

Reaction of a diepoxide with a diisocyanate in bulk

II. Use of an imidazole or a blocked isocyanate catalysts

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SUMMARY

Reactions between a diepoxide and a diisocyanate can lead to copolymers having isocyanurate and oxazolidone rings in their chemical structure. Using Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR), we have studied the influence of catalysts such as an imidazole or a blocked isocyanate on the polymer formation. We have identified the nature of the exotherms observed in DSC experiments with the aid of FTIR spectroscopy and observed the influence of the molar ratio of the functional groups and the amount of catalyst. We have compared the influence of these catalysts with results obtained previously with a tertiary amine.

INTRODUCTION

Copolymers obtained by reacting a diepoxide and a diisocyanate have two kinds of heterocycles in their chemical structure : isocyanurate and oxazolidone rings. Compared with classical epoxy networks these materials exhibit better thermal, mechanical and electrical properties as well as better dimensionnal stability because of the absence of labile hydrogens and of the presence of nitrogen atoms in the structure of the heterocycles (1-6).

In a previous paper (7), we have studied the influence of a tertiary amine on the formation of isocyanurate and oxazolidone rings. The purpose of this work is to identify and understand the influence of an imidazole and a blocked isocyanate on the formation of the same kind of networks.

EXPERIMENTAL

Materials

All the materials used in this study are commercially available and are low cost. They are described in detail in a previous work (7).

The liquid diisocyanate used was ISONATE 143 M from DOW CHEMICAL. This product is a mixture of 85% by weight of diphenylmethane-4,4'-diisocyanate and 15% of uretonimine. Its functionality is 2.2 due to the presence of trifunctional trimers.

The 2-ethyl 4-methylimidazole (EMI) was from ALDRICH. The blocked isocyanate "monouron" was obtained from the reaction of chloro-phenyl isocyanate with NN' dimethyl amine. It is commercially available as a solid dispersed in DGEBA (50% by weight), Bakelite 164.

All materials were used without further purification.

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Figure 1 : The two catalyst formulas
a) EMI and b) Monouron

The reaction between MDI and DGEBA with different ratios, r , was examined. This ratio is defined as the number of diisocyanate moles over the number of diepoxide moles. The mixtures were prepared as follows, depending on the kind of experiment :

i) the imidazole was mixed with the DGEBA at room temperature and the solid MDI was added after it was preheated to 50 °C in order to obtain a liquid

ii) the liquid MDI and the DER 332 were mixed at room temperature and then the monuron in paste form was added and mixed in order to obtain a homogeneous mixture.

Measurements

The DSC and FTIR apparatus used are described in detail in our previous publication (7). Viscoelastic dynamic measurements were taken with a Rheometrics viscoanalyzer. The heating rate was 2 °C/min and the frequency was 11 Hz.

RESULTS AND DISCUSSION

Use of the 2-ethyl 4-methylimidazole as catalyst

The literature reports that the formation of oxazolidone rings is favoured by the presence of an imidazole catalyst (1,2,8,9).

Typical thermograms of the MDI/DGEBA reaction in the presence of 0.5% EMI by weight of the total mixture are shown in Figure 2.

With an isocyanate excess ($r=2$) recrystallization and fusion of MDI occurs at 0 °C and 30 °C, respectively (Fig. 2b). This was not the case for r is 0.5 because of the dilution of MDI in DGEBA.

Both thermograms exhibit several exotherms which are not completely separated. The features of the exothermic regions between 90 and 300 °C depend on the ratio, r . This result has also been observed by other authors (1,5,9). When a tertiary amine was used as the catalyst (7), several exotherms occurred, too, but in this case two regions were well defined : at low temperatures, between 50 and 150 °C depending on r , isocyanurate formation occurred, while at higher temperatures, between 250 and 380 °C, oxazolidone rings were formed.

