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Study of adducts of tertiary amines with halo or isothiocyanato boranes as latent catalysts of epoxide-amine compositions

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Summary

Adducts formed by associating tertiary amines $RN(CH_3)_2$ with haloboranes or pseudo haloboranes BX_3 (X = Cl, NCS) were utilized as latent catalysts for curing epoxide-dicyandiamide compositions. Isothiocyanato borane adducts appeared as effective agents initiating the copolymerization reaction at 100 °C, whereas their chloro analogues principally produced an homopolymerization of the epoxide. The copolymerization was made possible by the tertiary amine, $RN(CH_3)_2$, released in the reaction medium by decomposition of the adduct. Compared to the chloro derivatives, the effectiveness of the isothiocyanato derivatives can be attributed to their ability to liberate the tertiary amine before the homopolymerization of DGEBA is initiated.

Introduction

Adducts formed by haloboranes (X = Cl, Br, I) or isothiocyanato boranes and tertiary amines are easily produced. Among these adducts, those containing boron trichloride and N,N-dimethyloctylamine (DMOA) or N,N-dimethylbenzylamine (DMBA) are latent catalysts of industrial interest for the polymerization of epoxy resins. During the past few years we have investigated applications of haloboranes and pseudo haloboranes adducts as latent catalysts for curing epoxide or epoxy-isocyanate mixtures. Using bromo derivatives instead of chloro derivatives was advantageous in some instances (1) and the iodo and isothiocyanato boranes also showed interesting properties as catalysts. The possibility of changing the amino counterpart was more limited because the nature of the amine has a great influence on the stability and the properties of the adduct. In fact, apart from initiating the polymerization under determined conditions, a latent catalyst of polymerization must be sufficiently stable towards hydrolysis to be handled in air and also to be soluble in the resin to form homogenous mixtures when incorporated in it. It was found that dimethylamines $RN(CH_3)_2$ where R contains at least four carbon atoms fulfilled this requirements. Conversely their diethyl analogues were too unstable. The mechanism by which these borane adducts initiate the polymerization of pure epoxide has also been investigated recently (2).

In this work we have examined the behaviour of the adducts DMOA-BX_3 and DMBA-BX_3 (X = Cl, NCS) when incorporated in an epoxide-DDA mixture (DDA = dicyandiamide). The epoxide used was diglycidyl ether of bisphenol A (DGEBA). A limited number of tests were performed on TMBDA-$(BCl_3)_2$ and TMBDA-$[B(NCS)_3]_2$ (where TMBDA is N,N,N',N' tetramethyl 1,4 butane diamine), because the same trends as with monoamine adducts were observed. The catalytic process was compared to those described for classical

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latent catalysts, the urones, and the properties of the more promising materials obtained using isothiocyanato borane adducts were briefly examined.

Experimental

Starring Materials

Standard inert atmosphere techniques were used for the syntheses of the BCl_3 and $B(NCS)_3$ adducts according to methods recently published (2). Their concentration in the resin is given in mol/ee : [catalyst] / [equivalent epoxide] molar ratio. DGEBA DER 332 (epoxide equivalent weight: 172-176 g mol^{-1}) was obtained from Dow Chemical and DDA (T_f : 210 °C) from Aldrich. Due to the 4 amino hydrogens of DDA, $(NH_2)_2$-C=N-C≡N, and the functionality 2 of DGEBA, the amino hydrogens to epoxy functions ratio was R = 4[DDA] / 2[DGEBA], [DDA] and [DGEBA] were the molar concentrations.

Preliminary polymerization tests in presence of curing agents led to higher Tg values for R = 0.6 than for R = 1. The former value was accepted as the more convenient in accordance with published results on the polymerization of epoxide-DDA mixtures (3,4).

