

Catalytic curing agents

A study of boron halide and boron isothiocyanate complexes with tertiary amines as catalytic curing agents for epoxide and epoxy-isocyanate mixtures

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Summary

The BY_3 ($Y = F, Cl, Br, I, NCS, H$) adducts with the tertiary amines *N,N*-dimethyl-*n*-octylamine (DMOA) and *N,N*-dimethyl-benzylamine (DMOA) were prepared, characterized and tested as catalytic curing agents for epoxy (DGEBA) and epoxy-isocyanate resins.

Evaluation of the storage stability and reactivity of the resins showed that the BBr_3 , BCl_3 , BI_3 and $B(NCS)_3$ adducts were good latent catalysts. No correlation could be found between the temperature of decomposition of the catalysts in an inert atmosphere or in contact with air and the catalytic properties. Consequently the reaction medium was involved in the activation process.

Introduction

Boron trifluoride-amine adducts have been described in the literature (1-6) as catalytic curing agents for epoxy resins and among these adducts, $BF_3NH_2C_2H_5$ has been widely used in epoxy technology (7). Such complexes are latent catalysts at room temperature. More recently the catalytic properties of boron trichloride adducts have been claimed (8) but to our knowledge no other boron trihalide has been studied. In the work reported here, we have investigated the properties of complexes formed from the Lewis acids BY_3 ($Y = Br, I, NCS, H$) as latent catalysts of epoxides or epoxy-isocyanate mixtures. These catalysts have been compared with the BCl_3 and BF_3 adducts. The Lewis acids were associated with the tertiary amines *N,N*-dimethyl-*n*-

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octylamine (DMOA) and *N,N*-dimethyl-benzylamine (DMBA). Monomeric mixtures containing the BCl_3 complexes formed with the previous amines exhibit higher storage possibilities (9) than those containing $\text{BF}_3\text{NH}_2\text{C}_2\text{H}_5$. The primary and secondary amines which can be used with BF_3 generally give unstable adducts with the other boron halides (10).

Choice of a suitable amine is also restricted by :

- a) adducts must be resistant to hydrolysis
- b) have reasonable solubility in the monomer mixture.

Experimental

Syntheses of the catalysts were carried out in a dry argon atmosphere, either in a glove box or by using Schlenck techniques.

BF_3 complexes : The BF_3 complexes with DMBA or DMOA were prepared by displacement of BF_3 from commercial boron trifluoride etherate, Et_2OBF_3 purified by distillation, i.e.



Et_2OBF_3 (0.105 mol.) was added dropwise to a solution of the amine (0.105 mol.) in 200 cm^3 of hexane vigorously stirred and cooled to 0°C . The crude complex was obtained after vacuum distillation of the volatile products from the reaction mixture.

BH_3DMBA : The preparation was the same as for the BF_3 complexes, the triethylamine complex Et_3NBH_3 being used to provide the BH_3 groups.

BCl_3 complexes : They were prepared by reaction of a suitable amine with commercial BCl_3 . In a typical reaction a 2 dm^3 round bottom flask containing 0.1 dm^3 of a dichloromethane solution of DMBA (20 g) was connected to a vacuum line and a gas line. The reaction vessel was cooled with liquid nitrogen until solidification began. After pumping off the residual gas from the reaction vessel, gaseous BCl_3 was slowly and continuously added through the gas line with vigorous stirring. The end of the reaction was indicated by a sudden pressure increase in the flask. The volatile products were evacuated from the reaction vessel and the BCl_3DMBA complex was dissolved in the minimum amount of dichloromethane and precipitated by addition of hexane. This work-up was not used for BCl_3DMOA , which was recovered as a waxy material at room temperature, readily converted to a crystalline solid when it was shaken with water.

BBr_3 , BI_3 and $\text{B}(\text{NCS})_3$ complexes : Commercially available BBr_3 was used. BI_3 was prepared from KBH_4 and iodine(11) and $\text{B}(\text{NCS})_3$ was obtained by the reaction of BBr_3 with AgNCS (12). Complex formation was achieved by slowly mixing hexane or CH_2Cl_2 solutions of acid and base at 0°C . Liquid chromatography was used to obtain pure DMBA complexes, the impurities remaining in the stationary phase when the CH_2Cl_2 solutions of the complex were passed through the column.

The complexes have been characterized in CH_2Cl_2 solution by ^{11}B NMR. Thus every BY_3 complex ($\text{Y} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) displayed a sharp singlet whereas a quadruplet due to the BF or BH coupling was observed

with the BF_3 and BH_3 complexes. The following chemical shifts (in ppm) were measured for DMBA complexes with $\text{B}(\text{OMe})_3$ as reference, $\text{Y} = \text{H} : -26.07$; $\text{Y} = \text{F} : -18.06$; $\text{Y} = \text{Cl} : -7.68$; $\text{Y} = \text{Br} : -21.96$; $\text{Y} = \text{I} : -71.91$; $\text{Y} = \text{NCS} : -28.59$. The chemical shifts for the corresponding DMOA complexes were the same (within 0.2 ppm) as those of the DMBA complexes.

Curing of epoxyde has been considered first and the evaluation studies of the catalysts were made using diglycidic ether of bisphenol-A (DGEBA) and complexes in a constant molar ratio of 1/0.046. The storage stability characteristics of these mixtures were followed at 35°C . The viscosity of the samples was measured at 20°C on a Brookfield viscosimeter. Termination of a sample life time (i.e. pot life) was taken to be when the viscosity reached a value of 10^5 m Pa s.