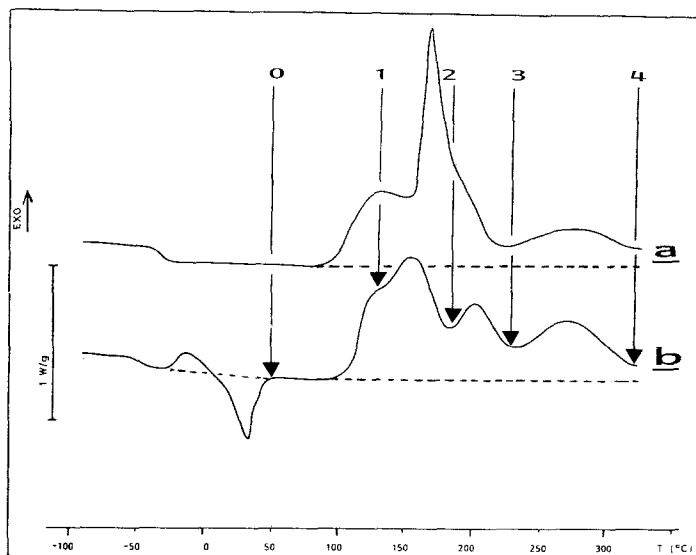


Figure 2 : DSC thermograms of MDI/DGEBA reaction catalyzed by 0.5% EMI by weight for a) epoxide excess ($r=0.5$) and b) isocyanate excess ($r=2$).

In order to identify the regions that we observe in the DSC thermograms when the reaction is catalyzed by an imidazole, FTIR analyses were performed before and after the different exotherms (points 1 through 4 in Figure 2). As was done in our previous work (7), we followed the evolution of the different FTIR peaks characteristic of the groups present in the initial material and of the formed products.

From Figure 3 we can identify the exotherms observed in the DSC runs : at arrow 1 the FTIR spectra show that the isocyanate peak strongly diminishes while the epoxy absorption does not change. A strong absorption peak appears at 1710 cm^{-1} . Also, the first exothermic peak that we observe is due to the isocyanurate formation for all values of r .

For other points two cases must be distinguished :

i) Epoxy excess ($r = 0.5$) :

After arrow 2 ($180\text{ }^{\circ}\text{C}$ in DSC scan) a strong absorption is observed at 1760 cm^{-1} while the isocyanurate peak becomes very small. At the same time the epoxy absorption becomes weaker. Thus the second DSC exotherm is due to oxazolidone ring formation. The two routes previously proposed for the oxazolidone formation (1,2,7) occur here at the same time. The epoxy functions react with the free isocyanate as well as with the isocyanurate rings already existing.

After this stage (arrows 3 and 4) the chemical reaction finishes : the isocyanurate rings almost disappear (no more absorption at 1710 cm^{-1} and a very weak one at 1410 cm^{-1}) and the oxazolidone rings become prominent. The epoxy groups have disappeared, too. This was not the case when the catalyst used was a tertiary amine (7); this can be explained by the fact

that imidazole is a more effective catalyst than tertiary a amine for the homopolymerization of the epoxy (10,11). However, etherification is not easily detectable by FTIR experiments, and NMR studies are currently in progress to understand this point.

