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Evaluation of Initiators and Fillers in Diallyl Phthalate Resins by Differential Scanning Calorimetry

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ABSTRACT

Seven organic peroxide initiators for the polymerization of diallyl-*o*-phthalate prepolymers were studied using differential scanning calorimetry. Included were *t*-butyl perbenzoate, dicumyl peroxide, α, α' -bis(*t*-butyl peroxy) diisopropyl-benzene, 2,5-dimethyl-2,5-di(*t*-butyl peroxy) hexane, 2,5-dimethyl-2,5-di(*t*-butyl peroxy)hexyne-3, di-*t*-butyl peroxide, and *t*-butyl hydroperoxide. Heats of reaction and reaction rate constants are presented for each initiator at 1, 2, 3, and 4 phr of diallyl-*o*-phthalate prepolymers. The differences in reaction temperature and rate are discussed. Effects of four types of commonly used fillers (asbestos floats, ground quartz, calcium silicate, and clay) on the heats of reaction of diallyl-*o*-phthalate prepolymers using *t*-butyl perbenzoate and dicumyl peroxide initiators show the large inhibiting effect of untreated kaolinite clays on this polymerization.

INTRODUCTION

Doehnert and Mageli [1] measured the decomposition of organic peroxide initiators in benzene and acetone solutions. Their method allowed the calculation of activation energies and rate constants for the decomposition of these initiators in dilute solutions. The technique had not been extended to studying the actual decomposition kinetics of these initiators in polymeric materials, although such work was proposed in their paper.

Barrett [2] studied the thermal decomposition of benzoyl peroxide and azobisisobutyronitrile in solutions of di-n-butyl phthalate. His method, based on differential scanning calorimetry (DSC), allowed the calculation of kinetic constants for thermal decomposition from a single DSC curve.

The present work involves the study of seven commercial peroxide initiators in diallyl phthalate prepolymer. The seven initiators studied were:

t-butyl perbenzoate

Di-Cup (registered trademark, Hercules, Inc.) (dicumyl peroxide)

Vul-Cup (registered trademark, Hercules, Inc.) (α, α' -bis(t-butyl peroxy)diisopropyl-benzene)

Lupersol 101 (registered trademark, Lucidol Division, Pennwalt Corp.) (2,5-dimethyl-2,5-di(t-butyl peroxy)hexane)

Lupersol 130 (registered trademark, Lucidol Division, Pennwalt Corp.) (2,5-dimethyl-2,5-di(t-butyl peroxy)hexyne-3)

di-t-butyl peroxide

t-butyl hydroperoxide

Table 1 summarizes the properties of the catalysts used in this study and gives 1 min half-life data in dilute solution in benzene.

These seven initiators were studied at four different concentrations in Dapon 35 (registered trademark, FMC Corp.), a prepolymer of diallyl-o-phthalate.

The data presented herein are in terms of initiator (or catalyst, as it is known in the industry) as parts per hundred of resin (phr). This convention is widely used in diallyl phthalate compounding.

The effect of four commonly used fillers was also determined with both t-butyl perbenzoate and Di-Cup initiators.

EXPERIMENTAL

DSC curves were taken with a Du Pont Model 900 Thermal Analyzer with a DSC cell. This instrument was interfaced to an analog to digital converter and punched paper tape generated as the scan was carried out as described previously [3].

TABLE 1. Catalyst Properties

| Material | Abbreviation used in this report | % Active oxygen | 1 Min half-life at T (°C) | 1 Min half-life at T (°F) |
|-----------------------|----------------------------------|-----------------|---------------------------|---------------------------|
| t-Butyl perbenzoate | TBP | 8.1 | 166 | 331 |
| Di-Cup | Di-Cup | 11.9 | 174 | 345 |
| Vul-Cup | Vul-Cup | 18.9 | 180 | 356 |
| Lupersol 101 | L-101 | 10.5 | 174 | 346 |
| Lupersol 130 | L-130 | 5.6 | 193 | 379 |
| Di-t-butyl peroxide | DTBP | 10.8 | 193 | 380 |
| t-Butyl hydroperoxide | TBHP | 12.7 | 179 | 354 |

Using the method of Barrett, activation energies and rate constants were determined for each of the concentrations of initiators.