Reactivity evaluation was made on 15 g of resin contained in a 5.5 cm diameter metallic dish. The reactivity was considered high when the sample appeared as a gel after having been cured for one hour in an oven at 120°C . When the gel state was attained after a new treatment of one hour at 150°C , the reactivity was qualified as medium. When the sample remained liquid in both cases, the reactivity of the catalyst was considered low. The glass transition temperatures, T_g , reported in Table I were determined after the two previous treatments. The maximum value of the exotherm peaks associated with the cure reaction have been observed by DSC on a Dupont 1090 instrument. The energy released during these transformations is also reported in Table I. The decomposition temperatures of the pure BDMA.BY_3 complexes were also measured by DSC in an argon atmosphere on a Mettler TG 3000 or Setaram DSC 111. Thermogravimetric analysis was also used to obtain information on the behaviour of some complexes in contact with air at various temperatures (Table III). The catalysts have also been used to cure an epoxy-isocyanate resin, the commercial 18311 ALSTHOM IVA resin. The gel time data were measured (Table II) at 135°C on 15 g samples contained in 1.4 diameter glass tubes on a TECAM Geltimer. The sample life time was the time required for a doubling of viscosity at 35°C .

Results and discussion

According to the data reported in Table I in particular the storage stability and reactivity, BBr_3 and BCl_3 complexes appeared the most interesting catalysts. The reactivity of resins containing BI_3 complexes was high whereas the storage stability was lower than in the case of chloro and bromo catalysts. According to its chemical properties, $\text{B}(\text{NCS})_3$ is often considered as intermediate between BI_3 and BBr_3 but its DMBA complex was less active than the corresponding iodo and bromo compounds. The life time of the resins containing the BF_3 -tertiary amine complexes was very low by comparison with the resins containing the other complexes. BH_3 .DMBA has little effect as a catalyst.

COMPLEX Lewis Acid Lewis Base	Storage stability Time (Days)	REACTIVITY	MAXIMUM TEMPERATURE of the Exotherm peak (in °C)	ENERGY RELEASED (in J g ⁻¹)	T _g (in °C)
BH ₃	20	Weak	163	86	41
BF ₃	Exothermic reaction when the catalyst was added to the resin				
BF ₃	< 10	High	315.4	135	liquid
BCl ₃	51	High	139 and 176 *	106.5	80.5
BCl ₃	> 150	High	150 and 173 *	339	141
BBr ₃	> 250	High	166.5	227	93.5
BBr ₃	55	High	173.5	239	117.5
BI ₃	7	High	157	256	89.5
BI ₃	15	High	161	279	120.5
B(NCS) ₃	14	Medium	151	51.6	118

Table I : Behaviour of a DGEBA resin in the presence of various boron catalysts
* Two peaks were present on the DSC plots in the case of BCl₃ complexes

In the case of epoxy-isocyanate resins, BBr_3 , BCl_3 and BI_3 complexes (Table II) showed the most interesting properties, although the other complexes behaved as active catalysts but with lower storage stabilities.

COMPLEX		Storage Stability Time (Days at 35°C)	Gel Time 135 °C (in min)
Lewis Acid	Lewis Base		
BH_3	DMBA	< 9	28
BCl_3	DMBA	8	26
BCl_3	DMOA	21	9
BBr_3	DMBA	18	77
BBr_3	DMOA	20	38
BI_3	DMBA	15	74
BI_3	DMOA	8	13
$B(NCS)_3$	DMBA	8	18

Table II : Behaviour of an epoxy-isocyanate (ALSTHOM IVA 18311) resin in the presence of various boron catalysts

In the case of amine-boron trifluoride complexes (1) it has been assumed that the epoxide resin was cured at the dissociation temperature of the complex but this assertion has now been rejected (7). We have attempted to find some correlation between the decomposition temperature and the activity of the catalyst. The decomposition temperature data reported in Table III for the DMBA complexes have been obtained separately by thermogravimetric analysis and by differential scanning calorimetry.

DMBA Complex With	Temperature of decomposition by	
	TGA (in °C)	DSC (in °C)
BH_3	134	185
BF_3	157	250
BCl_3	208	230
BBr_3	154.6	210
BI_3	157	155
$B(NCS)_3$	152	275

Table III : Temperature of decomposition for DMBA complexes, data measured in contact with air by TGA and in a dry argon atmosphere by DSC

The discrepancy between these data is mainly due to the fact that the TGA data were obtained for decomposition occurring in contact with air whilst the DSC data were taken in an inert atmosphere. No correlation could be found between these decomposition temperatures and the catalytic behaviour : the decomposition temperature measured by TGA is nearly the same for the BF_3 , BBr_3 , BI_3 and $\text{B}(\text{NCS})_3$ complexes but their activities and storage stabilities are very different. It turns out that the activation of the latent catalyst does not depend upon the catalyst alone, but that the reaction medium is also involved in this process.

Finally all the complexes of boron halides or boron triisothiocyanate with dimethyl-benzylamine or dimethyl-octylamine except the adduct $\text{BF}_3\text{-DMOA}$ were latent catalysts for curing epoxy or epoxy-isocyanate resins. Among them the BBr_3 complexes have proved to be more interesting than the well known BCl_3 complexes.

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