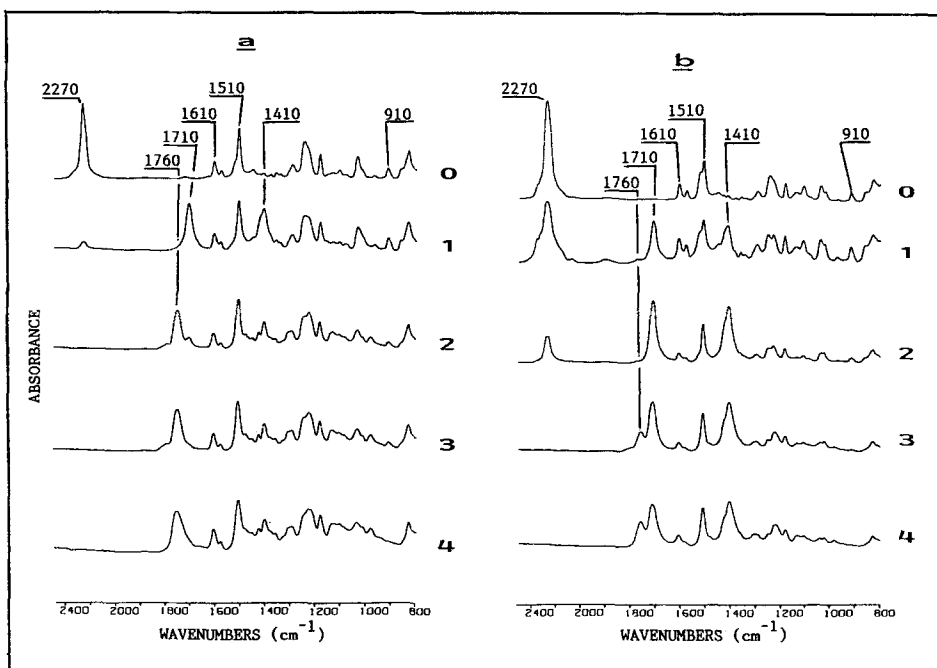


Figure 3 : Evolution of the FTIR spectra of the MDI/DGEBA mixture in the presence of EMI during the DSC experiments.
a) $r = 0.5$ and b) $r = 2$

ii) Isocyanate excess ($r = 2$) :

After arrow 2, the isocyanurate peak grows and the isocyanate functions disappear. The absorption of the epoxy becomes weaker perhaps because of homopolymerization of the epoxy. At the higher temperature (arrow 3, 210 °C) the oxazolidone absorption is visible while isocyanate and epoxy groups are absent. At the last step of the DSC scan (Fig. 3.4), the oxazolidone peak is stronger than the isocyanurate peak. Here too, residual epoxy groups have reacted with the isocyanurate trimer. The final material is a mixture of the two heterocycles with probably some homopolymerized epoxy in the network also.

Figure 4 shows that increasing the amount of catalyst displaces all of the exothermic regions to lower temperatures. This effect could not be seen in the case where a tertiary amine was used as the catalyst, especially for the oxazolidone exotherms.

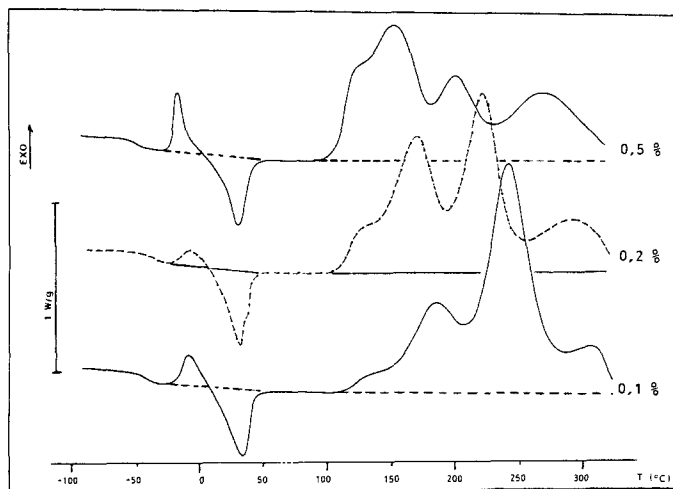


Figure 4 : Evolution of the DSC thermograms when the amount of EMI is increased in the case of $r = 2$ (excess of isocyanate). % of EMI by weight of total mixture.

Thus the imidazole promotes the formation of oxazolidone heterocycles better than a tertiary amine and the reaction takes place at lower temperatures (250°C rather than 300°C in the case of BDMA). However, the comparison of the FTIR spectra of completely polymerized materials for both types of catalyzed systems does not show any differences in the amount of the isocyanurate and oxazolidone formed. The main difference is in the amount of epoxy homopolymerization which is higher when an imidazole is used. Some authors have stated that imidazole catalysts favour the formation of oxazolidone rings (1,2,8), which means that these cycles are built at lower temperatures but not that a greater amount of oxazolidone is formed in the polymer.

