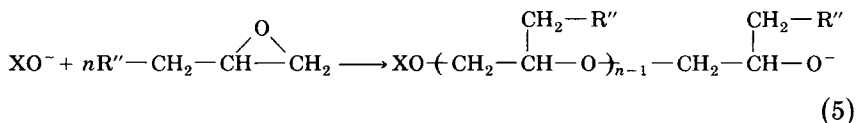
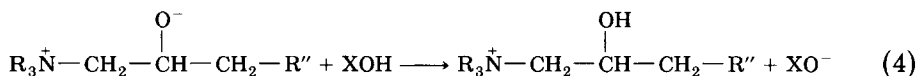
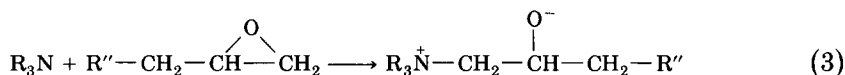


When the nature of R and R' is such that the basicity of the tertiary amine is enhanced, an anionic homopolymerization of epoxides takes place through the following mechanism²:



A termination step must also be present to account for the observed arrest of reaction in dynamic DSC runs, when unreacted epoxy functionalities are still available.^{3,4} The need to have OH groups in the formulation in order to generate the initiator through step (4) has been experimentally confirmed.⁴

Therefore, substituted ureas may be used as latent initiators for the anionic homopolymerization of epoxy resins. This is precisely the case of the commercial product 1,1-dimethyl-3(*p*-chlorophenyl)urea (Monuron). In this case, the release of dimethylamine at moderate temperatures leads to a rapid polymerization of epoxy groups. An experimental study carried out by Byrne et al.,⁵ as well as a previous unpublished work performed by J. Bornstein and B. R. LaLiberte, as reported by the former authors, confirmed that the progress of the reaction takes place along steps (1)–(5). Thus, it was found that Monuron disappeared by reaction after approximately 0.5 h of heating at 120°C and an oxazolidone was formed, as denoted by the appearance of an IR peak at 1760 cm⁻¹ (attributed to the carbonyl of the oxazolidone). The homopolymerization of the epoxy groups was shown by the presence of a strong IR peak at 1145 cm⁻¹ assigned to the aliphatic ether produced in the propagation step. Moreover, step (4) was indirectly confirmed by the disappearance of amino alcohol addition products, as determined by HPLC.

Recently, Pearce et al.⁶ reported the use of 1,1-pentamethylene-3-phenyl-urea, prepared by the reaction of phenyl isocyanate with piperidine in dry benzene, to cure a tetraglycidyl methylenedianiline resin (TGMDA), toughened with a CTBN rubber. These formulations showed an excellent stability at 23°C and led to a high *T_g* product when cured at 170°C.

As substituted ureas result from the reaction of a secondary amine with an isocyanate (RNCO), a great variety of latent initiators may be generated by dissolving a convenient amount of a secondary amine in the epoxy resin and adding a stoichiometric amount of an isocyanate. By adjusting the addition rate of the isocyanate the evolution of reaction heat may be kept under control. Moreover, as the isocyanate reacts very much faster with secondary amines than with any secondary OH present in the epoxy molecule (a dibutylamine excess is used to quench the reaction between NCO and OH groups^{7,8}), and no reaction is observed between NCO and epoxides at moderate temperatures,⁹ the substituted urea is the only product generated in the reaction medium.

The proposed *in situ* generation of the substituted urea may be used with advantage to replace the use of a volatile secondary amine, such as piperidine, in the cure of epoxy resins. In this case, it has been reported that an increase in the curing temperature leads to a decrease in the glass transition temperature T_g .^{10,11} Losses of piperidine (bp = 106°C) during the cure lead to a decrease in the maximum epoxy conversion³ and, consequently, to a reduction in the T_g value. To avoid both the volatilization of piperidine and the reaction advance in the fresh mixture,³ it is possible to convert the piperidine into a substituted urea by adding a stoichiometric amount of an isocyanate. This will increase the latency of the initial formulation and give reproducible curing schedules.

