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THERMAL STABILITY OF EPOXY COMPOUNDS CURED WITH BORON TRIFLUORIDE COMPLEXES

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The thermal resistances of epoxy resins cured with complexes of boron trifluoride with benzylamine, 2-benzylaminoethanol and 2-anilinoethanol were examined. Thermal analysis data were used to compare the thermal resistances of epoxy compositions cured with polyamines (aliphatic and aromatic), acid anhydrides and complexes of boron trifluoride with the above amines.

One of the most essential factors influencing the processing characteristics and pratical use of epoxy materials is the type of hardener used.

The curing of epoxy resins proceeds according to a polyaddition mechanism (primary and secondary polyamines, acid anhydrides) or to polymerization (tertiary amines, Lewis acids).

The curing of epoxy resins with complexes of boron trifluoride (BF_3) with amines proceeds according to a cationic polymerization mechanism. The use of boron trifluoride complexes as the catalysts for the cross-linking of epoxy resins leads to a considerable reduction of the curing agent consumption per unit mass of a resin, as compared with typical hardeners such as polyamines or acid anhydrides.

Another feature of the behaviour of BF_3 amine complexes as epoxy resin hardeners is frequently the latent character of the action. This feature, i.e. a rapid cross-linking reaction above a certain temperature specified for each complex, is utilized in processing practice.

The above mentioned advantages of using BF_3 complexes, as well as the favourable properties of epoxy compounds cured with these complexes, turned our interest to this class of curing agents. Our studies were carried out with compositions consisting of epoxy resin and BF_3 amine complex. The fundamental properties concerning the curing (or gelation) of the epoxy resin were evaluated, as well as the thermal resistance of the hardened resin.

Experimental

During the tests both commercially manufactured BF_3 complexes and ones developed and prepared [1] in our laboratory were used. The complex of BF_3 with benzylamine (Experimental Department of PZNF, Poznań, Poland) was delivered in solid form or as a solution in glycol. Complexes of BF_3 with amines synthetized in our laboratory are listed in Table 1.

As epoxy component we used either a fraction of the diglycidyl ether of bisphenol A (EDGB) [2], having an epoxy number of 0.581 g equiv/100 g, or the low molecular weight epoxy resin Epidian 6 (Chemical Works, Sarzyna, Poland) with an epoxy number of 0.533 g equiv/100 g.

Only pure compositions were tested, i.e. without fillers, modifying agents etc. The thermal resistances of epoxy materials cured with BF_3 complexes or for comparison, with representatives of other classes of curing agents, were determined.

Thermal tests on epoxy compounds were carried out with a Paulik–Paulik–Erdey Derivatograph (MOM, Budapest).

Maximum temperatures corresponding to the peaks of exothermic effects were determined according to Ref. [3], using 5 g samples.

Results and discussion

In order to evaluate the prepared complexes of BF_3 with aromatic and aliphatic–aromatic amines, curing tests on EDGB were carried out, directly in the platinum pot of the derivatograph, the composition being heated from ambient temperature up to 573 K. The data obtained from these studies enabled us to determine the curing temperatures of a particular system: the EDGB complex of BF_3. The gelation curves were recorded according to [3], at specified, characteristic temperatures for a given composition of resin and BF_3 amine complex.

The peak temperatures corresponding to the exothermic effects (T_{max}), determined from the gelation curve, as well as the gelation times (t_g) at the curing temperatures (T_u), are listed in Table 1.

For the curing of Epidian 6 resin, two of the BF_3 complexes listed in Table 1 (complexes with 2-benzylaminoethanol and 2-anilinethanol) were used, besides commercial complexes with benzylamine. The hardened epoxy materials were tested for thermal resistance, mass loss during heating in the derivatograph being evaluated within the temperature range from 293 to 773 K, in air atmosphere.

The temperature of 1 and 5% mass loss of epoxy materials cured with BF_3 complexes were measured. For comparison, other compositions were also tested; these were cured with a triethylenetetramine (Z–1) adduct of methylenedianiline with the epoxy resin (ad–MDA), and with phthalic (PA) and hexahydrophthalic anhydride (HHPA). Test results are shown in Table 2 (sample hardening procedures are also given) and in Fig. 1.

Table 1 Curing parameters of EDGB–BF_3 complex systems (T_u = curing temperature, T_{max} = maximum temperature during gelation test, t_g = gelation time)

Complex of BF_3 with	Complex concentration, phr *	T_u/T_{max}, K/K	t_g min
$C_6H_5–S–(CH_2)_2–NH–C_6H_5$	2	323/425	3
	3	323/368	4
4 Cl–C_6H_5–S–$(CH_2)_2$–NH–CH_3	2	343/353	15
	2	353/495	6
$C_6H_5–CH_2–NH–(CH_2)_2–OH$	4	403/411	18
	4	413/483	8
$C_6H_5–NH–(CH_2)_2–OH$	0.5	333/357	9
	1.0	333/436	7
$C_6H_5–NH_2$	5	403/428	5
	5	413/465	3

* phr = parts per hundred parts of resin.