Similar thermograms have been observed by SENGHER et al. (9) and their FTIR observations of the resulting material lead to the same conclusions as ours.

Use of a blocked isocyanate as the catalyst

From an industrial point of view, catalyst systems such as tertiary amines or even imidazole cannot be used for certain applications because they are too reactive and the pot-life is too short (a few minutes in both case). Moreover, the use of solid MDI is not industrially acceptable because of its crystallinity. For applications such as solventless varnishes, a long pot-life and a good reactivity during the polymerization are required. If rigid materials are required, the formation of isocyanurate rings should be promoted in order to obtain a high cross-linked network. For this reason we have tried to produce an industrially acceptable system. Therefore, the study of the reaction between the DGEBA and the liquid MDI with a blocked isocyanate was performed.

As shown by SON et al. (12) the blocked isocyanate dissociates at 150°C into isocyanate and amine and the latter can react rapidly with the epoxy groups to give a tertiary amine (in Fig. 6, first thermogram, "monouron

alone"). Then the formed tertiary amine can catalyze the reactions between the epoxy and isocyanate groups. Figure 5 summarizes these reaction mechanisms.

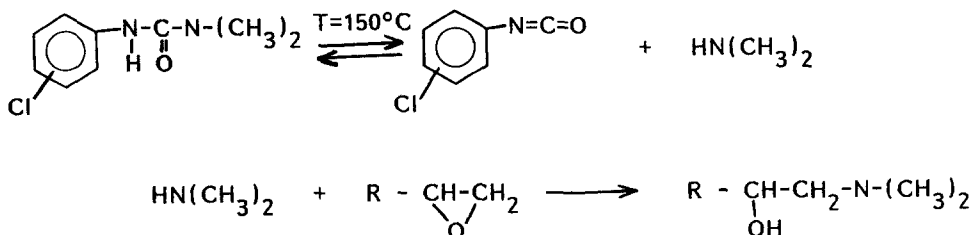


Figure 5 : expected deblocking mechanism of the monouron pasted with epoxy oligomers.

However, FASCE et al. (13) showed that the chloro-phenyl isocyanate can also react with epoxy groups to further give oxazolidone rings.

Thus we have studied, using DSC, the reaction between DGEBA and liquid MDI in the presence of different amounts of monouron. A molar ratio of 2 (excess of isocyanate) was used in order to favour the formation of isocyanurate rings (Figure 6).

As opposed to the thermograms obtained with other types of catalysts, only one exotherm is observed in the thermogram of the monouron-catalyzed reaction.

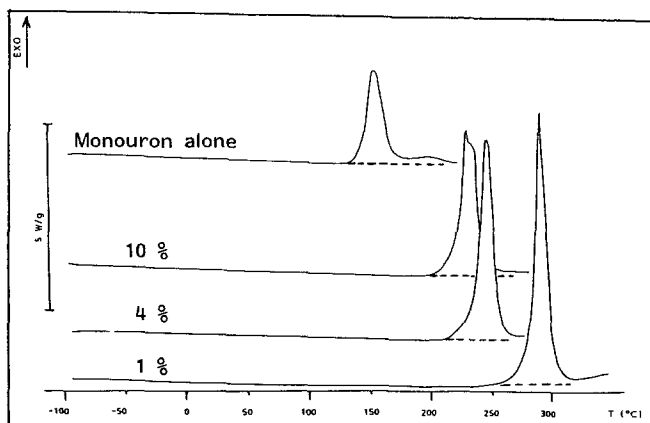


Figure 6 : Evolution of the DSC thermograms of the reaction between DGEBA and liquid MDI ($r=2$) in the presence of various amounts of monouron (heating rate : 10 °C/min). Comparison with monouron alone (50% by weight in DGEBA).