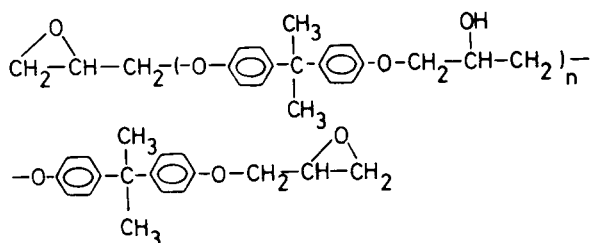
The aim of this work is to show the feasibility of curing epoxy resins with *in situ*-generated substituted ureas and to discuss some aspects related to the reaction mechanism. Due to its practical application, a formulation based on piperidine will be selected.

EXPERIMENTAL

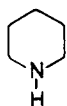
Materials

The formulas of the chemical reagents are shown in Figure 1. The epoxy resin was a commercial bisphenol-A diglycidylether (DGEBA), Araldit GY 250 (Ciba-Geigy), with a weight per equivalent, WPE = 187 g/eq. This gives

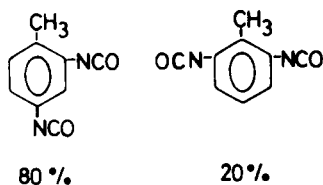
EPOXY RESIN:



PIPERIDINE:



TDI 80:20



80%

20%

Fig. 1. Chemical formulas.

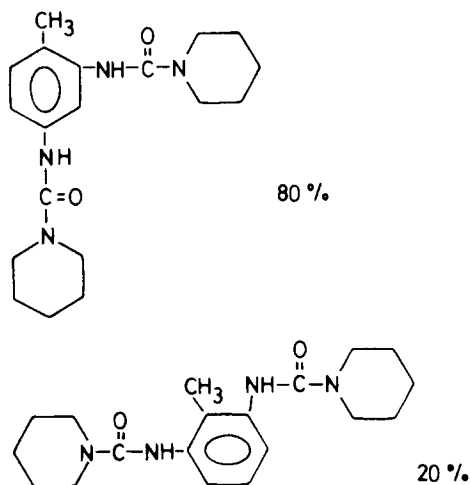


Fig. 2. Substituted diurea.

$n = 0.12$ in the structural formula. The resin was carefully dehydrated at 85°C , under vacuum, before use. Piperidine was a p.a. reagent (Carlo Erba). Toluene diisocyanate (99.9% purity, TDI, was available as a mixture of 80% 2,4 and 20% 2,6 isomers).

Characterization Techniques

A DuPont 990 thermal analyzer provided with a differential scanning calorimetry pressure cell (DSC 910), was used either in the scanning ($10^{\circ}\text{C}/\text{min}$) or isothermal modes under a nitrogen atmosphere. The device was

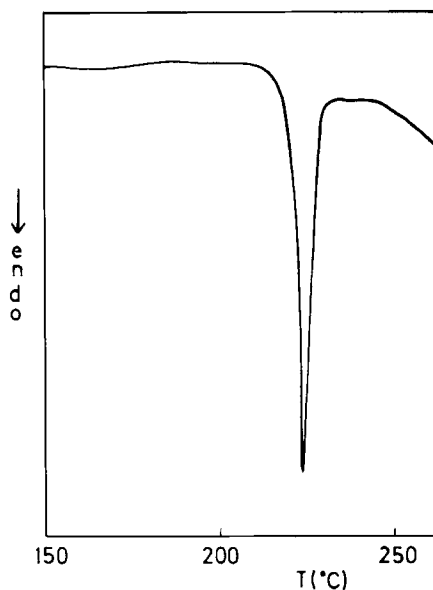


Fig. 3. DSC thermogram of the substituted diurea.

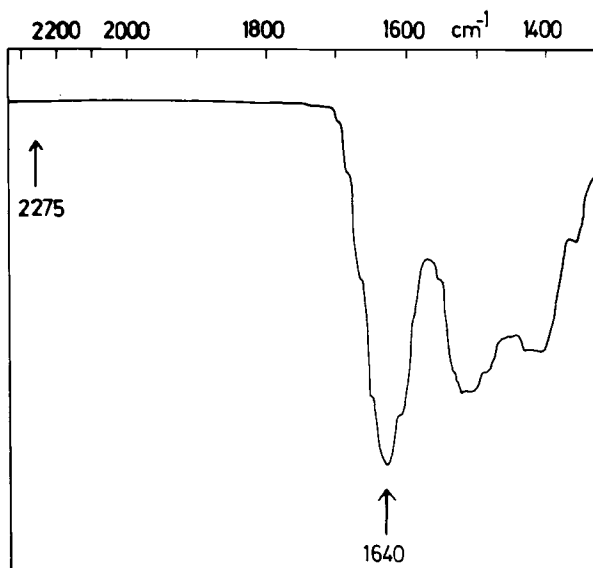


Fig. 4. IR spectrum of the substituted diurea. The arrow at 2275 cm^{-1} shows the absence of free NCO groups whereas the arrow at 1640 cm^{-1} shows the presence of urea groups.