DSC and TGA measurements

The DSC analyses were performed on a TA 3000 Mettler apparatus under an argon atmosphere, reaction enthalpies were measured on 15 mg samples and the temperature was raised from -50 °C to 230 °C at a 7.5 °C mn^{-1} rate. After cooling down a new scan was performed at 10 °C mn^{-1} to measure the residual enthalpy and determine the Tg value. DDA is a solid difficult to scatter in the epoxy resin explaining that a sharp endotherm corresponding to the melting point of residual DDA was observed in the DSC curves at 208 °C (Fig. 1).

A B70 Setaram apparatus was used for TGA measurements.

FT Infrared spectrometry

The IR spectra were recorded on a Nicolet 550 spectrometer. The prepreg was heated just above its melting point (45-50 °C) and one drop was laid between two CsI plates pre-heated at 50 °C. The plates were placed in a copper vessel maintained at a constant temperature (temperature range: 100-140 °C). After this isothermal treatment the plates were cooled down and the spectrum was recorded. Several chemical groups were affected by the polymerization reaction (epoxy, amino, ether, hydroxy groups), their band intensities were normalized relative to the CH and CH_3 bending (1360 cm^{-1}) and stretching (2870 cm^{-1}) vibrations.

Thermal stability and storage properties.

The DGEBA-DDA-borane adduct prepregs could be stored for several months in a closed vessel at temperatures below 10 °C without any noticeable change in the physical and chemical properties but when kept at higher temperature, the alteration became really apparent. After 2 days at 40 °C, the DSC thermograms of samples containing DMOA-$B(NCS)_3$ or DMBA-$B(NCS)_3$ (4 mol, %) displayed no more endothermic peak due to the DGEBA melting, but the shape and area of the exothermic peaks were similar to those observed for fresh prepeg. After a 6 day storage time the shape of the exothermic peaks had changed and their area was decreased by more than 60 %.

The thermal stability of the mixture has been evaluated : the DSC curves of DGEBA-DDA mixtures containing no amine borane adduct showed a sharp exothermic peak in the 190 °C-200 °C region attributed to the copolymerzation reaction. This peak was followed by a broad exothermic peak with a maximum at 250 °C due to the thermal degradation of the material as confirmed by a weight loss shown by the TGA curves The weight loss remained unchanged when less than 5 mol.% amine-isothiocyanatoborane adduct was incorporated into the resin. We concluded that no oxidization degradation of the material occured at temperatures lower than 230 °C.

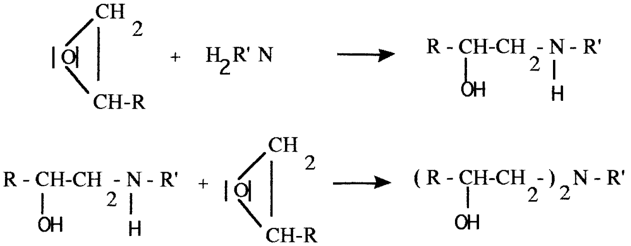
Preparation of pellets

A DGEBA-DDA mixture was vigorously stirred at 50 °C for 30 mn in order to scatter the amine into the resin. The mixture was then degased for one hour under vacuum at room temperature and DMOA-B(NCS)$_3$, the adduct showing the more promising properties as latent catalyst, was added. The mixture was cast into a duralumin mould which was placed in an oven maintained at a constant temperature (in the 100-140 °C temperature range). During the isothermal treatment a device allowed a continuous rotation of the mould to prevent the sedimentation of DDA. 1 mm thick and 4 mm thick pellets were prepared. To measure the water absorption, tests specimen were immersed in water at 80 °C.

