

Cyanoacetamide Accelerators for the Epoxide/Isocyanate Reaction

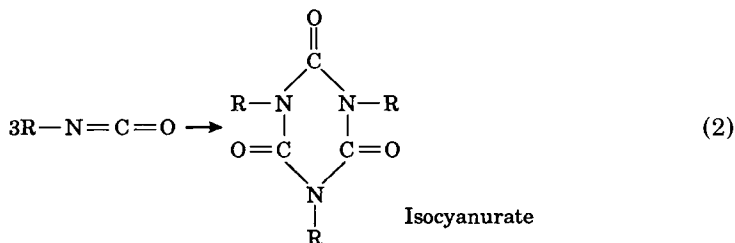
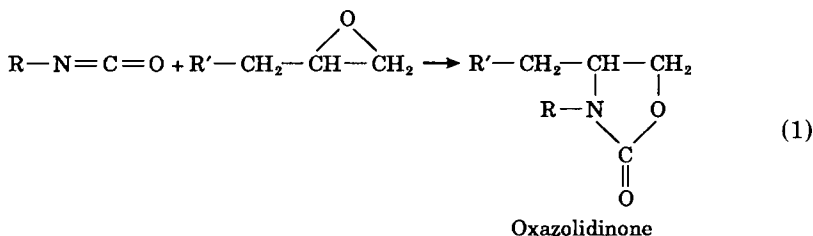
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Synopsis

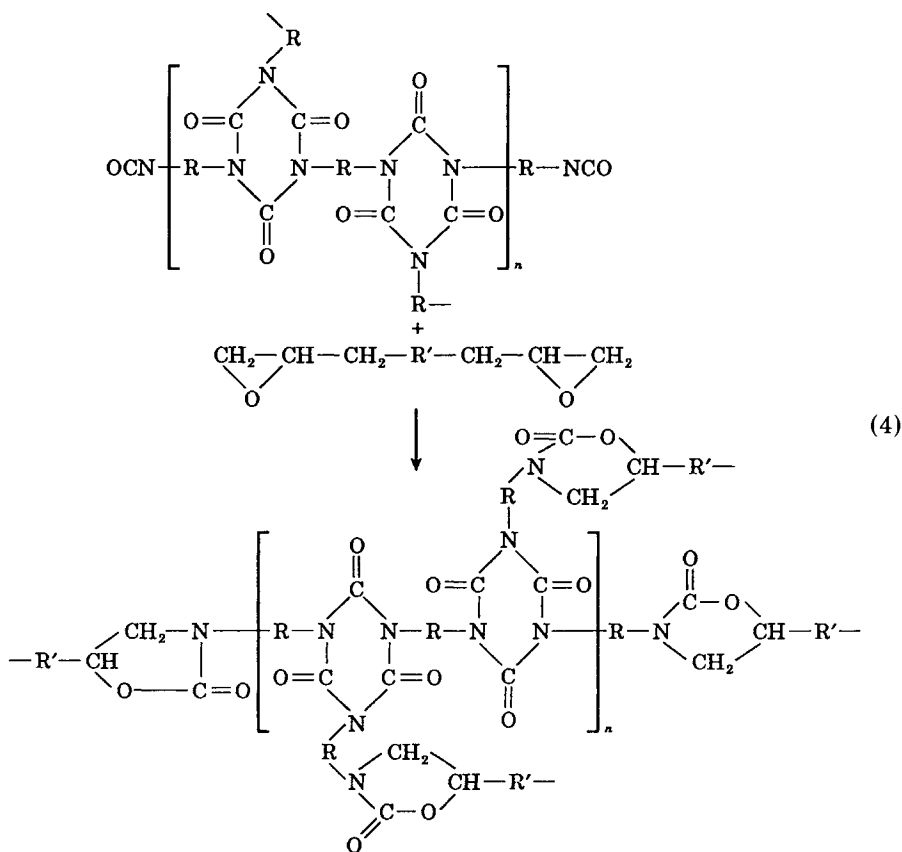
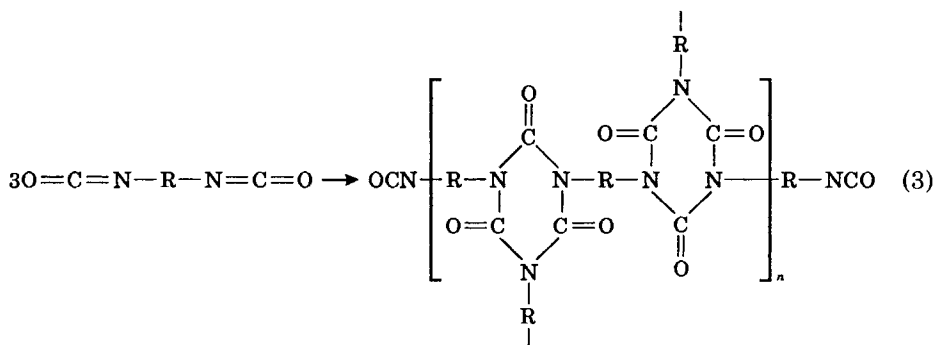
The cyanoacetamides $\text{NC}-\text{CH}_2-\text{CO}-\text{NH}-\text{R}_1-\text{N}(\text{R}_2)(\text{R}_3)$ are a new family of accelerators for the epoxy/isocyanate (EP/IC) reaction. Results obtained from systematic structure variations indicate that they belong to the "deactivated tertiary amine" type of catalyst with the cyanoacetamide group as the deactivating moiety. Reactivity can be controlled via the R_1 substituent (cyanoacetamide) and/or by R_2/R_3 . A reaction mechanism is proposed. The results of a factorial design experiment and IR determination of the oxazolidinone (OX)/isocyanurate (ICR) extinction maxima ratios were used to develop an optimized EP/IC system. A trial formulation (filled) is given in which rapid gelation, a high T_g value, and excellent mechanical properties were achieved with an accelerator concentration of less than 0.2%.

