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THERMAL STABILITY OF EPOXY ADHESIVES

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A study was made of the thermal stability of epoxy compounds which were unfilled or contained metallic fillers such as aluminium dust, aluminium flakes, powdered bronze, powdered brass and silver flakes. The properties of the compounds were modified by the use of various hardeners.

The intensive development of the electronics industry has led to the need to manufacture various special-purpose materials, and polymer compounds play an important role among them.

Such materials include conductive and non-conductive adhesives, used among other things for cementing semiconductor structures with base.

Most recently manufactured adhesives contain epoxy resins as a polymer matrix. These resins exhibit a considerable adhesion to metal surfaces. These adhesives should also be characterized by high purity, high thermal resistance and stability of the electric characteristics at elevated temperatures [1].

The thermal stability of epoxy compounds depend primarily on the chemical structure of the epoxy resin and on the type of hardener [2]. Depending on the types of resin and hardener, the glass transition temperatures of the epoxy compounds used vary within the range 100–270° [4].

The thermal stability of typical epoxy resins made from bisphenol A, constituting 80 to 90% of the world production of epoxy resin, can be increased by the use of ring compounds as curing agents, for example aromatic amines and anhydrides [3], novolaks [4], bismaleimides, e.g. di-(*p*-maleimidophenyl) methane [5], as well as imidazole derivatives [6, 7], which improve the homogeneity of the structure of the hardened composition [8].

Experimental

Liquid epoxy resin with an epoxy equivalent weight of 180 was used for tests, together with the following hardeners: *p,p'*-diaminodiphenylmethane (AR), adducts of p,p'-diaminodiphenylmethane with epoxy resin with an epoxy equivalent weight of 182, with different amine to resin molar ratios (AAR), diaminodiphenylsulphone (SF), adducts of BF_3 with benzylamine (KBF-1 and KBF-2), hexahydrophthalic anhydride (HHP) and series of imidazoles: 2-methylimidazole (MI), 2-ethanol-2-methylimidazole (EMI), 1-allyl-2-methylimidazole (TL), 1-ethyl-β-cyano-2-methylimidazole (PAC) and the potassium salt of 1-β-carboxylethyl-2-methylimidazolic acid (IK).

The effect of the type of hardener on the thermal resistance of the composition was studied. The effect of metallic filler added in an amount of 70% was also determined, using aluminium powder and flakes, powdered brass and bronze, and silver flakes. The thermal stabilities of the compositions were determined with a dynamic method (heating rate 6 deg/min), using a MOM, Budapest (Hungary) derivatograph.

Results and discussion

Tests on unfilled epoxide compositions

The thermal stabilities of the tested compositions were determined on the basis of the temperature of commencement of rapid decomposition of the epoxy composition. The epoxy compositions used as adhesives in electronics should be applied at temperatures where there is no decomposition of the binding agent and hence no evolution of volatile products of macromolecular chain degradation, and at temperatures at which the thin layer of adhesive on the metal surface does not deteriorate and maintains its physical and mechanical properties.

Examinations on unfilled epoxy compositions showed that most of them exhibited short-term thermal resistance at 220–250° (Figs 1 and 2). The mass losses of the tested compositions did not exceed 1.5% at these temperatures, whereas rapid decomposition commenced above 250°. Compositions containing imidazole derivates, excluding the MI derivate, undergo a mass loss of 1.5% or less below 300° (Fig. 2). The compositions hardened with PAC, EMI and TL imidazole derivatives achieve the maximum thermal decomposition rate at 420–440°. The composition hardened with 2-methylimidazole MI had a markedly lower thermal resistance than those of compositions hardened with typical hardeners such as aromatic amines and sulphone.

From the above examinations it appears that the use of imidazole derivatives as hardeners for epoxy compositions leads to an improvement of the short-term thermal resistance by about 50° compared with typical, currently used hardeners.

Examinations of metal-filled epoxy compositions

Two methods were used to test epoxy compositions containing 70% powdered metallic fillers: studies of the effect of the metallic filler type on the thermal resistance of the composition, and more extensive studies of the influence of the hardener type on the thermal properties of compositions containing a particular type of metallic filler. For the majority of tested compositions the temperatures of commencement

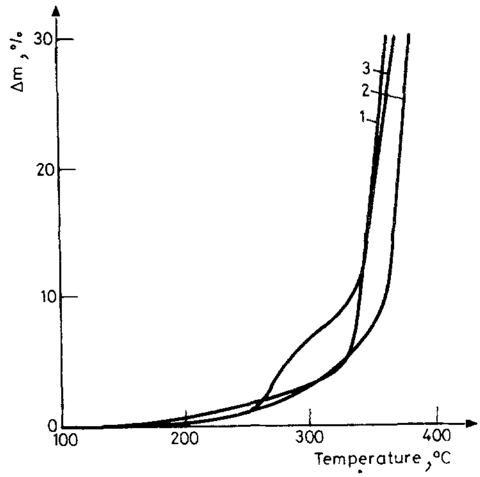

Fig. 1 TG curves of unfilled epoxy compositions. 1 – AAR, 2 – SF, 3 – AR

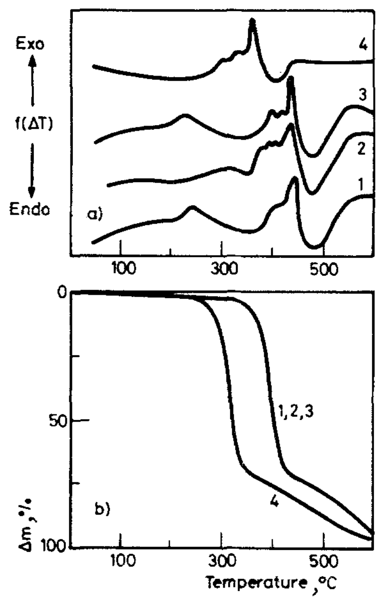

Fig. 2 TG and DTA curves of unfilled epoxy compositions hardened with imidazole derivatives 1 – PAC, 2 – EMI, 3 – TL, 4 – MI

of rapid thermal decomposition of the filled compounds were approximately the same and did not depend on the type of filler used (Fig. 3). On the other hand, the type of the hardener had a substantial influence on the course of thermal decomposition of compositions containing one type of filler (Fig. 4). Depending on the type

