the epoxy–isocyanate system causes a side reaction of NCO group trimerization. Aliphatic isocyanates containing nitrogen do not provoke a reaction of isocyanurate formation. Kinetic parameters of oxazolidone formation were calculated. It is shown that this process is in full agreement with the first order reaction equation and is distinguished by a high activation energy of 129.2–193.9 kJ mol^{-1}. Most active in the reaction of oxazolidone formation are the aliphatic epoxy oligomers and isocyanates; the aromatic oligomers are least active. The epoxy cycle of the alicyclic epoxy oligomer does not react with NCO groups without a catalyst.

The dependence of the epoxy–oligomer structure effect on the relative activity of its secondary hydroxyl groups in the reaction of urethane formation was determined. The reactivity of secondary OH groups of epoxy oligomer decreases in the order aliphatic > aromatic > aliphatic–alicyclic.

In epoxy–isocyanate oligomer compositions formed at room temperature under isothermal conditions the component ratio and curing conditions have a significant effect on system interaction. With a ratio of 1:1 eq. for NCO and OH groups and with tertiary nitrogen present in the composition of one of the oligomers, urethane formation is the basic reaction in bulk and in thin layer on the substrate. With a change in component ratio in the epoxy–isocyanate system to 2:1:1 eq. for NCO, OH and epoxy groups, trimerization of the isocyanate component emerges as the basic reaction. In a thin layer on substrate the process of polymer formation is supplemented by the reaction of urea formation.

It has been found that the structural changes in epoxy–isocyanate polymer, depending on the synthesizing temperature and relations between urethane formation, cyclotrimerization of isocyanates and formation of oxazolidones, result in changes in the degree of the cross-linking and, correspondingly, in changes of topological and supermolecular structures of polymers. Elevation of polymer formation temperature from 25 to 160°C leads to a loss of segmental mobility in the polymer matrix and to the appearance of distinct phase separation.

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