INTRODUCTION

The reaction between epoxides and isocyanates is now relatively well known and would appear to be at least 50 years old.¹ The main reaction products are oxazolidinones and isocyanurates.^{2,3}



In a 2/2 bifunctional system the main reactions are apparently as follows: The isocyanurate will trimerize first at temperatures $\leq 130^\circ\text{C}$, and this reaction step is followed, at temperatures in excess of 130°C , by further reaction between the isocyanurate prepolymer and the bisepoxide^{4,5}:

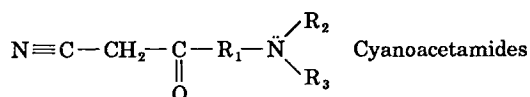


Reaction scheme (4) shows that the final structure consists of linked isocyanurate and oxazolidinone rings. Both are reported to exhibit excellent thermal resistance.⁶⁻⁸ Of equal importance is the fact that due to the different functionalities of the isocyanurate and oxazolidinone moieties (3 and 2) and also to the generally more flexible nature of R' in a commercial epoxide resin, an increase in the amount of oxazolidinone linkages will lead to a decrease in crosslink density and therefore to more flexible systems with improved mechanical properties. Conversely a high percentage of isocyanurate linkages would be synonymous with a high T_g /high modulus structure. It is this combination

of high temperature resistance and variable mechanical properties that accounts for the techno/commercial interest shown toward this relatively new product group in recent years.^{5,9-11}

Catalysts are generally employed for the epoxide/isocyanate reaction. Apart from specific catalysts such as lithium compounds and lithiumhalide complexes¹²⁻¹⁴ or more recently organoantimony iodide,¹¹ the main body of proposed catalysts would seem to fall into one of four categories, viz. onium salts (e.g., quaternary onium salts),^{15,2} Lewis bases (e.g., tertiary amines such as imidazoles),^{4,16} Lewis acids (such as ferric chloride),¹⁷ and complexes between Lewis acids and Lewis bases.^{16,18}

In this study we shall report on work with a new group of products that have proven to be highly effective as catalysts for the epoxy/isocyanate reaction: the cyanoacetamides.



EXPERIMENTAL

Synthesis and Materials

The cyanoacetamides were made by amidation of ethyl cyanoacetate¹⁹ and purified via high-vacuum distillation. 3-Dimethylamino-1-propylamine and cyanoacetamide were obtained from Fluka AG, Buchs, Switzerland. EPN 1139 is a standard CIBA-GEIGY epoxy novolac resin; the product used had an epoxide content of 5.7 eq/kg (or an epoxide equivalent weight of 175). ZK HR 1862 (CIBA-GEIGY) is a polypropylene-oxide-diglycidylether; the epoxide equivalent weight of the batch used in this study was 392. Diphenylmethane-diisocyanate (MDI) was obtained from Merck-Schuchardt, West Germany; the product used had an -NCO equivalent weight of 128.

