Curing of Epoxy Resins with Dicyandiamide and Urones

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SYNOPSIS

The curing of epoxy resins using dicyandiamide (DICY) and combinations of DICY with several uron accelerators as curing agents is investigated. DSC, FTIR, mechanical, and sorption measurements indicate complex multistage curing processes. There is no evidence that the curing reaction is catalyzed by DICY. The optimum stoichiometry is determined as 7 epoxy units per 1 molecule DICY. Contour plots for curing reactions with DICY in presence of Fenuron **3c** or TDI-uron **3d** give some information for optimizing technical formulations. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Dicyandiamide (DICY) has been used as a curing agent for epoxy resins since their commercialization in the 1950s. The application of this curing agent ranges from adhesives to composites and from printed circuit boards to powder coatings. Despite a vast number of investigations regarding the mechanisms of the reaction between DICY and epoxy compounds,[1-7] no precise and complete mechanism has yet been established. The stoichiometry of the epoxy–DICY reaction has been determined to be between 3 : 1 and 7 : 1.[1,8] Because of this wide range, until now, only empirically optimized formulations of epoxy resins and DICY are used for technical applications.

$$H_2N \diagdown \atop H_2N \diagup C = N - CN$$
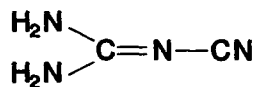
DICY

Some recent investigations show DICY to have a functionality of > 4 toward epoxy resins, although

due to the presence of 4 NH bonds, a functionality of 4 would be expected.[1,7,9] It was demonstrated that the reaction of DICY with epoxy compounds gives the same structural units as from the reaction of cyanamide with epoxy compounds, e.g., 2-imino-1,3-oxazolidines **1**,[1,7] 2-amino-1,3-oxazolines **2**,[1,9] and tertiary amines.[7] Obviously, N-alkylated cyanoguanidines do not represent main structures of the completely reacted system.[7] Some authors suppose DICY to be a catalytic curing agent causing homopolymerization of the epoxy groups exceeding the stoichiometry of 4 : 1.[1,2,5,9]
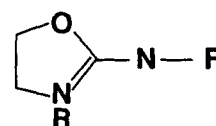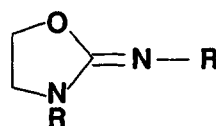
DICY is a high melting solid (mp 212°C), nearly insoluble in most epoxy compounds.[6] Therefore, it is necessary to use solvents or an extremely micronized solid DICY to ensure a nearly homogeneous reaction. Most of the model experiments in solution suffer from restricted comparability to systems in technical use.

Using DICY for curing epoxy resins, temperatures of around 180°C are necessary. To reduce the curing

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temperature, accelerators are normally used. Some accelerators, e.g., the aryldimethylurea compounds Monuron **3a**, Diuron **3b**, and Fenuron **3c**, give a latency at room temperature necessary to formulate single-component systems. Upon heating, these compounds dissociate into isocyanate and dimethylamine (Scheme 1). Both fragments are active components: Dimethylamine reacts with an epoxy group to give a tertiary amine that catalyzes the reaction of DICY with epoxy groups, and the isocyanate reacts with other epoxy unit forming an 1,3-oxazolidin-2-one.[9]

3a: R¹=Cl, R²=H

3b: R¹=Cl, R²=Cl

3c: R¹=H, R²=H

3d: R¹=CH₃, R²=NH-CO-N(CH₃)₂
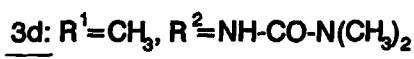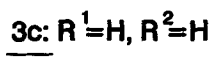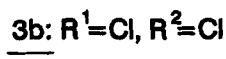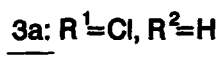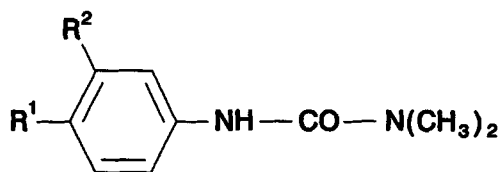
The objective of the present investigation is to clarify the stoichiometry of the reaction between DICY and epoxy resins. No effort was made to separate and to identify the reaction products. All measurements dealt with technically relevant properties to evaluate the optimum dosage of DICY and urones for curing epoxy resins.

