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APPLICATION OF THERMAL ANALYSIS IN THE STUDY OF ALKYD–ALLYL MOULDING COMPOUNDS

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Alkyd–allyl moulding compounds containing diallyl orthophthalate as networking monomer and five other unsaturated polyester resins were investigated by DTA. Analysis of DTA curves allowed choice of the alkyds forming well-cured moulding compounds within the investigated monomer. The thermal resistance and acetone absorption of the cured sample confirmed the choice of the alkyd.

The influence of 6 different powder fillers on the exothermic effect of curing of alkyd–allyl moulding compounds was evaluated by DTA.

Alkyd–allyl moulding compounds are used to make a wide variety of insulation and construction elements for the electrotechnical industry and for hermetization in electronics.

Alkyd–allyl moulding compounds are made from unsaturated polyester resins cross-linked with allyl monomers: diallyl orthophthalate or diallyl isophthalate. They occupy an intermediate position between polyester moulding compounds from unsaturated polyester resins cross-linked with styrene and allyl moulding compounds. They approach the allyl moulding compounds in manufacture and utilization qualities, yielding only to the latter compounds in resistance to moisture and to elevated temperature. They are characterized by better stability and definitely better manufacture and utilization qualities as compared to the polyester moulding compounds. Further, the utilization of allyl monomers permits elimination of the disadvantages due to the presence of styrene, i.e. an unpleasant, sharp odour, the toxicity and the short life of the uncured moulding compounds. At the Department of Plastics of the Technical University in Szczecin, investigations were undertaken to develop the technology of alkyd–allyl moulding compounds based on unsaturated polyester resins of home make.

In this publication we present data on part of the procedure for alkyd–allyl moulding compounds, relating to thermal analysis by means of thermal analysis.

Experimental

Preparation of samples

Commercial unsaturated polyester resins (alkyds):

- from saturated oligomer obtained from ethylene polyterephthalate, subjected to glycolysis, reacted with maleic anhydride and propylene glycol (P-142),
- from maleic anhydride and ethoxylated 2,2-di-(4-phenyl) propane (P-173),
- from maleic anhydride, glycerol and 2,2-di-(4-phenyl) propane (P-132),
- from maleic anhydride, phthalic anhydride and propylene glycol (P-109),
- from the addition product of 2-naphthol to maleic anhydride and propylene glycol (ANE).

Characteristics of these alkyds, the absorbing power of acetone, and the hardness of the moulding compunds, are given in Table 1.

Table 1 Characteristics of alkyds, absorbance of acetone, and hardness of moulding compounds obtained with various alkyds

	Alkyds				Moulding compounds cured	
type	softening temp., °C	iodine number	acid number	hydroxyl number	absorbance of acetone	hardness °Barcol
P-142	28–35	4.5	34.3	47.7	0.04	53
P-132	46–55	50.2	12.9	33.7	0.31	45
P-109	38–48	6.9	43.5	31.4	4.08	45
ANE	69–80	9.6	36.2	59.1	10.11	43
P-173	55–62	36.5	24.6	86.1	2.85	40

Diallyl orthophthalate (*o*-DAP) was used as cross-linking monomer. Moulding compunds of identical composition (alkyd + *o*-DAP + initiator + powder fillers + releasing agent + thickening agent), differing from each other only in the type of alkyd used, were prepared for investigations.

The effect of the type of powder filler in the moulding compounds studied with the use of alkyd P-142 and *o*-DAP. The moulding compounds were obtained by the fusion method in a single curve blade mixer at about 80°. The curing of moulding compounds was carried out by the pressing method at 180° and 8.5 MPa, using a pressing time of 1 min per 1 mm thickness of sample.

Uncured moulding compounds and samples of the same materials after curing were analysed with a derivatograph in order to select alkyds best fitted to yield alkyd–allyl moulding compounds.

Thermoanalytical methods

Simultaneous recording of the T, TG, DTG and DTA curves was achieved with a Derivatograph OD-102 (MOM, Budapest). A heating rate of 6 deg/min^{-1} was applied.

Results and discussion

The DTA curves of the uncured moulding compounds indicate the essential differences between the materials prepared with the use of various alkyds (Fig. 1).

The highest exothermic effect, estimated from the area enclosed by the DTA curve, was exhibited in the case of moulding compounds prepared from alkyd P-142. The next in order of effectiveness was the setting effect of the moulding compound that contained alkyd P-132. The exothermic setting effect of the moulding compound made from alkyd P-173 proved to be unexpectedly small. The reason for such a course of copolymerization of this alkyd with *o*-DAP might be that the relatively large content of phenolic groups inhibits the cross-linking process. The endothermic setting effect of the moulding compound containing the resin ANE is also relatively small. If it is assumed that the value of the effect gives evidence of the reactivity of the individual alkyds and the degree of curing of the moulding compounds obtained from these alkyds, the best will be alkyd P-142, followed closely by alkyd P-132.