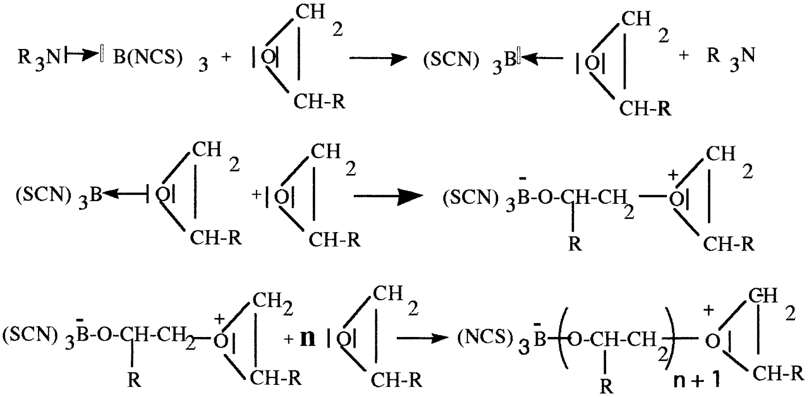
Results and discussion

Although the curing process of dicyandiamide and epoxy prepolymer is generally complicated (3-10), it should mainly consist in a competition between the addition of amine to epoxy (condensation reaction) and the epoxy homopolymerization.

Condensation reaction :



Homopolymerization reaction :



Side reactions could involve the hydroxyls formed by the addition of amine to epoxy or present in low concentration in the initial DGEBA. These hydroxyls could react together or with the epoxy groups or also with the nitrile groups. The reaction of the adducts with DGEBA observed in the absence of DDA should also occur here.

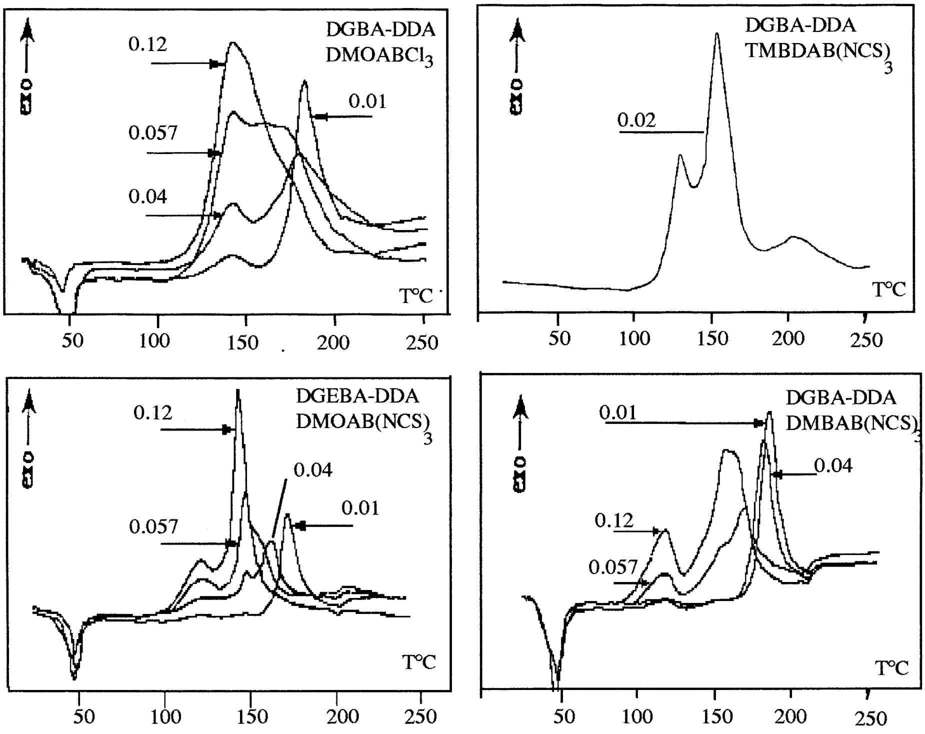


Fig. 1 : DSC thermograms obtained with different tertiary amine adducts.