EXPERIMENTAL

Common technical products were selected as raw materials. The epoxy resin (Epikote® 828 from Shell) was used as received. The epoxy equivalent weight was determined as 187 g/mol. DICY was used in a micronized form (Dyhard® 100 SF from SKW) with 98% w/w < 5.3 μm, 50% w/w < 1.8 μm; its SiO₂ content of 3% w/w was subtracted for calculating the molar ratios. The two urones chosen were Fenuron **3c** (N,N-dimethyl-N'-phenylurea, Dyhard UR 300 from SKW) and TDI-uron **3d** [N,N''-(4-methyl-1,3-phenylene)bis(N',N'-dimethylurea),

Dyhard UR 500 from SKW]; both substances were micronized to 98% < 10 μm.

The samples used in the present experiments were prepared by mixing the epoxy resin with the desired amount of DICY and the uron accelerator. To avoid sedimentation of DICY, 4% w/w of the thixotroping agent Aerosil® R 805 (from Degussa) were added. All formulations were dispersed by a three-roll mill.

DSC measurements were carried out on a Mettler TA 4000 system with a DSC 20 cell calibrated with an indium standard. Onset temperatures were recorded using a temperature program of 30–200°C at 10 K/min with a subsequent 30 min at 200°C. After cooling, the T_g was measured with 10 K/min. Reaction enthalpies were measured from 30 to 300°C at 10 K/min. According to recommendations of the International Confederation for Thermal Analysis, exothermal enthalpies were taken as positive values. FTIR data were measured as absorbance values using KBr pellets on a Perkin-Elmer 1740 spectrometer.

Test specimens for mechanical and immersion testing were prepared by using an open mold made of V4A and PTFE, dimensioned 70 × 50 mm². The appropriate amount of the resin mixture to give a cured specimen thickness of 3 mm was inserted and degassed.

Because of the high exotherm, the mold was prereacted 15 min at the previously measured DSC onset temperature; subsequently, the temperature was raised and held at 200°C for 2 h. Test specimens of 70 × 10 × 3 mm³ were cut using a water-cooled diamond saw.
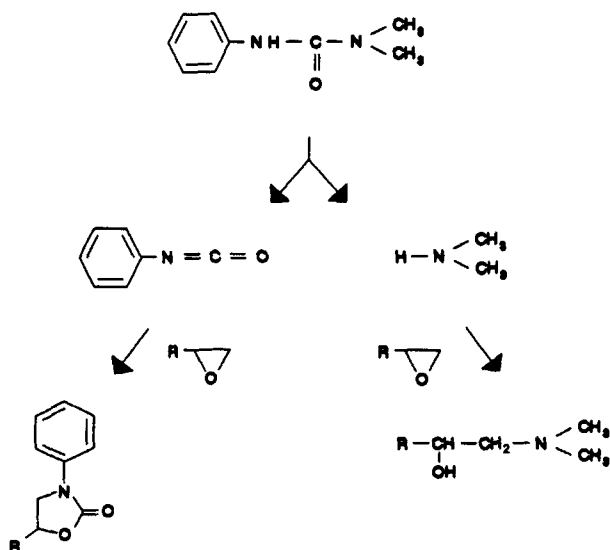
Scheme 1   Mechanism of the uron/epoxy reaction according to Ref. 9.
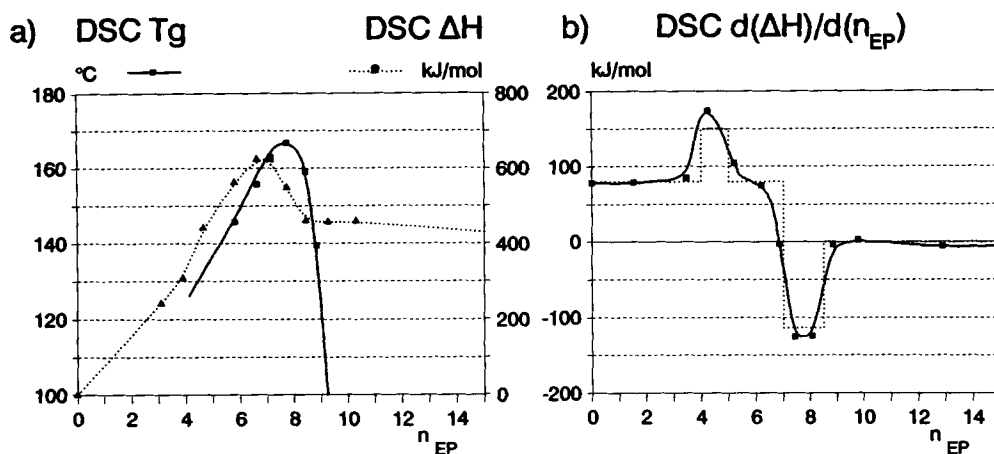
Figure 1 (a) Overall reaction enthalpy per mol of DICY (kJ/mol) and glass transition temperature for the cured resin (°C). (b) Differential enthalpy of the reaction of n_{EP} mol epoxy units with 1 mol DICY. The dotted curve shows the assumed theoretical enthalpy behavior mentioned in the text.