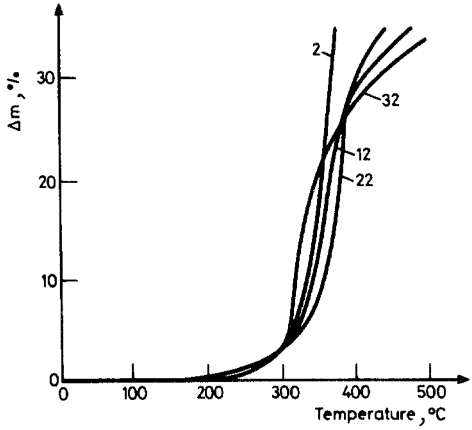

Fig. 3 TG curves of epoxy compositions hardened with amine (SF) and containing different metallic fillers: 2 – unfilled, 12 – aluminium dust, 22 – aluminium flakes, 32 – powdered bronze

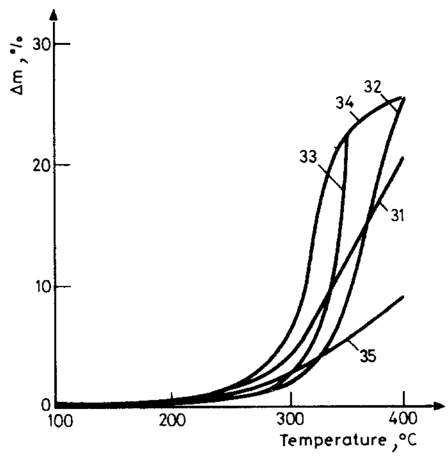

Fig. 4 TG curves of epoxy compositions filled with powdered bronze: 31 – AAR, 32 – SF, 11 – AR, 34 – KBF-1, 35 – KBF-2

of hardener, at 250° these compounds exhibit mass losses ranging from 0.8 to 2.0%, in the following sequence:

SF < AR < KBF-2 < AAR < KBF-1

If the electric characteristics are considered (the lowest resistance), the compositions with silver proved to be most interesting. Figure 5 shows the thermogravimetric curves of the compositions exhibiting the best of the remaining properties, such as electrical properties, adhesion to metal surfaces, the quality of the joint, lack of

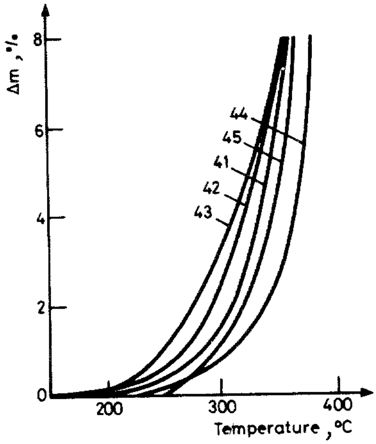

Fig. 5 TG curves of epoxy compositions filled with silver flakes: 41 – KBF-1, 42 – KBF-2, 43 – HHP, 44 – IK, 45 – PAC

blistering and mechanical strength. The effect of the hardener on the course of thermal decomposition, both within the range from 200° to 300° and above 300°, is clearly visible.

Conclusions

The thermal stabilities of epoxy compositions, both with and without metallic fillers, in the form of powder of flakes, depends primarily on the type of hardener used. Of the tested compositions with different hardeners, both filled and unfilled, the compositions containing imidazole derivatives showed the best thermal resistance.

References

1 B. Pieńkowska and P. Chrobak, Elektronika, (pol.), 17 (1976) 363.
2 U. Gruber, Papers of AVK 17 Internationale Tagung über verstärkte Kunststoffe, Freudenstadt, 1981, 26/1.
3 U. G. Petter, Epoxide Resins, London, Iliffe Books, 1970.
4 Austrian Pat. 332 129 (1975).
5 P. Penczek, W. Kosińska, E. Drągowska and A. Wanat, Polimery (pol.), 19 (1974) 613.
6 US Pat. 3 903 480 (1975).
7 Pol. Pat. Appl. 234 885 (1982).
8 T. Takahama and P. H. Geil, Makromol. Chem. Rapid Commun., 3 (1982) 389.

Zusammenfassung — Es wurde die thermische Stabilität ungefüllter und gefüllter Epoxidkompositionen untersucht. Als metallische Füllstoffe wurden Aluminiumpulver und -flocken, Messing- und Bronzpulver sowie Silberflocken eingesetzt. Die Eigenschaften dieser Kompositionen wurden mit verschiedenen Härtern modifiziert.

Резюме — Изучена термоустойчивость эпоксидных смол без наполнителя и с металлическими наполнителями такими, как алюминиевая пыль, алюминиевые и серебрянные волоски, а также порошки бронзы и латуни. Использование различных отвердителей вызывало изменение свойств эпоксидных соединений.