calibrated in the temperature range of interest, using known values of the heat capacity of alumina. Infrared spectra were monitored on a Perkin-Elmer 599 IR spectrophotometer, using KBr pellets mixed with a solid (or impregnated with a liquid) sample.

Generation of Substituted Urea

In order to characterize the substituted urea, the reaction was first carried out by adding a diluted solution of piperidine in chloroform to a similar diluted solution of TDI in the same solvent. By controlling the addition rate and adjusting the dilution, the heat evolved could be kept at small levels to prevent any vaporization of piperidine. After addition of a stoichiometric proportion of piperidine (in equivalents), the solvent was vaporized and the substituted diurea obtained (Fig. 2). Its melting point was $mp = 224^\circ\text{C}$, as determined by DSC (Fig. 3). An IR spectrum (Fig. 4) showed the presence of urea groups at 1640 cm^{-1} and the absence of free NCO groups at 2275 cm^{-1} . Chemical titration with dibutylamine confirmed the absence of free NCO groups.

In Situ Generation of Substituted Urea

To a mixture of epoxy resin containing 5 phr piperidine, by weight, a stoichiometric amount of TDI with respect to piperidine was slowly added to control the heat evolution. The resulting solution was transparent, indicating complete solubility of the initiator in the epoxy matrix. An IR spectrum of the resulting product is shown in Figure 5. The same spectrum was obtained when a solution of substituted urea in chloroform was added to the epoxy resin, keeping the same proportions and after solvent evaporation. On occa-

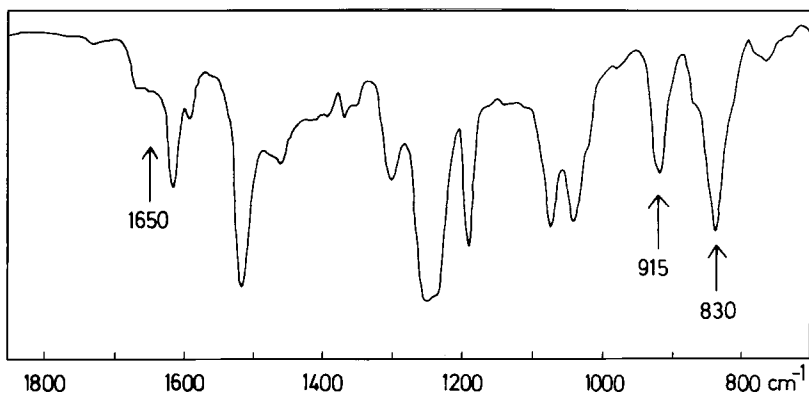


Fig. 5. IR spectrum of the epoxy resin containing the *in situ*-generated substituted diurea. The shoulder at 1650 cm^{-1} is attributed to urea groups, the peak at 915 cm^{-1} corresponds to epoxy functionalities, and the one at 830 cm^{-1} , assigned to *p*-phenylene groups, is taken as an internal standard.

sions, a small peak at 1730 cm^{-1} was present in the IR spectra of samples where the substituted diurea was formed *in situ*. This peak is attributed to urethane linkages arising from the reaction of a slight isocyanate excess over the stoichiometric value, with secondary OH groups belonging to DGEBA.

Relevant features of the IR spectrum are: the absence of free NCO groups at 2275 cm^{-1} (region not shown in Fig. 5), a shoulder at 1650 cm^{-1} corresponding to urea groups, a peak at 915 cm^{-1} assigned to epoxy groups, and several peaks that may be used as internal standards to calculate absorption ratios. After measuring the relative intensity of different peaks in samples cured to different conversions, it was concluded that the absorption ratio of peaks at 1255 cm^{-1} (aryl ether) and 830 cm^{-1} (*p*-phenylene¹²) was constant for every sample within the experimental error. Therefore, the peak at 830 cm^{-1} was taken as an internal standard.