For mechanical measurements, a Netsch 401/3 flexural strength testing apparatus with a 3-point geometry and a support span of 50 mm was used. Young's modulus and the strain to rupture were calculated according to ASTM D-790.

To measure the water absorption, test specimens of $30 \times 10 \times 3$ mm^3 were immersed in water at 90°C for 168 h. Absorption of methyl ethyl ketone (MEK) was measured after 24 h immersion at 23°C.

Evaluation of most measurements was done using contour plots. The dosage of DICY was calculated as mol of epoxy units per 1 mol of DICY (n_{EP}). The amount of urones was calculated as mol of N,N-dimethyl urea functionality per 1 mol of DICY (n_{UR}).

Curing without Accelerators

As mentioned before, high temperatures are necessary to cure epoxy resins with DICY. The observed DSC onset temperatures range from 180 to 186°C. Doubling the amount of DICY reduces the onset temperature by 3–5 K due to the higher total particle surface.

The reaction enthalpy [Fig. 1(a)] shows a remarkable dependence on n_{EP}. This behavior is elucidated by evaluating the differential enthalpy per mol epoxy unit [Fig. 1(b)]. A formulation containing up to 4 mol epoxy units per mol DICY reacts by releasing an average differential enthalpy of 80 kJ/mol epoxy units. This enthalpy, obviously related to addition reactions of NH to epoxy groups (see Scheme 2), corresponds to those reported for reactions of aliphatic amines with epoxides.[10]

Curing a formulation containing up to 5 mol epoxy units per mol DICY ($4 < n_{EP} < 5$) releases an enthalpy of [$4 \times (80$ kJ/mol) + ($n_{EP} - 4$) $\times (150$ kJ/mol)]. This formula is based on the assumption that 4 mol of epoxide react with the same enthalpy as above (80 kJ/mol) and any epoxy functionality exceeding $n_{EP} = 4$ gives the much higher reaction enthalpy of 150 kJ/mol. Supposedly, this higher reaction enthalpy corresponds to addition reactions of the nitrile groups.

Reacting DICY with 5–7 mol of epoxy units ($5 < n_{EP} < 7$) releases the normal differential enthalpy of 80 kJ/mol for the epoxide groups exceeding 5 mol. Obviously, the reaction of the nitrile group forms two additional reactive groups. Formulations containing more than 7 epoxy groups per mol DICY release less overall enthalpy than those with $n_{EP} = 7$. Epoxy groups exceeding $n_{EP} = 8.5$ do not contribute any thermal effect and are supposed to be unreactive in the absence of an accelerator.

FTIR measurements of the cured resin show further evidence for a mechanism involving several different reaction steps (Fig. 2). Residual epoxide absorbance at 920 cm^{-1} sharply increases at $n_{EP} > 7$. Nitrile absorption at 2180 cm^{-1} is at a minimum at $n_{EP} = 5$, whereas imine absorption at 1685 cm^{-1} decreases up to $n_{EP} = 7$. The weak absorption at 1560 cm^{-1}, tentatively classified as a cyanamide structural unit, minimizes at $n_{EP} = 7$ and slightly increases up to $n_{EP} = 8.5$. This behavior correlates to the reaction mechanisms proposed in Scheme 2.

The network stiffness, measured as glass transition temperature T_g [Fig. 1(a)], shows a marked maximum at $n_{EP} = 7.7$, which is slightly higher than

the optimum given by enthalpy measurements. Using formulations with a higher n_{EP} sharply reduces the T_g and gives insufficient curing at $n_{EP} > 9$. Using less than 7 epoxy units per mol DICY also continuously decreases the T_g.