Infrared Studies

The infrared spectra of the cured epoxide/isocyanate systems were taken with a Perkin-Elmer FT-IR 1710 spectrophotometer equipped with a Perkin-Elmer data station PE 3600:

Samples: 1 mg in 350 mg KBr.

Isocyanurate (ICR) ν (C=O) analysis absorption: 1710 cm^{-1} .

Oxazolidinone (OX) ν (C=O) analysis absorption: 1758 cm^{-1} .

The carbonyl absorption frequencies observed and given here were in excellent agreement with literature values.^{4,7} The ratio of the extinction maxima at 1758 cm^{-1} to that at 1710 cm^{-1} [$E_{1758(\text{OX})}/E_{1710(\text{ICR})}$] for the systems studied were determined using part of the Perkin-Elmer QUANT program (method RATIO).

Gel Time Data

The gel times were determined on 0.5-g samples on thermostatically controlled hot plates. The temperature variance was $\pm 0.1^\circ\text{C}$.

Physical Properties

Glass transition temperatures (T_g) were determined via thermomechanical analysis (TMA). The module used was a DuPont 943 coupled to a DuPont 9900 thermal analysis system. Samples of 1 mm were used. The heating rate was 10°C/min.

The mechanical properties were determined according to the various ISO, Swiss (VSM), and German (DIN) norms. Other properties were determined according to CIBA-GEIGY internal standards. The norms or standards are indicated in the appropriate tables.

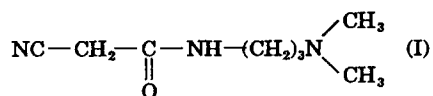
RESULTS AND DISCUSSION

In preliminary work several dozen new compounds were screened as accelerators for the epoxy/isocyanate reaction. Equivalent amounts (1/30 mol/mol epoxy) of accelerator candidates were tested in a standard epoxy/MDI system:

EPN 1139	100 pbw
ZK HR 1862	100 pbw
MDI	250 pbw

The main screening criteria were reactivity and curability (the ability to form a "normal," homogeneous, ca. 4-g sample casting after a standardized cure cycle).

The compounds screened were representative of the four known classes of catalyst for the epoxide/isocyanate reaction, viz. onium salts, Lewis bases, Lewis acids, and Lewis acid/base complexes. Very few candidate accelerators fulfilled the two primary screening requirements. One that did was *N,N*-dimethyl-*N*-propyl-3-cyanoacetamide (DIMPCY) I:



With the ultimate objective of developing an accelerator (or accelerators) with maximum possible efficiency out of this product group, systematic structure variations were carried out in order to gain insight into the possible modus operandi. This is shown in Table I. With reference to the general formula the chain length between the cyanoacetamide group and the tertiary amine (R_1) was varied first.

A slight decrease in reactivity is caused by reducing R_1 from C_3 to C_2 and a very marked decrease by reducing R_1 further to C_0 (cyanoacetamides I-III). If the cyanoacetamide group is removed completely (compound IV) catalytic activity is increased dramatically. Cyanoacetamide itself (compound V) is not active as an accelerator, neither is the "neutrally" substituted cyanoacetamide $\text{N}\equiv\text{C}-\text{CH}_2-\text{CO}-\text{NH}-i-\text{Bu}$ (not shown in the table).

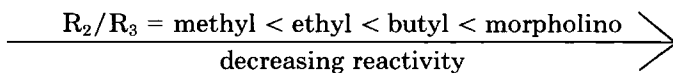
TABLE I
Influence of Cyanoacetamide Structure on the Reactivity of an Epoxy/Isocyanate System