Nevertheless, the FTIR spectrum of the sample polymerized for 5 hours at 150 °C (Figure 7) shows that isocyanurate and oxazolidone rings are present.

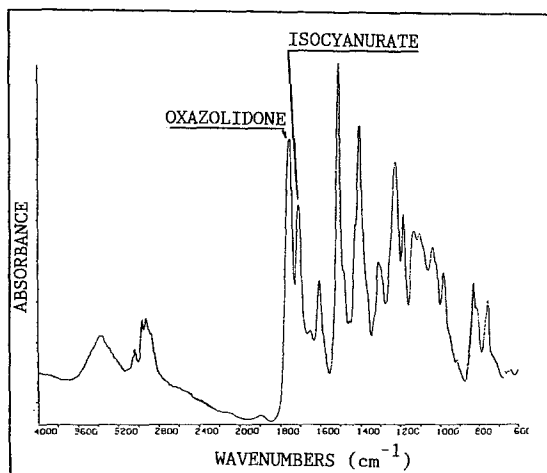


Figure 7 : FTIR spectra after the complete reaction between DER 332 and LMDI ($r=2$) in the presence of 10% of monouron.

These results indicate that three possible reactions take place simultaneously in a small temperature range : isocyanurate and oxazolidone formations, and epoxy homopolymerization. This system exhibit a pot-life longer than one month at room temperature, and a specimen cured for 5 hours at 150 °C exhibits a glass-transition temperature of 200 °C. This is higher than the T_g obtained with specimens cured in the presence of BDMA which was 165 °C.

The viscoelastic properties of the copolymer prepared with monouron as the catalyst have been determined (Figure 8).

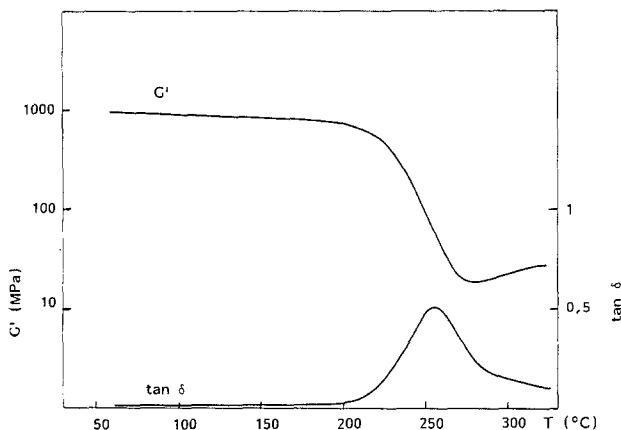


Figure 8 : viscoelastic properties of the copolymer cured for 5 hours at 150 °C with monouron as the catalyst.

The initial results show that this kind of material is interesting : its high elastic modulus (20 MPa) and its low lost factor (maximum of $\tan \delta = 0.3$) are promising for applications like insulating varnishes. Our results agree with those obtained by KINJO et al. (2,3) except that their copolymers

seem to exhibit higher glass-transition temperatures than ours (they found a T_g of 200 °C by viscoelastic experiments for $r=1$ but do not indicate the heating rate). The catalyst they used is an imidazole and this could explain this difference, too.

Further characterization to explain the polymerization mechanisms need to be done, but these initial results indicate that this system could be very interesting for industrial applications.

CONCLUSION

The imidazole catalyst is effective for promoting the diepoxide-diisocyanate reaction which occurs at lower temperatures than with a tertiary amine as the catalyst. It especially promotes the oxazolidone formation. The resulting polymer has a higher crosslinking density when an excess of isocyanate is introduced because the isocyanurate formation is then favoured. Homopolymerization of the epoxy groups occurs at a much higher rate than with the tertiary amine catalyst.

An industrially suited system has been investigated using liquid diisocyanate and a blocked isocyanate as the catalyst. Preliminary results show that this system polymerizes easily at 150 °C to give a copolymer having two heterocycles in its structure. Its glass-transition temperature is 200 °C and its pot-life is longer than one month at room temperature.

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