All samples were prepared by ball milling the initiators into the powdered prepolymer. Replication of tests showed the homogeneity of the mixtures. All DSC curves were taken in a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}/\text{min}$. Sample weights were approximately 30 mg and consisted of preforms made by cold pressing the prepolymer-initiator mixtures at pressures of 100,000 psi at room temperature in a 1/4-in. pellet press die. This procedure insured that all samples had the same density and surface volume relationships regardless of particle size. This technique is also applicable to the study of molding compounds where granular size can influence the results obtained by DSC.

RESULTS AND DISCUSSION

Figure 1 presents the DSC curves for seven commercial peroxide initiators at a concentration of 1 pph of Dapon 35 prepolymer. There is a wide range in temperature activity of these peroxides, ranging from 169°C for t-butyl perbenzoate up to as high as 224°C for t-butyl hydroperoxide. The peak temperatures indicated on the figure are

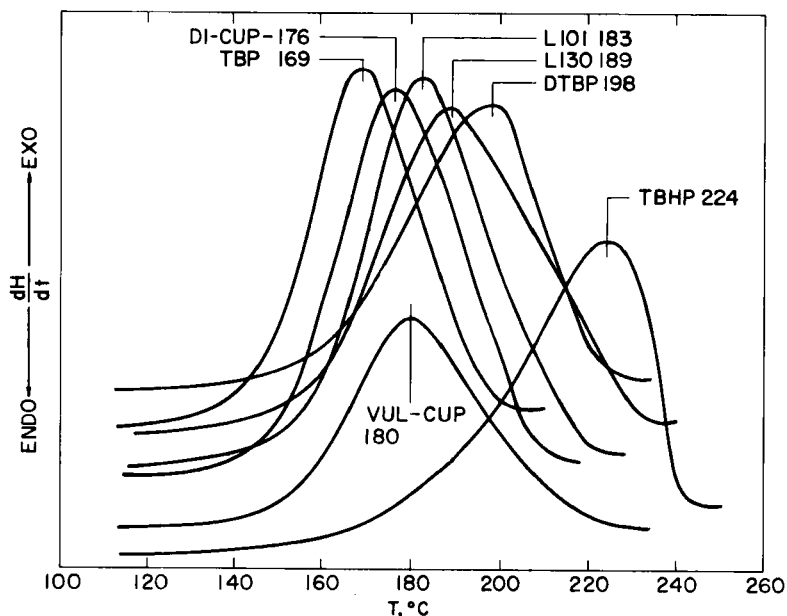


FIG. 1. Effect of catalyst type.

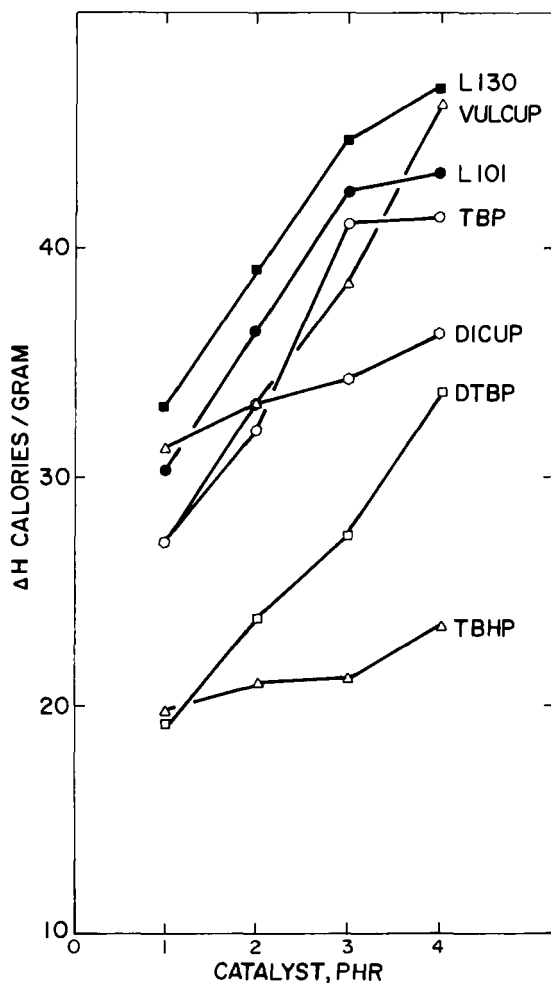


FIG. 2. Catalyst type and level vs heat of reaction.

the peaks in the DSC curve, representing the temperature at which the reaction is proceeding at its maximum rate. These figures can be used to compare the activity of the various peroxides in the diallyl phthalate prepolymer.

The data from the DSC curves, as punched paper tapes, were analyzed by computer program [3] and the total heat of reaction (area under the DSC curve) was determined as a function of concentration for each initiator.