Epoxy/isocyanate model system ^a without accelerator	Gel time at 180°C
Epoxy/isocyanate model system with cyanoacetamide accelerator ^b ↓	30'
$\text{I} \quad \text{NC}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N} \begin{matrix} \text{R}_2 \\ \text{R}_3 \end{matrix}$	2'
$\text{II} \quad \text{NC}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{N} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	3'
$\text{III} \quad \text{NC}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{N} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	≥30'
$\text{IV} \quad \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{N} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	<30"/120°C
$\text{V} \quad \text{NC}-\text{CH}_2-\text{CO}-\text{NH}_2$	≥30'
$\text{VI} \quad \text{NC}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N} \begin{matrix} \text{CH}_2-\text{CH}_3 \\ \text{CH}_2-\text{CH}_3 \end{matrix}$	7'
$\text{VII} \quad \text{NC}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N} \begin{matrix} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{matrix}$	21'
$\text{VIII} \quad \text{NC}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N} \begin{matrix} \text{CH}_2-\text{CH}_2 \\ \text{CH}_2-\text{CH}_2 \end{matrix} \text{O}$	40'

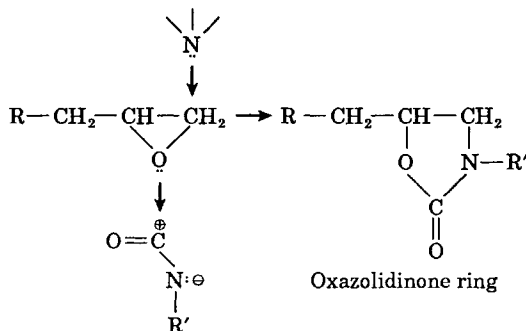
^a EPN 1139, 100; ZK HR 1861, 100; MDI, 250.

^b 1/30 mol/mol epoxide.

These results clearly indicate that the tertiary amine is the catalytically active species and that this activity is reduced by the cyanoacetamide group. In the second part of the table results are given for three further cyanoacetamides (VI-VIII). Here, R₁ has been kept constant and R₂ and R₃ varied. As would now be expected, the catalytic activity of the cyanoacetamides can also be influenced by "direct" substitutions at the tertiary N. The reactivities measured are in the expected order, i.e.,

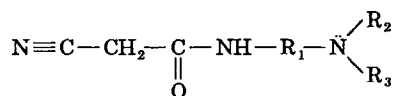


Tertiary amines fall under the general heading "Lewis bases," and the catalyses of the epoxide/isocyanate reaction with Lewis bases is well known, as has already been mentioned in the introduction. In spite of this, no reaction mechanism for this catalysis has, to our knowledge, been proposed in the literature. This may be due to the fact that the epoxide/isocyanate reaction in the presence of a tertiary amine can easily be formulated as a relatively straightforward Lewis base/Lewis acid reaction:



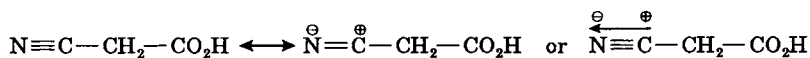
The tertiary amine attack on epoxy carbon would decrease the electropositivity at this carbon atom, thereby weakening the carbon/oxygen bond. This in turn would facilitate coordination between the oxygen electron pair and an electrophilic center of the isocyanate molecule. This formulation would be in agreement with generally known Lewis base/Lewis acid reactions with epoxide groups.²¹ The tautomeric form given for the isocyanate is, of the four given in the literature,²² the only one which can lead to the formation of the oxazolidinone ring. Indirect support for the catalysis of an *epoxide/isocyanate* reaction as opposed to tertiary-amine-catalyzed epoxide homopolymerization and/or tertiary-amine-catalyzed isocyanurate trimerization²⁰ comes from a recently published article in which another "inhibited" tertiary amine, 1-cyanoethyl-2-phenyl-imidazole, was clearly shown to catalyze oxazolidinone formation.⁹ Nevertheless, the latter reactions cannot be excluded.

The second point to be discussed is a possible mechanism for the deactivation of the tertiary amine moiety in the cyanoacetamide molecule:



We have clearly demonstrated that the cyanoacetamide group is responsible for this deactivation and would therefore first try to identify an electropositive center within this moiety that might coordinate with (and thereby deactivate) the lone electron pair of the tertiary nitrogen atom. Our suggestion is that the electropositive center is the carbon atom of the cyano group. The cyano group

of cyanoacetic acid is known to have a strong dipole with a positive charge oriented toward the carboxyl group²³:



As a result of this the K_a values of acids containing this substituent are markedly higher than those that do not. Furthermore the dipole effect is known to be proportional to the distance between the dipole and the carboxyl group as demonstrated by a decrease in K_a values in the series α -, β -, and γ -chlorobutyric acid. We propose therefore by analogy—the cyano group or, more precisely, the cyan dipole of the cyanoacetamide molecule is responsible for the deactivation of the catalytically active tertiary nitrogen. This proposal would also readily explain the increasing deactivation with decreasing distance between the cyanoacetamide and tertiary amine groups (substituent R_1) as shown in Table I.