Curing Schedule

Samples of epoxy resin containing the *in situ*-generated substituted urea (prepared from 5 phr of piperidine/epoxy, by weight), were cured in small glass tubes, during 24 h, at the following temperatures: 40, 60, 80, 100, and 120°C . To establish any possible effect of a postcure step, a sample cured at 120°C was heated at 160°C during another 24 h. Samples were also cured in the DSC at 100°C for a prolonged time necessary for the return of the signal to the base line (approximately 5.5 h).

RESULTS AND DISCUSSION

Figure 6 shows IR spectra in the $800\text{--}1200\text{ cm}^{-1}$ range, for samples cured at different temperatures. The conversion of epoxy groups may be defined as

$$x_E = 1 - [A_{915}A_{830}(0)]/[A_{915}(0)A_{830}] \quad (6)$$

Table I shows the resulting conversion after 24 h heating at constant temperature. At 100°C , a complete conversion of epoxy functionalities is

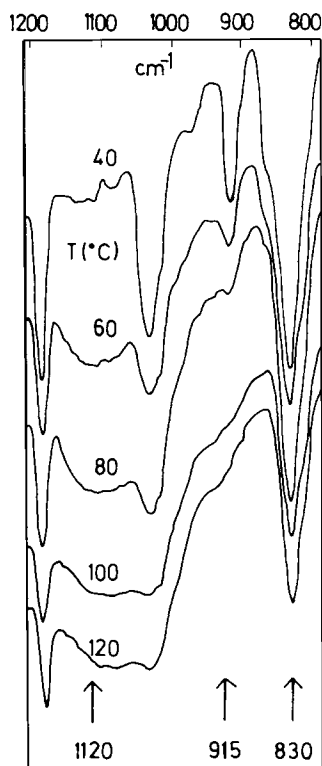


Fig. 6. IR spectra in the 800–1200 cm^{-1} range for samples cured at different temperatures. Relevant peaks are: 830 cm^{-1} (reference peak), 915 cm^{-1} (epoxy groups), and 1120 cm^{-1} (aliphatic ethers).

observed. A simultaneous increase in the IR absorption at 1120 cm^{-1} , attributed to the aliphatic ethers produced in the homopolymerization [eq. (5)], is shown in Figure 6.

Glass transition temperatures of samples cured to a complete epoxy conversion were determined using DSC at a 10°C/min heating rate. A value of $T_{g\infty} = 102^\circ\text{C}$ was obtained. A similar value arose from the cure of DGEBA with 5 phr piperidine, without the previous addition of an isocyanate. Then, the cure of the epoxy resin with the substituted urea leads to a network similar to the one arising from the direct use of the corresponding secondary amine. However, the previous conversion of the amine into an urea enhances

TABLE I
Conversion of Epoxy Groups after 24 h Heating at Different Temperatures

T ($^\circ\text{C}$)	x_E
40	0.11
60	0.60
80	0.84
100	1
120	1

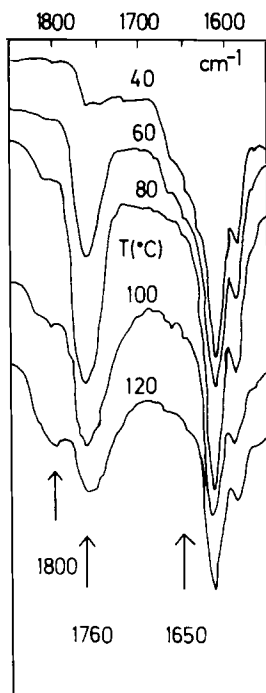


Fig. 7. IR spectra in the 1550–1850 cm^{-1} range for samples cured at different temperatures. Relevant peaks are: 1650 cm^{-1} (urea groups), 1760 cm^{-1} (oxazolidone), and 1800 cm^{-1} (unknown, see text).

the latency of the formulation and avoids the amine volatilization when using high curing temperatures.^{10,11}

Figure 7 shows IR spectra in the 1550–1850 cm^{-1} range, for samples cured at different temperatures. Relevant features are the increase in the absorption of the oxazolidone peak at 1760 cm^{-1} , and a corresponding decrease in the urea shoulder at 1650 cm^{-1} , when increasing the curing temperature. Moreover, by plotting the oxazolidone concentration, calculated as the ratio A_{1760}/A_{830} of IR absorptions for samples cured at 40, 60, 80, and 100°C, as a function of epoxy conversion, a straight line results as shown by Figure 8.