Figure 2 shows the data obtained and indicates the steep concentration dependence of these initiators. Note that for Lupersol 130 at 4 parts of initiator phr, the thermal output is approximately 47 cal/g. At 1 phr, the thermal output is only 33 cal/g. Similar concentration dependencies are shown for the other initiators. This finding is important to the manufacturer of commercial molding compounds since lowering catalyst concentration may give very low degrees of cure in the compound.

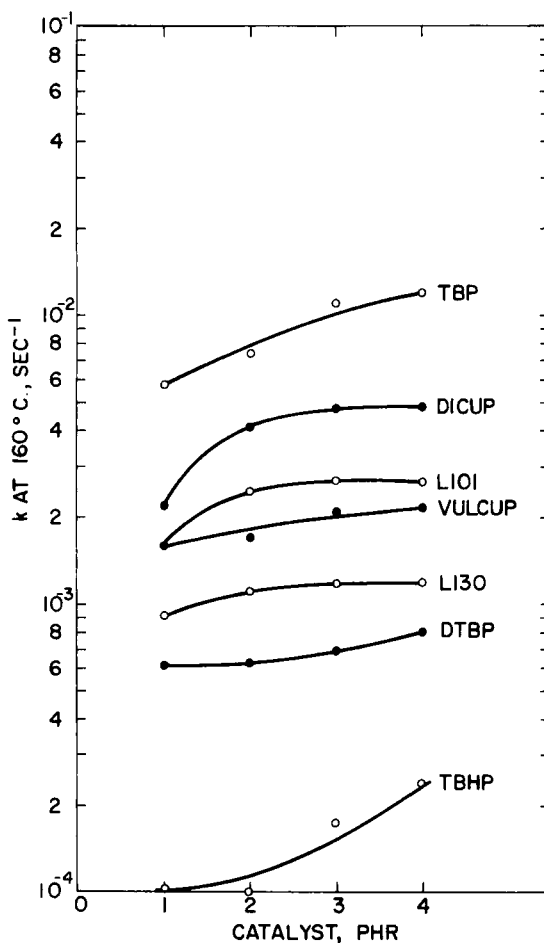


FIG. 3. Catalyst type and level vs reaction rate constant.

There is also a wide difference in the total heat of reaction obtainable with the various initiators, and this initiator efficiency should be known if such catalyst systems are to be used in commercial compounds. Thus *t*-butyl perbenzoate (TBP), which is a commonly used commercial material, is much more efficient than *t*-butyl hydroperoxide or di-*t*-butyl peroxide.

Reaction rate constants were calculated, and Fig. 3 presents the reaction rate constants at 160°C in sec^{-1} as a function of concentration. With the exception of *t*-butyl hydroperoxide (TBPH), there is not as large a concentration dependency in the case of reaction rate constant k as there is in the case of heat of reaction ΔH . However, since these data in Fig. 3 are presented at 160°C, a commonly used molding temperature for diallyl phthalate, the activity of the initiators covers almost two decades of reaction rate constant. Thus the compounder who uses *t*-butyl hydroperoxide at conventional molding temperatures will find the reaction proceeding almost 100 times slower than that of TBP.

Solomon [4, 5] has found that certain kaolinite clays seriously degrade the performance of peroxide initiators in polymerization reactions. He found that kaolinite clays were particularly effective in decomposing organic peroxide initiators because of the high acidity of the clay surface.

In order to test these effects in diallyl phthalate prepolymers, mixtures of four common fillers at the 50% level were made with Dapon 35 using two different organic peroxide initiators. Four materials used were: asbestos 7 TF-1 floats (Johns-Manville), silica 219 (ground quartz) (Harshaw Chemical Co.), Wollastonite T-1 (natural calcium silicate) (Cabot Corp.), and an untreated kaolinite clay (ASP 400) (Georgia Kaolin Co.). These materials were added at equal weights to Dapon 35 catalyzed with 3 phr of *t*-butyl perbenzoate giving a 50% by weight filler loading. DSC curves were then run on these compositions. As shown in Fig. 4, total heat of reaction was least affected by the ground quartz (silica 219) which gave a ΔH value of 20.6 cal/g, which is exactly half the value obtained for Dapon 35 and 3 parts *t*-butyl perbenzoate with no filler. Wollastonite reduced the total heat reaction slightly, as did asbestos. The clay reduced the value to 13.1 cal/g or 64% of the value obtained with silica 219.