System Variation

The effects of accelerator concentration, epoxy/isocyanate (EP/IC) ratio, and flexibilizer concentration upon system processing and end properties were now investigated. In order to determine not only primary but also secondary and possibly higher order effects (i.e., interactions), a factorial experiment was used:

Factors		Levels	
		(-)	(+)
A:	EP/IC	0, 4	1, 2
B:	Flexibilizer	10	40 mol % ^a 1/30 mol % ^b
C:	Accelerator	1/210	% ^b

^a Based upon epoxy.

^b Per mole epoxy.

The properties included in the factorial experiment were flexural strength and flexural angle (the maximum angle of deflection during the flexural strength measurement), impact strength, T_g , gel time, water absorption, and oxazolidinone (OX)/isocyanurate (ICR) infrared extinction maxima ratios of the cured systems. The experimental design and numerical results for two responses, viz. T_g and impact strength, are given in Table II.

Further results are given in Figures 1 and 2 for flexural strength and water absorption. Two of the infrared absorption spectra (experiments 1 and 4) are reproduced as Figures 3 and 4. The OX and ICR $\nu(\text{C}=\text{O})$ absorptions are clearly visible at 1758 and 1710 cm^{-1} , respectively, with more ICR having been formed in experiment 1. In experiment 4 the opposite would appear to be the case. The corresponding extinction maxima ratios are 0.5156 and 1.8851.

The average effects were determined according to the Yates method,²⁴ and the significance was determined graphically using half-normal plots.^{25,26} The

TABLE II
Factorial Experiment: Epoxy/Isocyanate Model System^a

Factorial design				Results	
Experiment	Factors			T_g (°C)	Impact strength (kJ/m ²)
	A	B	C		
1	-	-	-	264	6.7
2	+	-	-	79	11.9
3	-	+	-	205	8.5
4	+	+	-	51	16.5
5	-	-	+	260	6.3
6	+	-	+	115	15.1
7	-	+	+	51	6.7
8	+	+	+	55	16.4

^a Influence of EP/IC ratio (factor A), flexibilizer concentration (factor B), and accelerator concentration (factor C) on T_g and impact strength. Cure conditions for all formulations: 3 h/80 + 3 h/140 + 18 h/200°C.

significant factors for the various properties (in descending order of magnitude where appropriate) together with the corresponding signs are as follows:

Property	Significant Factor(s)
T_g	A (-)
Flexural strength	B (-), AB (-)
Impact strength	A (+)
Water uptake	B (+), A (+), AB (+)
Gel time	A (-), C (-)
OX/ICR (extinction ratios)	A (+)

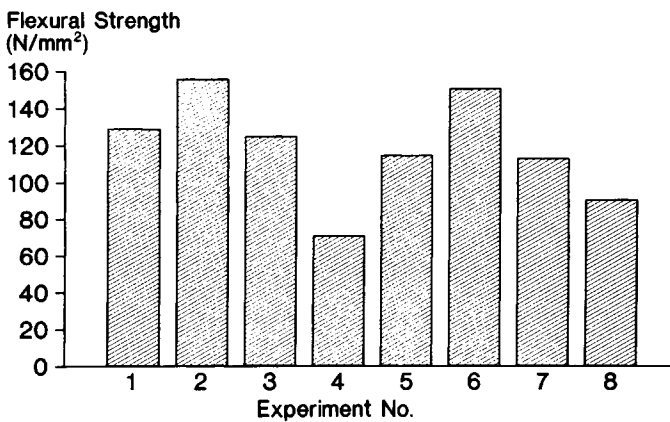


Fig. 1. Influence of EP/IC ratio, flexibilizer content, and accelerator concentration on flexural strength.