These results can be explained by a stoichiometric reaction between DICY and epoxy resins, but not by homopolymerization reactions of the epoxy groups catalyzed by DICY. The thermochemical and FTIR data are in agreement with a multistep mech-
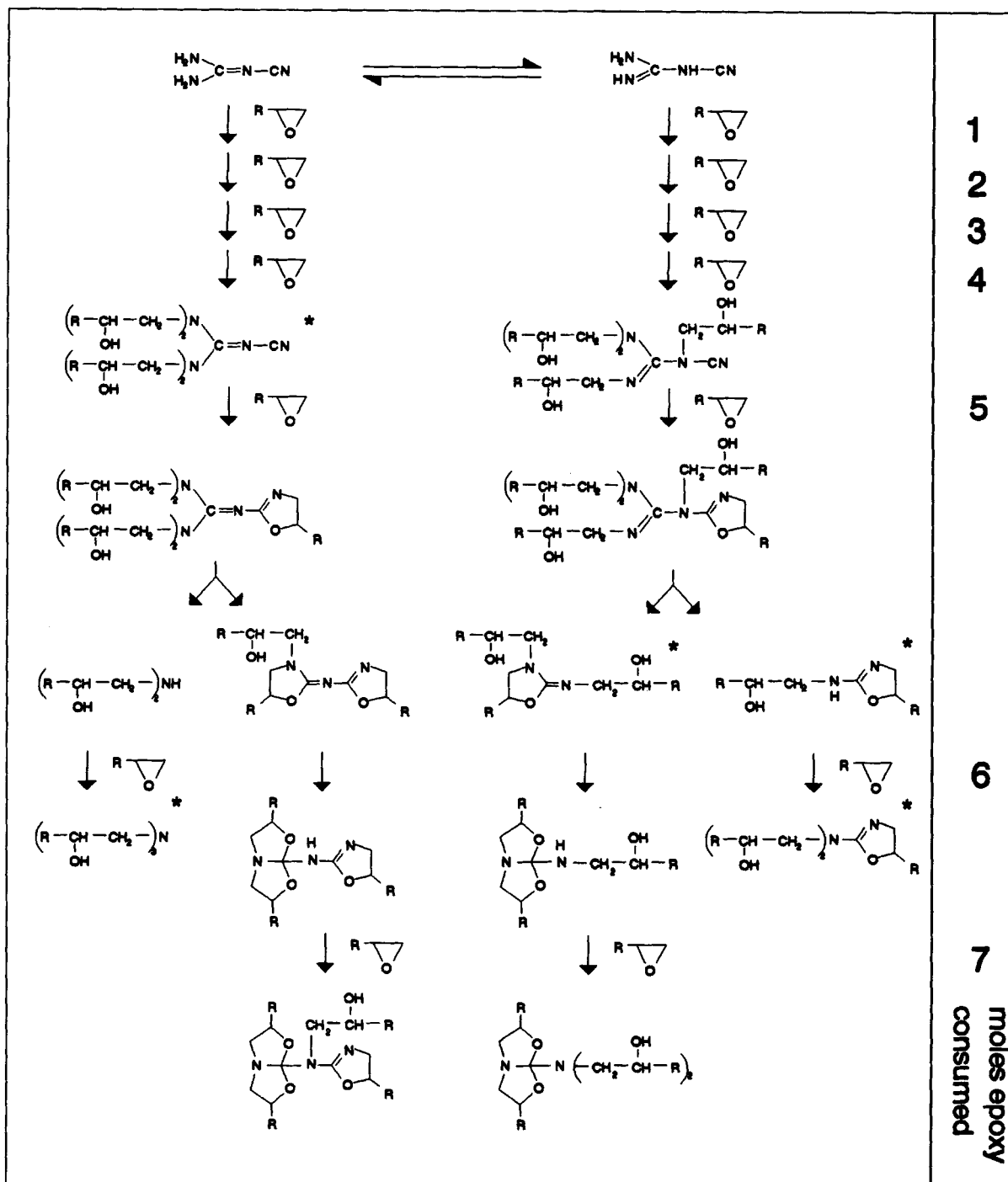
Scheme 2 Proposed pathways of the DICY/epoxy reaction. The reaction steps involve NH/epoxy additions, cyano/epoxy additions (mediated through nucleophilic agents), and elimination/cyclization reactions. Intermediates isolated in Refs. 1, 7, or 9 are marked by an asterisk.
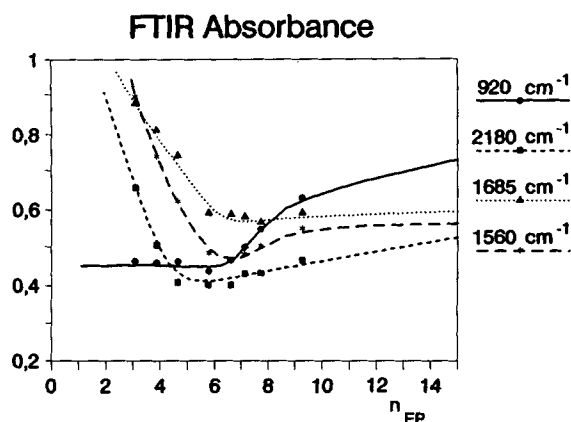
FTIR Absorbance