When Di-Cup (dicumyl peroxide) initiator was used in the same 50% filler loading with these fillers, the effect of the untreated kaolinite clay, ASP 400, was extremely high. Figure 5 shows the DSC curves using Di-Cup initiator. Here the silica value is lower than that obtained with *t*-butyl perbenzoate (which we would expect from the relative reactivities of TBP and Di-Cup). However, in the case of ASP 400 clay, total heat of reaction drops to 0.3 cal/g which is 1.6% of the value obtained with silica 219 in this initiator system.

Obviously, the use of ASP 400 clay in Di-Cup initiated systems may result in materials which will not cure due to decomposition of the initiator by the acidic clay surface.

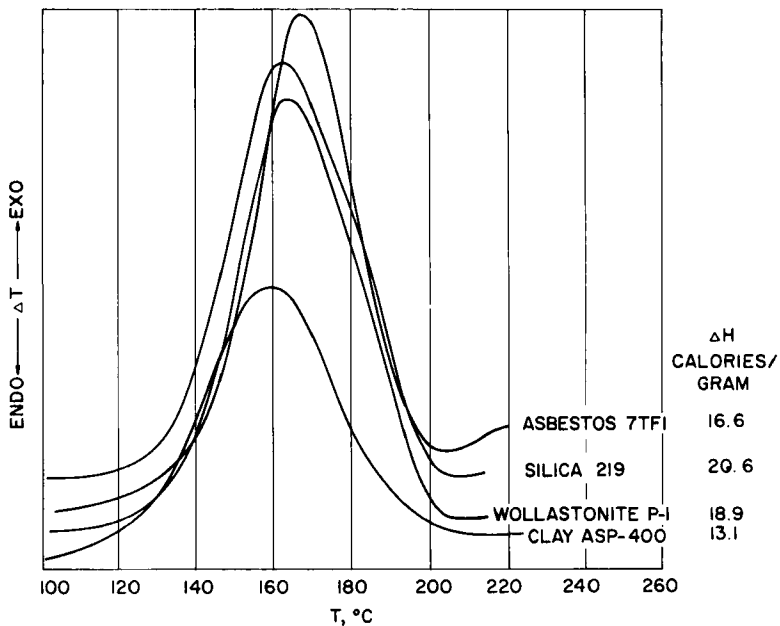


FIG. 4. Effect of fillers on cure-TBP.

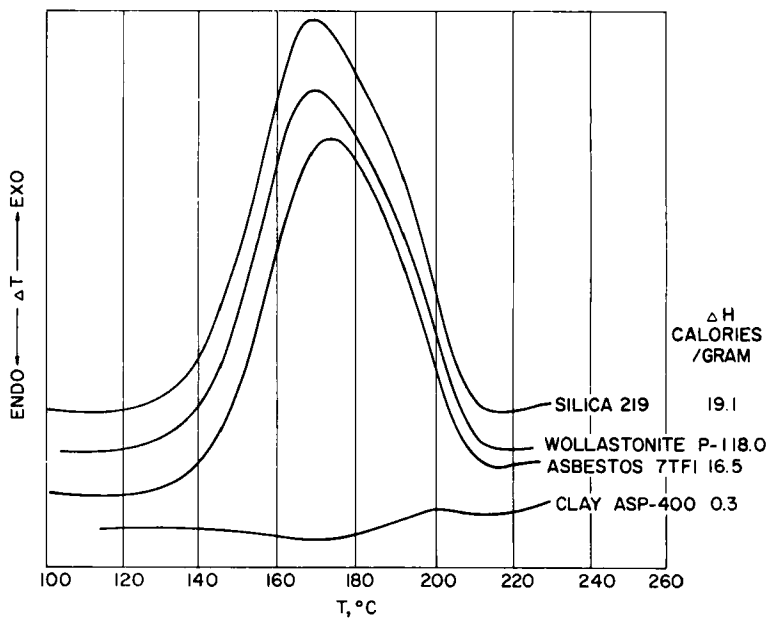


FIG. 5. Effect of fillers on cure-Di-Cup.

The use of DSC to measure activity of initiators for the diallyl phthalate system and to determine the effects of fillers on total heat of reaction allows rapid screening of initiator systems and compounding ingredients to determine their activities in the polymerization. By using small quantities of materials to obtain DSC curves, it is possible to survey large numbers of compositions which would be impossible to study using conventional compounding molding and physical testing techniques. DSC allows the rapid and inexpensive screening of these systems to allow predictions of polymerization performance.

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