Table 2 Thermal resistance of epoxy compounds

	Curing agent, concentration, phr	Curing conditions				Mass loss temp. K	
		curing		heating-up			
		temp., K	time, h	temp., K	time, h	1%	5%
1	Z–1 */13	333	2	373	3	504	564
2	ad–MDA/34	333	2	373	3	514	599
3a	BF_3 • benzylamine solid/7	408	3	–	–	529	561
3b	solution of 3a in butylene glycol/7	423	3	–	–	496	572
3c	solution of 3a in ethylene glycol/7	423	3	–	–	484	572
4	BF_3 • 2-benzylaminoethanol, solution in glycerol /5	423	1	–	–	458	565
5	BF_3 • 2-anilinoethanol, solution in glicerol/5	353	1	–	–	393	575
6	PA/70 + DMF–3**/0.5 as curing accelerator	423	3	–	–	450	537
7	HHPA/70 + DMF–3**/0.5	423	3	–	–	550	605

* Symbols of curing agents: see text; ** DMF–3 is commercial 2,4,6-tri(dimethylaminomethyl) phenol (Chemical Works, Sarzyna, Poland).

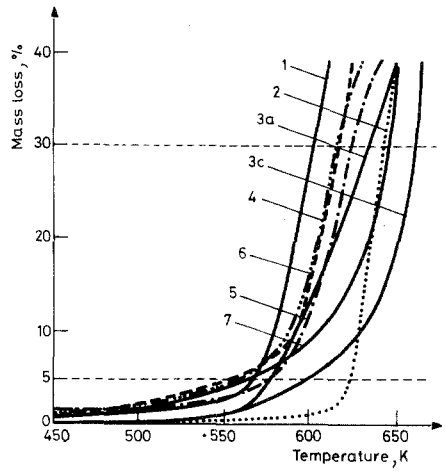

Fig. 1 TG curves of epoxy compounds described in Table 2

The results revealed that the epoxy compositions cured with BF_3 · benzylamine complex have higher thermal resistances than those of materials hardened with aliphatic amines. By selection of the optimum curing conditions for the composition epoxy resin–BF_3 · benzylamine (form of introduction of complex into resin, concentration of complex in resin, curing temperature), materials with thermal resistance similar to those of compositions cured with aromatic amines and acid anhydrides were obtained.

Curing of Epidian 6 resin with complexes of aliphatic–aromatic amines (2-anilinoethanol, 2-benzylaminoethanol) leads to epoxy materials with thermal resistances intermediate between those of materials cured with aliphatic and aromatic polyamines (see Table 2 and Fig. 1). The advantage of the use of these two latter BF_3 complexes is that light-coloured, transparent materials are obtained [1].

Conclusions

There is a possibility of enlarging the range of BF_3 complexes used up to date, as curing agents for epoxy resins. Depending on the type of amine bonded with BF_3, the processing properties and stability of epoxy materials hardened with such complexes can be modified. By selecting proper conditions for curing, one can obtain epoxy materials cured with BF_3–amine complexes with thermal resistance parameters comparable with those of materials cured with aromatic amines or acid anhydrides.

References

1 Polish Pat. Appl. P 245 770 18.01.1984.
2 T. Spychaj and A. Błędzki, Polimery – tw., in press.
3 Polish National Standard: PN-74/C-89085.

Zusammenfassung – Der Wärmewiderstand von mit Komplexen von Bortrifluorid mit Benzylamin, 2-Benzylamino-äthanol und 2-Anilino-äthanol gehärteten Epoxyharzen wurde untersucht. Anhand thermoanalytischer Daten wurden die Wärmewiderstandswerte von mit (aliphatischen und aromatischen) Polyaminen, Säureanhydriden und Komplexen von Bortrifluorid mit den oben angeführten Aminen gehärteten Epoxy-Kompositionen miteinander verglichen.

Резюме – Исследована термоустойчивость эпоксисмол, отвержденных комплексными соединениями трехфтористого бора с бензиламином, 2-бензиламиноэтанолом и 2-анилинэтанолом. Данные термического анализа были сопоставлены с термоустойчивостью этих же эпоксидных смол, отвержденных аминами (алифатическими и ароматическими) и ангидридами кислот.