Catalyst	Mol/ee	$-\Delta H$ (J.g^{-1})	Beginning T°(°C)	End T°(°C)
DMOA-B(NCS)$_3$	0	117	180	205
	0.01	152	103	200
	0.04	173	101	190
	0.057	253	100	180
	0.12	499	95	175
DMOA-BCl$_3$	0.01	142	115	210
	0.04	189	110	240
	0.057	397	105	240
	0.12	450	102	210
DMBA-B(NCS)$_3$	0.01	123	90	204
	0.04	155	85	200
	0.057	388	80	190
	0.12	405	75	180
DMBA-BCl$_3$	0.01	148	110	200
	0.04	231	93	220
	0.057	241	90	210
	0.12	240	85	190
TMBDA-[B(NCS)$_3$]$_2$	0.04	403	94	240
TMBDA-(BCl$_3$)$_2$	0.04	219	115	250

Table 1 : DSC data for different DGEBA-DDA-latent catalyst systems.

As illustrated by the DSC curves shown in Fig 1, an adduct acts according to : (i) its chemical composition (chloro and isothiocyanato adducts behave differently), (ii) its concentration and (iii) its physical state.

Two distinct exothermic peaks were observed when the reaction was initiated by the chloro adduct and three well separated exothermic peaks were generally observed when the isothiocyanato adducts were used. The first exothermic peak appeared at a lower temperature for the isothiocyanato adducts than for the chloro adduct. DMBA-B(NCS)$_3$ required higher concentrations than DMOA-B(NCS)$_3$ to produce an equivalent effect, because the former was a solid difficult to disperse in the resin whereas the latter was a wax which dissolved easily. We could also observe in all cases that the higher the adduct concentration was, the lower the final reaction temperature was. The values of the polymerization enthalpy, the initial and final reaction temperatures for various compositions are given in table 1 and the Tg values are shown in Fig. 2. DMOA-B(NCS)$_3$ appeared as the most interesting latent catalyst because it gave both the higher Tg values and the lower final reaction temperatures.

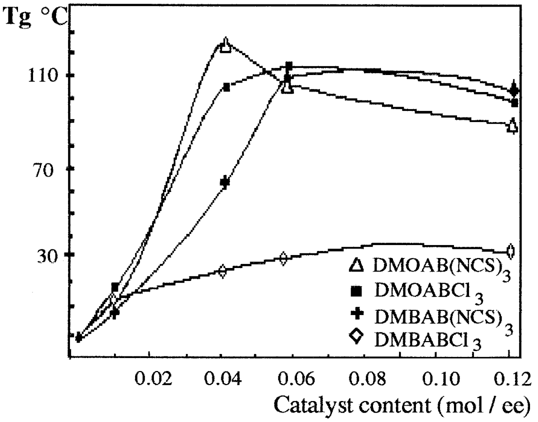


Fig 2 : Dependence of the Tg value on the catalyst content

However, all the adducts studied here initiate the homopolymerization of DGEBA and the temperature range of the dynamic DSC runs includes the 190-200 °C region of the DGEBA-DDA thermic copolymerization reaction. In this respect, the highest temperature peaks observed on the thermograms for low adduct content prepegs may be attributed to this reaction. Considerations about DSC data were not sufficient to determine in which cases catalysis of the copolymerization reaction took place but most indicative results were obtained using IR spectrometry. The IR spectra of a cured DGEBA-DDA resin containing DMOA-B(NCS)$_3$ as catalyst (**A**) and an incured sample (**B**) are shown in Fig. 3. The polymerization reaction resulted in a decrease in the intensity of the band at 915 cm^{-1} due to the epoxide ring. The NH$_2$ stretching vibrations of pure DDA are located at 3150 cm^{-1} ($V_a(NH_2)$) and 3400 cm^{-1} ($V_s(NH_2)$). The NH absorbances in the 3150-3200 cm^{-1} decreased indicating that most of the amino hydrogens had disappeared. The phenomenon observed between 3200 and 3550 cm^{-1} is more difficult to interpret because both the OH and the NH$_2$ groups absorb in this region, the overall effect was an increase in absorbance due to the formation of hydroxyls. The homopolymerization of DGEBA resulting in the formation of C-O-C ether bonds gave rise to a strong absorption at 1110 cm^{-1}. An important modification of the spectrum can be observed between 2000 and 2200 cm^{-1}, the initial spectrum displayed two bands due to DMOA-B(NCS)$_3$ at 2053 cm^{-1} and 2107 cm^{-1} ($V_s(C{=}N)$ and $V_a(C{=}N)$) and one band due to the nitrile group of DDA at 2200 cm^{-1}. After heating, only the band attributed to the nitrile group remained. As previously observed for thermosets containing