The presence of oxazolidone in IR spectra of cured samples reassures the validity of the reaction path [eq. (1)]. The direct proportionality of epoxy conversion to oxazolidone concentration enables us to infer a similar proportionality with respect to tertiary amine concentration, e.g., assuming that eq. (2) takes place to a complete extent. The proportionality between epoxy conversion and tertiary amine concentration has been recently reported by Galy et al.,⁴ for the cure of DGEBA prepolymers with a tertiary amine (BDMA).

The increase of the curing temperature to 120°C shows that secondary reactions do also take place as revealed by the IR peak at 1800 cm^{-1} (Fig. 8). This peak appears at 80°C, increases at 100°C, and is significant at 120°C. A simultaneous decrease in the absorption intensity of the oxazolidone peak at 1760 cm^{-1} was evidenced for the sample cured at 120°C. Thus, one may infer that alternative steps to eq. (1) may be present in the reaction mechanism. In

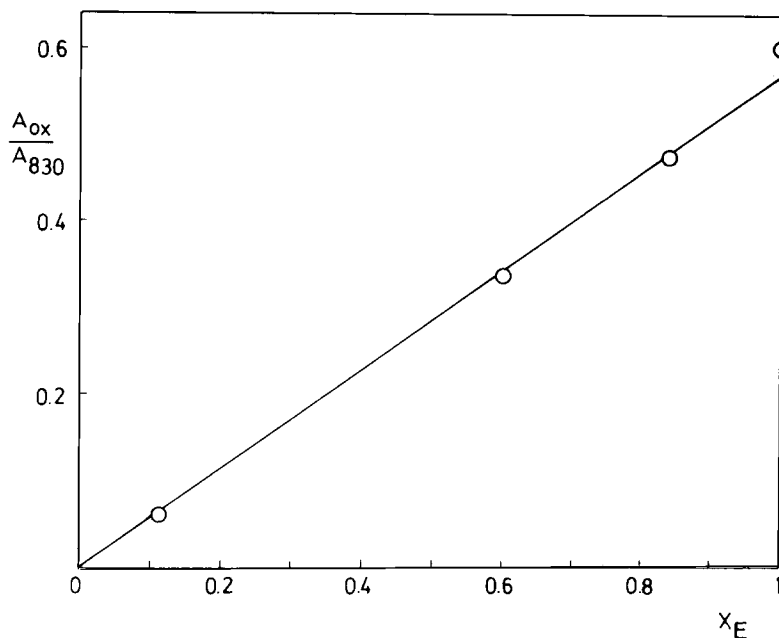


Fig. 8. Oxazolidone concentration in arbitrary units vs. epoxy conversion (both calculated from IR absorption peaks).

a recent review of the curing reactions of epoxy resins, Tanaka and Bauer¹³ discuss other possible reaction products obtained from the reaction of an epoxy resin with a substituted urea, e.g., hydroxyalkyl ureas or urethanes with a secondary amine group. However, no one of these possibilities explains the IR peak at 1800 cm^{-1} . A possible assignment for this band is to an open chain anhydride ($\text{R}-\text{CO}-\text{O}-\text{CO}-\text{R}'$), a structure which has two absorption bands at about $1800\text{--}1820$ and $1740\text{--}1760\text{ cm}^{-1}$, the former being stronger.¹⁴ A band at 1808 cm^{-1} , appearing during thermal degradation of epoxy resins, has been assigned to open chain anhydrides by Lin et al.¹²

In order to provide more information of the IR band at 1800 cm^{-1} , samples cured at 120°C were subjected to two different treatments: (i) postcure at 160°C for 24 h, (ii) hydrolysis with $1N$ NaOH (boiling during 1 h). IR spectra of resulting samples showed that the heating at 160°C did not produce any noticeable change; however, the hydrolysis in NaOH led to the disappearance of the IR peak at 1800 cm^{-1} , without any other significant change (Fig. 9). Thus, assignment of this peak to an open chain anhydride may be possible, although no mechanism explaining its appearance in the reaction scheme may be proposed at present. This aspect of the reaction remains as an open question.