Figure 2 Influence of the DICY epoxide molar ratio on FTIR absorbancies of the cured resin. The frequencies correspond to epoxy ($920\,\text{cm}^{-1}$), cyano ($2180\,\text{cm}^{-1}$), imino ($1685\,\text{cm}^{-1}$), and, presumably, cyanamino groups ($1560\,\text{cm}^{-1}$). The abscissa lists absorbancies relative to those of the phenyl band ($830\,\text{cm}^{-1}$), which was taken as an internal standard.

anism involving addition and cyclization reactions formerly proposed.[1,7] These reactions create additional reactive groups that enable consumption of up to 7 mol epoxy units per DICY, resulting in the ultimate polymer network. Additional epoxy groups exceeding $n_{EP} = 7$ can be incorporated in the network in a manner unexplained until now, simultaneously reducing the overall reaction exotherm and the rigidity of the network.

Curing with DICY and Urones

Urones sharply decrease the curing temperature (Fig. 3). Regression analysis indicates a negative exponential function for **3c** and **3d** with 4.1 and 4.9

K decreases in onset on doubling the accelerator concentration n_{UR}. The lowest achievable onset is 140°C for **3c** and 130°C for **3d**. Variation of n_{EP} has no effect on the onset temperature exceeding the influence of the total particle surface mentioned before.

T_g measurements (Fig. 4) show an overall maximum at $n_{EP} = 7.7$, $n_{UR} = 0$. This means that the addition of any amount of an uron accelerator to an epoxy/DICY formulation reduces the T_g. Due to its bifunctionality creating additional crosslinks, **3d** generally gives a higher T_g than does **3c**.

Each mol of uron functionality theoretically consumes 2 mol of epoxy units due to isocyanate and dimethylamine reactions (see Scheme 1). The dependence of n_{EP} yielding the maximum T_g relative to n_{UR} shows a significant deviation from the theoretical slope. This may be explained by the catalytical activity of the uron enabling etherification reactions of excessive epoxy units.[9]

Young's modulus is not influenced by n_{EP}, n_{UR}, or the structure of the uron. The measured values of 2.82 ± 0.30 GPa (**3c**) and 2.92 ± 0.24 GPa (**3d**) correspond to those reported in Ref. 11.

The strain to rupture (Fig. 5) increases with n_{UR} due to a more flexible network, **3c** being slightly more effective. Regarding test specimens with n_{EP} > 8, the flexibility shows a rapid decrease nearly independent of n_{UR} for n_{UR} > 0.05. This may be explained by excessive epoxide, which embrittles the network by forming polyether bounds via homopolymerization reactions.