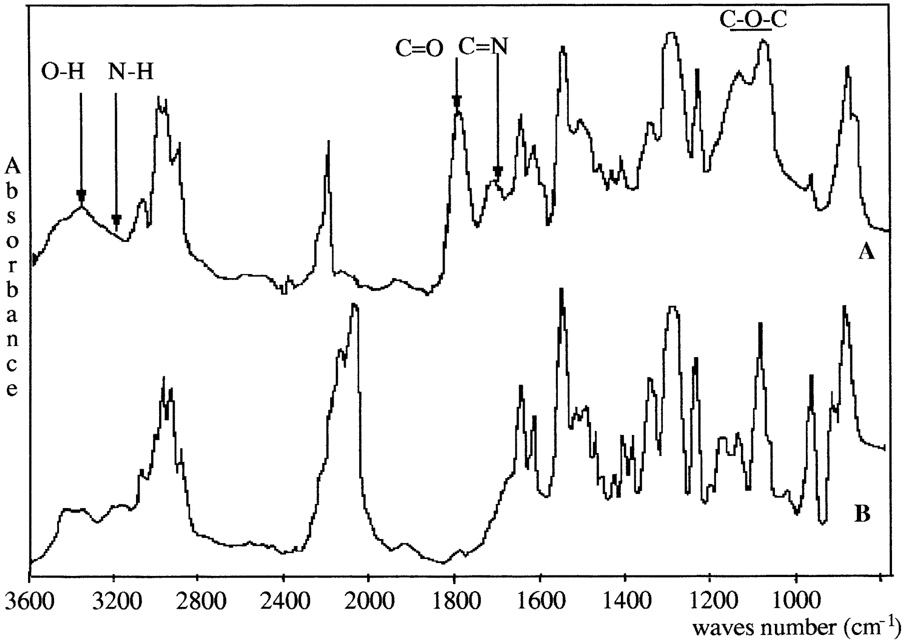


Fig. 3 : IR spectra of a cured DGEBA- DDA resin containing DMOA-B(NCS)3 as catalyst (A) and of an incured sample (B).

DGEBA and B(NCS)$_3$ adducts (2), the NCS groups disappeared giving rise to the formation of oxazolidone rings characterized by the absorption of the C=O bond at 1750 cm^{-1}. The absorbance in the region where the OH and NH$_2$ stretching vibrations overlap has been studied: the change in absorbance at 3340 cm^{-1} as a function of time is shown in Fig. 4 for different temperatures, the thermosets contained 0.04 mol/ee of DMBA-B(NCS)$_3$.

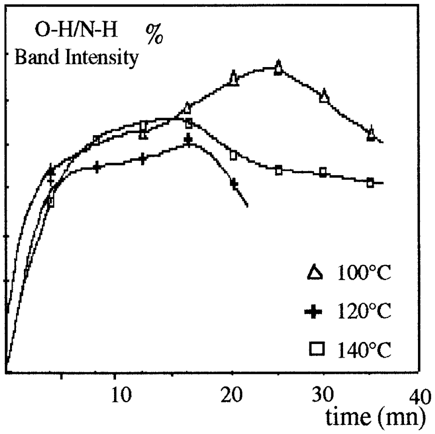


Fig. 4 : Time dependence of the OH/NH2 band intensity at 3340 cm^{-1}.