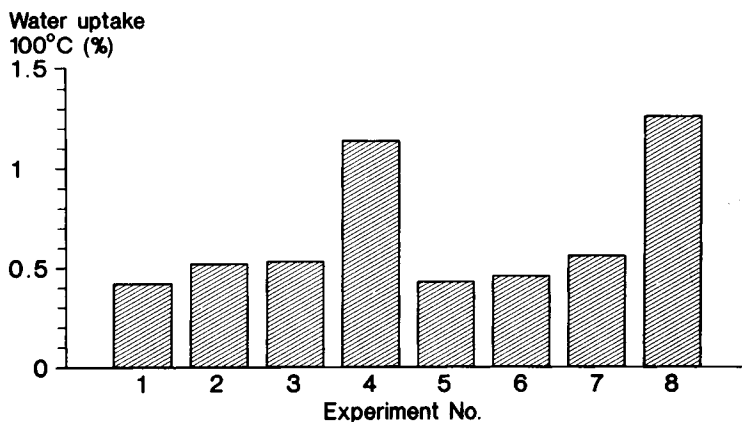


Fig. 2. Influence of EP/IC ratio, flexibilizer content, and accelerator concentration on water uptake (100°C).

Starting with factor C, the accelerator concentration, the only property affected is the gel time. The effect is negative, as would be expected, i.e., increasing the accelerator concentration from 1/240 to 1/30 mol % has led to a significant decrease in gel time. Of particular interest is the fact that the gel time can be influenced even more strongly by factor A = EP/IC ratio. Here, it is the threefold increase in the initial epoxy content of the formulations that has led to significantly shorter gel times. However, regulating gel times with the EP/IC ratio alone would not be advisable because almost all the other properties would be simultaneously affected, as can be seen from the table.

A further point of interest in connection with the accelerator concentration (within the range investigated in this experiment) is that it has shown no effect on the OX/ICR extinction ratios of the cured systems. From this, one would

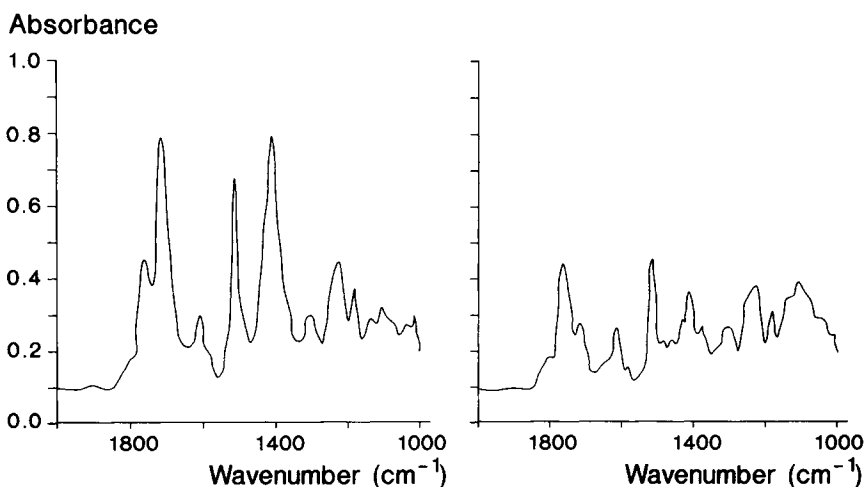


Fig. 3. Infrared spectrum of experiment 1 from factorial design.

Fig. 4. Infrared spectrum of experiment 4 from factorial design.

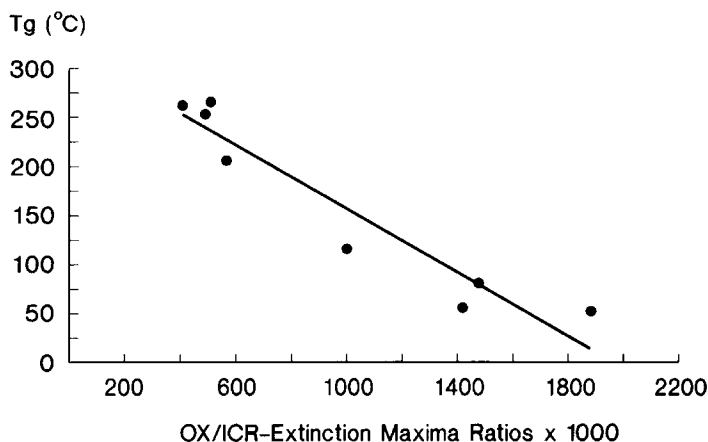


Fig. 5. EP/IC correlation between the glass temperature T_g and the OX/ICR extinction maxima ratios.

expect final properties also to be unaffected, and this is indeed the case. Factor A, the EP/IC ratio, is the dominant factor and influences all the properties measured either directly or via interaction with factor B, the flexibilizer concentration (e.g., flexural strength, water uptake).