The network penetrability, measured as MEK absorption (Fig. 6), increases with n_{EP}. In the case of **3d**, using more accelerator decreases the network penetrability, even if excess epoxide is present. **3c** has the same effect at low levels, but raises the network penetrability at higher amounts due to a less
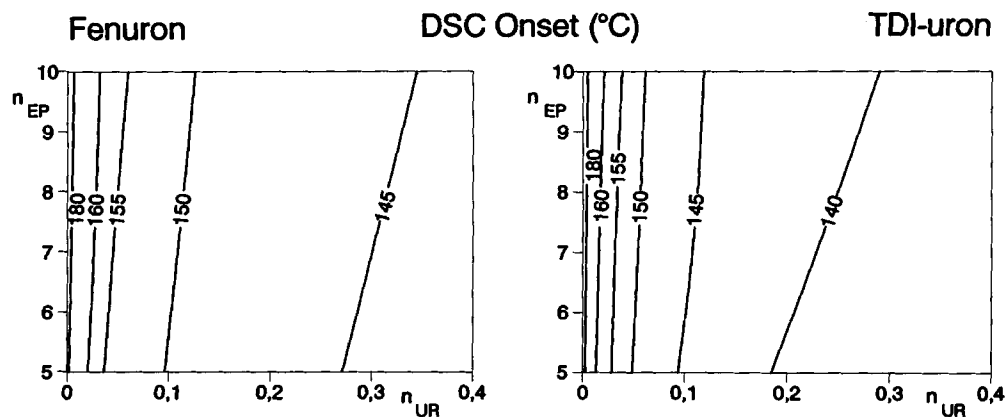

Figure 3 Influence of epoxy (n_{EP}) and uron (n_{UR}) molar ratios for **3c** and **3d** on DSC onset. Contour lines are given in °C.
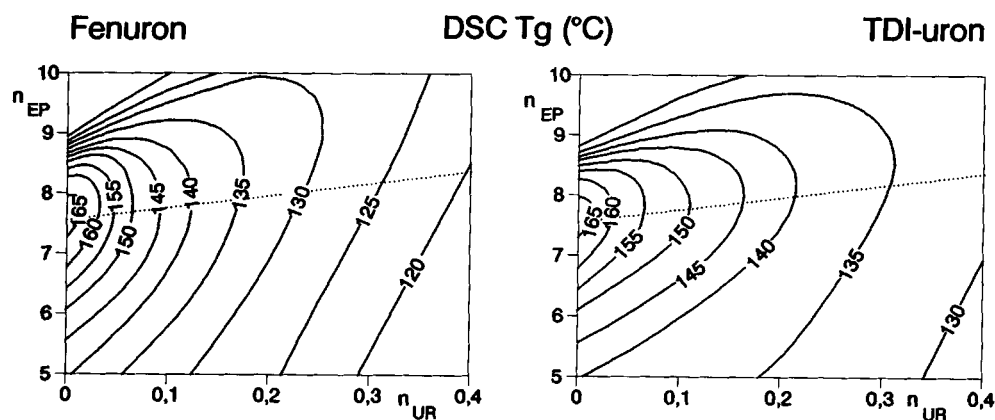
Figure 4   Variation of the glass transition temperature on n_{EP} and n_{UR} for formulations containing **3c** or **3d**. Contour lines are given in °C. The slope of the dotted lines indicates the theoretical epoxide consumption through reactions of epoxide with uron fragments.
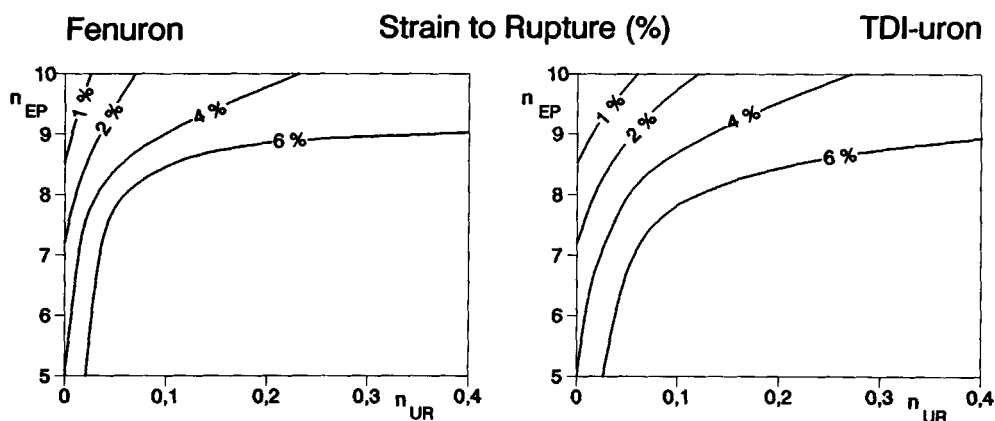
Figure 5   Flexural strain to rupture (in %) for formulations containing DICY and **3c** or **3d**. The maximum reliable strain for the given measuring geometry was 6%.
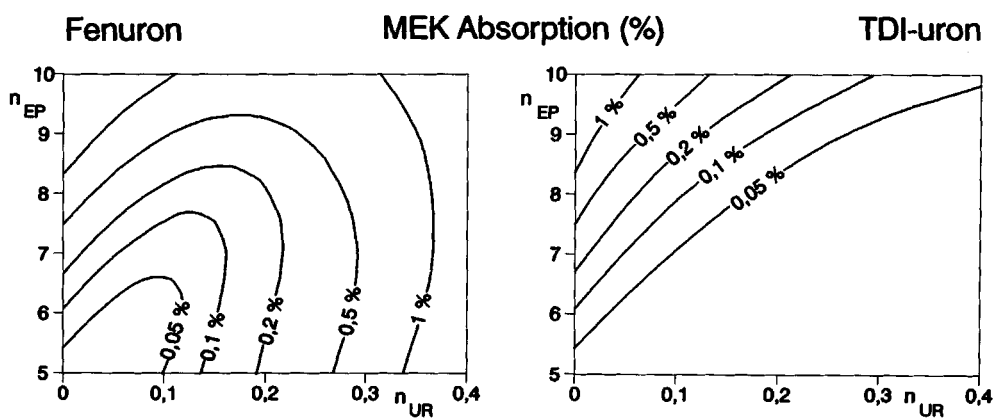
Figure 6   MEK absorption (24 h at 23°C) for formulations containing DICY and **3c** or **3d**.