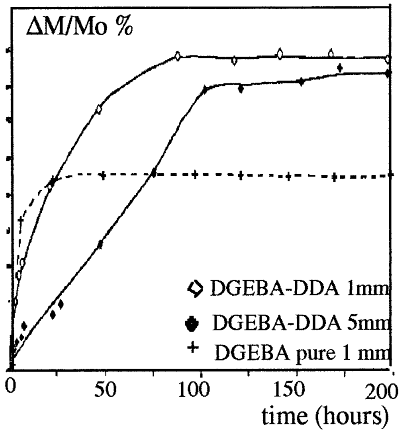


Fig. 5 : Time dependence of water absorption of cured pellets.

The decrease in absorbance observed after the maximum was due to reactions involving the hydroxy groups. These hydroxy groups are very reactive and can play an important role in the polymerization process (3,12-14). They can also react with the nitrile groups (10) consistently with a decrease in the intensity of the absorption at 2200 cm^{-1} observed for long reaction times. When the thermosets containing BCl_3 adducts instead of $B(NCS)_3$ adducts were maintained at 120 °C for one hour, only a new very weak C-O-C band appeared at 1110 cm^{-1} in the IR spectrum, the other bands remained unchanged. At 140 °C the homopolymerization of DGEBA became important whereas the amino groups of DDA were not significantly affected. BCl_3 adducts did not act as effective accelerators of the reaction of amines with epoxy in the 100-140 °C temperature range and so contrasted with their $B(NCS)_3$ analogues. DMOA-$B(NCS)_3$ (0.04 mol/ee) was used for the preparation of pellets and the data obtained from DSC measurements on these materials are reported in Table 2. For a reaction time of 90 mn at 140 °C the conversion appeared as almost complete ($-\Delta H = 0$). When immersed in water, the water absorption reached values of 8 weight percent (Fig. 5). Epoxy resins cured with DDA generally have a high water absorption because highly polar structural units are formed during cross-linking (15).

Temperature (°C)	Curing time	Tg (°C)	Remaining DDA (w %)	$-\Delta H$ residual (J/g)
100	2h30mn	86	18	54
120	30mn	92	12	47
	1h30mn	135	8	29
	2h30mn	140	7	28
140	30mn	144	3	8
	1h30mn	161	0	0

Table 2 : DSC data for the pellets after different curing times.

The catalytic effect produced by $RN(CH_3)_2$-$B(NCS)_3$ adducts can be interpreted from their behaviour in presence of pure epoxy resine (2). It has been demonstrated that the initiation process of the polymerization reaction at temperatures higher than 100°C involved the release of free $RN(CH_3)_2$, but these amines had only a little effect on the homopolymerization of epoxides. Only the isothiocyanato borane part of the adduct was considered as active and the mechanism involving an oxonium cation described above was proposed. By contrast with their behaviour in presence of pure epoxide, the amines $RN(CH_3)_2$ are very effective catalysts of polymerization of DGEBA-DDA systems (10). The reaction of DDA with DGEBA that we have observed was certainly initiated by the tertiary amine, liberated from the adduct by an exchange reaction involving an epoxide or an amine function of DDA. Comparatively the inactivity of the chloro adducts can be attributed both to their higher stability (the amine is less easily liberated) and their higher capacity to initiate the homopolymerization of DGEBA. It is worth noting that analogies appeared when the polymerization was intiated by the above isothiocyanato adducts instead of the widely used Monuron. In both cases : (i) an amine is liberated and is supposed to activate the copolymerization process and (ii) the formation of oxazolidinone rings considered as not essential to the cure has been observed (15-18). The amine liberated from Monuron is diethylamine but it is converted into a tertiary amine by reaction with epoxides. Both types of initiators behave as latent sources of amine, but they are different in their ability to initiate the homolymerization reaction of epoxides, the isothiocyanato borane adducts being more effective.

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