Direct correlations were found between the OX/ICR extinction ratios, the glass temperature T_g , and the flexural angle. The correlation coefficients are 0.95 and 0.93, respectively (Figs. 5 and 6).

Final Results

The results of the factorial experiment described here proved to be extremely useful when it came to formulating an epoxy/isocyanate system with a best possible combination of properties. In the trial formulation

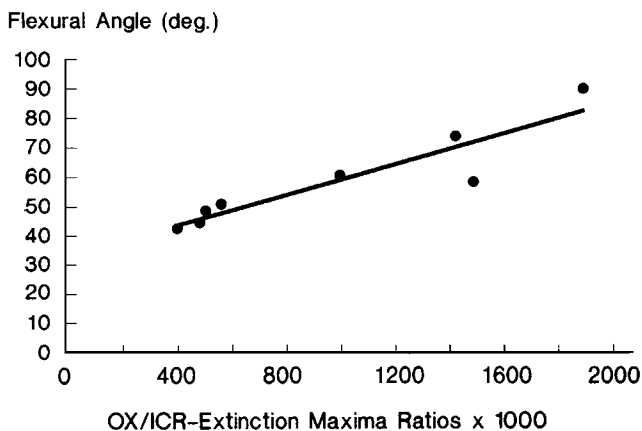


Fig. 6. EP/IC correlation between the flexural angle and the OX/ICR extinction maxima ratios.

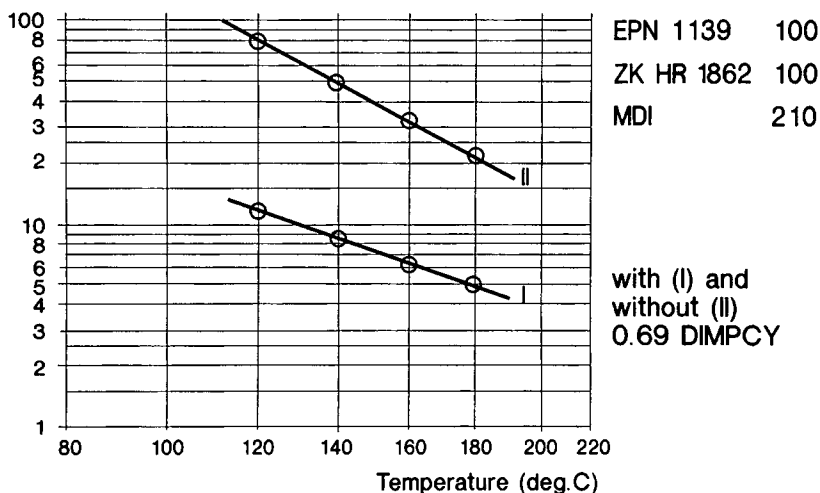


Fig. 7. Gel time as a function of temperature for trial formulation: EPN 1139, 100; ZK HR 1862, 100; MDI, 210 with (I) and without (II) 0.69 DIMPCY.

EPN 1139	100 pbw
ZK HR 1862	100
MDI	210
DIMPCY*	0.69

* 1-*N,N*-dimethylamino-3-cyanoacetamido-propane.

the EP/IC ratio has been raised from 0.42 to 0.5 in order to improve impact strength and the expected reactivity increase partially compensated by (greatly) reducing the accelerator concentration from 1/30 to 1/200 mole/mole epoxy. This approximately sevenfold reduction in accelerator concentration should certainly have a positive effect upon system pot life. In spite of this extremely low concentration, 0.17% or 1.7 ‰, the cyanoacetamide accelerator is extremely effective as demonstrated by the gel time plots given in Figure 7. An indication of final system properties follows:

Flexural strength (MPa) (ISO/R 178)	137	(134–140)
Impact strength (kJ/m ²) (ISO/R 179)	10.5	(9.5–11.5)
Heat distortion (°C) (ISO 75)	237	

These values, which are excellent for a filled system, were obtained when the trial formulation was formulated with 65% silica flour and cured for 4 h/140 + 16 h/225°C.

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