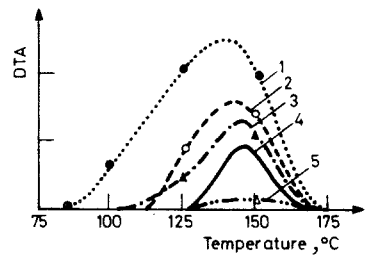

Fig. 1 DTA curves of curing of moulding compounds containing various alkyds: 1 – P-142, 2 – P-132, 3 – P-109, 4 – ANE, 5 – P-173

The DTA curves reveal a slight shift in maximum setting temperatures towards higher values for the moulding compounds containing less reactive alkyds.

On analysis of the TG curves of the moulding compounds, it is seen that the compounds which contain alkyds P-142 and P-132 are characterized by thermal resistances much better than the others (Fig. 2).

The extent of mass decrement after heating is associated with the chemical structure and the degree of cross-linking. All the resins except alkyd P-109 have good thermal resistance. Thus, the differences in the TG curves may be attributed to the weak cross-linking of moulding compounds composed of alkyd P-173 and resin ANE.

It should be noted that other investigations of the cured moulding compounds, carried out at the same time, entirely supported the results of thermal analysis.

The absorbing capacity of acetone (Table 1), a parameter which permits indirect evaluation of the degree of cross-linking, is thus the least (the highest degree of cross-linking) for the moulding compounds with alkyds P-142 and P-132, but very high for that with alkyd P-173. By analogy, a correlation (though not so distinct) is observed between the hardness of the noulding compounds and the values of the DTA effects.

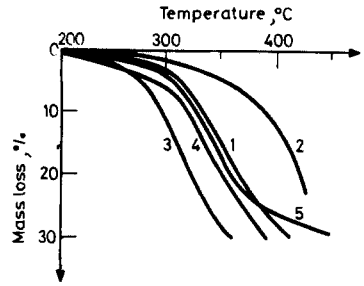

Fig. 2 Mass losses by TG of cured moulding compounds containing various alkyds: 1 – P-142, 2 – P-132, 3 – P-109, 4 – ANE, 5 – P-173

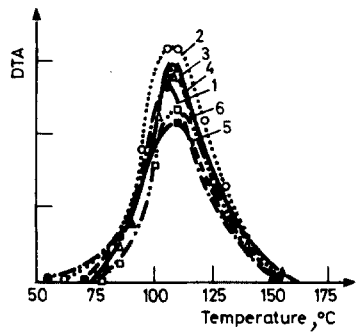

Fig. 3 DTA curves of curing of moulding compounds with various fillers: 1 – diatomite, 2 – talc, 3 – whiting, 4 – kaolin, 5 – alumina trihydrate, 6 – silica flour

The DTA curves of moulding compounds which contain various powder fillers but the same alkyd (P-142) show the influence of the type of filler upon the value of the exothermic setting effect (Fig. 3). A particularly unfavourable effect upon the curing was exhibited by alumina trihydrate.

Conclusion

Differential thermal analysis and thermogravimetry proved very useful for fixing the compositions of alkyd–allyl moulding compounds. The moulding compounds whose setting effect were the highest (with alkyd P-142 and P-132) happened to have the best utilization qualities as well. The DTA method also allows estimation of the effects of a variety of fillers upon the curing of moulding compounds.

Zusammenfassung — Mittels DTA wurde die Härtung von Alkyd—Allyl Preßmassen aus o-Diallylphthalat und fünf Polyestern untersucht. Anhand der DTA-Kurven konnten gut gehärtete Preßmassen ergebende Alkyde ausgewählt werden. Thermische Stabilität (TG) und Acetonaufnahme bestätigen die Zuverlässigkeit dieser Auswahlmethode. Mit dieser Methode wurde auch der Einfluß von sechs verschiedenen Füllstoffen auf die Wärmeeffekte des Härtungsprozesses bestimmt.

Резюме — Методом ДТА исследованы алкид—аллильные соединения для формовкки и сожащие в качестве сетчатого мономера орто-диаллилфталат и пять других ненасыщенных полиэфирных смол. Анализ кривых ДТА позволил выбрать алкиды, образующие с исследованным мономером хорошо затвердевающее формовочное соединение. Исследования термоустойчивости и поглощения ацетона затвердевшим образцом подтвердили выбор алкида. Методом ДТА проведена оценка влияния шести различных порошковых наполнителей на экзотермический эффект отвердения алкид-аллильного формовочного соединения.