Fenuron   **Water Absorption (%)**   **TDI-uron**
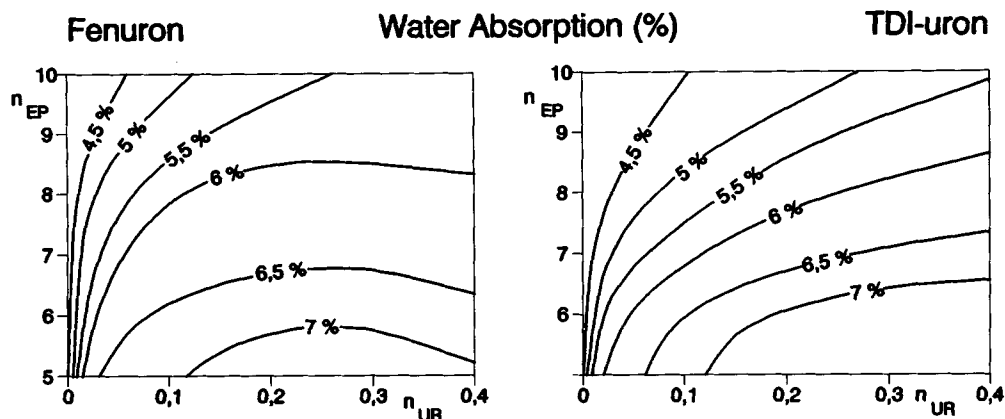
Figure 7   Water absorption (168 h at 90°C) for formulations containing DICY and **3c** or **3d**.

dense network caused by chain termination with the monofunctional isocyanate.

Epoxy resins cured with DICY generally have a high water absorption (Fig. 7), because highly polar structural units are formed during cross-linking. Increasing n_{EP} decreases the water absorption in the same way that it deteriorates most other properties. If the uron content is increased, the water absorption is further increased, forming additional polar groups. Very high contents of **3c** slightly reduce the water uptake because of its hydrophobic phenyl groups.

CONCLUSION

DICY was found to be a stoichiometric curing agent for epoxy resins. The molar ratio was confirmed to be near 7 mol of epoxy units per 1 mol of DICY. Most technologically relevant properties of the cured resins maximize at this ratio, giving minimum concentrations of residual reactive groups.

The type of uron to be chosen as the accelerator depends on the application field. The bifunctional **3d** provides higher reactivity, higher T_g, and a higher network density than do monofunctional urones, e.g., **3c**. Optimum usage of the curing agents often improves the performance of the cured resin so that the application of more costly specialty resins can

be avoided. The contour plots simplify the optimization of the formulations.

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