Figure 10 shows a DSC thermogram in the isothermal mode for a polymerization carried out at 100°C . Total reaction heat expressed per initial epoxy equivalent is $(-\Delta H)_T = 61\text{ kJ/eq}$. Thus, the reaction heat is significantly reduced with respect to the case of epoxy-amine polymerizations, $(-\Delta H)_{E-A} = 102\text{ kJ/eq}$,^{15,16} or epoxy homopolymerizations, $(-\Delta H)_{E-E} = 92\text{ kJ/eq}$.¹⁷ This effect, which arises from the endothermic nature of the epoxide-sub-



Fig. 9. IR spectra in the $1550\text{--}1850\text{ cm}^{-1}$ range for: (a) sample cured 24 h at 120°C , (b) sample (a) after hydrolysis in boiling $1N$ NaOH during 1 h.

stituted urea reaction [eq. (1)], may be important to reduce the large temperature gradients generated in the cure of thick parts.¹⁸

The reaction heat associated with the epoxide-urea reaction, $(-\Delta H)_{\text{E-U}}$, may be estimated as follows. The proportions used in the initial formulation are such that for 1 eq of epoxy groups there are 0.11 eq of piperidine, generating the same amount of substituted urea. On the other hand, according to IR results, we may assume that at the end of reaction all substituted urea has reacted and there are no unreacted epoxy groups. Then, on the basis of 1

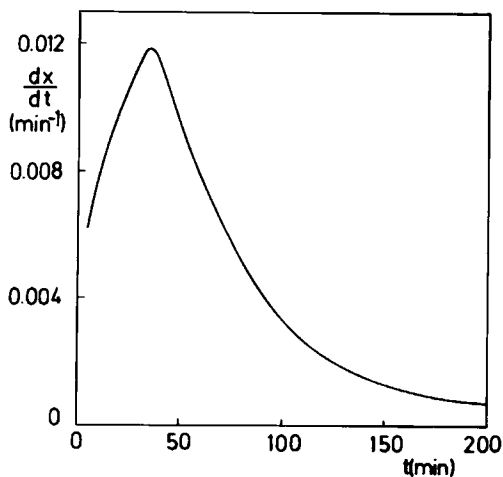
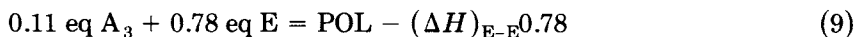
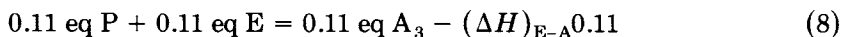
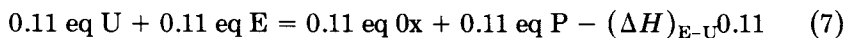


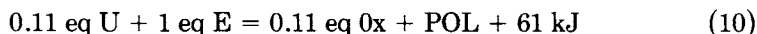
Fig. 10. DSC thermogram in the isothermal mode for the cure at 100°C ; $dx/dt = (-dH/dt)/\Delta H_T$.

eq epoxy groups, the reaction scheme may be written as:



where U, E, Ox, P, A₃, and POL indicate, respectively, the substituted urea, epoxy groups, oxazolidone, piperidine, tertiary amine, and the polymer network.

The overall reaction may be written as



From eqs. (7)–(10), we get

$$(\Delta H)_{\text{E-U}} = (-\Delta H)_{\text{E-A}} + (-\Delta H)_{\text{E-E}}(0.78/0.11) - 61/0.11 = 200 \text{ kJ/eq}$$

Obviously, this value must be only taken as a rough approximation due to the propagation of errors associated to the low amount of the initiator.

CONCLUSIONS

Substituted ureas generated from the reaction of a secondary amine with an isocyanate in the presence of the epoxy resin may be used as latent initiators for the polymerization. The resulting epoxy network has similar properties, e.g., the same $T_{g\infty}$, as the one arising from the cure with the secondary amine, but the process has the following advantages:

- Increase in the latency of the initial formulation (the secondary amine is generated by a reaction that proceeds very slowly at room temperature).
- Reproducible curing schedule due to the fact that the volatilization of the secondary amine is avoided.
- Less reaction heat per epoxy equivalent, an effect which is convenient for the cure of thick parts.

These advantages may be particularly applied to replace formulations based on piperidine as a curing agent.

The possibility of generating the substituted urea in the reaction mixture enables the processor to select a large variety of secondary amine/isocyanate combinations, giving different degrees of latency.

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