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KINETICS OF THERMAL DEGRADATION OF CURED EPOXY RESINS BASED ON TRIGLYCIDYL-*p*-AMINOPHENOL

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ABSTRACT

Epoxy resin prepared from *p*-aminophenol was cured with six different curing agents, viz. diaminodiphenyl sulfone, diaminodiphenyl methane, diaminodiphenyl ether, benzidine, *m*-phenylene diamine and diethylenetriamine. Kinetics of thermal degradation of the cured epoxy resins were studied by thermogravimetry in a static air atmosphere at a heating rate of 10 °C min^{-1}. The effect of the structure of the curing agent on the thermal stability of the cured epoxy resins was investigated on the basis of temperature characteristics such as initial decomposition temperature, temperature of half volatilization and the integral procedural decomposition temperature, as well as the kinetic parameters. The thermal degradation reactions were found to proceed in a single step having an activation energy in the range 90–122 kJ mol^{-1}. They were first-order reactions.

INTRODUCTION

A major impetus for the growth and interest in the thermally stable polymers is attributable to their extensive applications in aeronautics and in supersonic appliances. Considerable research has been undertaken [1] on the thermal stability of polymers to derive the polymers which may be useful for high temperature applications. However, the important class of thermoset polymers, the epoxy resins, have not been studied thoroughly in terms of their thermal characteristics, with the exception of a more general epoxy resin, diglycidyl bisphenol-A (DGEBA) [2,3]. The thermal behaviour of this type of epoxy resin over a wide range of temperature can be better understood by dynamic thermogravimetric analysis. Triglycidyl-*p*-aminophenol (TGAP), the trifunctional epoxy resin which is being used increasingly in adhesives and composites and in aircraft compositions [4], has been selected in the present investigation as no systematic thermal study has been reported so far. Thus the present paper deals with the study of the thermal stability of TGAP cured with diamines and with the study of the effect of the structure of curing agent on the thermal stability. In addition, the epoxy fortifiers which have been reported to affect the cure kinetics of

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epoxy resins are studied for their effect on the thermal stability by incorporating them in the selected resin systems prior to cure.

EXPERIMENTAL

Materials

The epoxy resins used in the study were the diglycidyl ether of bisphenol-A (DGEBA) and the triglycidyl-*p*-aminophenol (TGAP). DGEBA was prepared following the reported method [5]. TGAP was prepared following the method reported in the patent (ref. 6). Two epoxy fortifiers were prepared [7] by reacting 4-hydroxy acetanilide (HA) separately with phenyl glycidyl ether (PGE) and vinyl cyclohexene dioxide (VCD) using 0.1 wt.% diethylamine hydrochloride as catalyst. These were coded respectively as PGEHA and VCDHA. The analyses of these materials, DGEBA, TGAP, PGEHA and VCDHA are reported in our previous communications [8,9].

The curing agents (amines) were laboratory reagents. The aromatic diamines were used after recrystallization from the appropriate solvents.

Curing procedure

The epoxy resin and the amine were mixed in the composition corresponding to one amine proton per epoxy group. Curing was achieved by heating at a required temperature for about 3 h . The cure temperatures were determined by differential scanning calorimetry (DSC) using a Du Pont 900 differential scanning calorimeter. The completion of the cure was checked by carrying out DSC scans of the cured resin samples.

Thermogravimetric analysis (TGA) of the cured epoxy samples

Thermogravimetric analysis was performed on the cured epoxy samples using a Du Pont 951 thermogravimetric analyzer. The thermograms were obtained at a heating rate of 10°C min^{-1} using 10 mg of the powdered sample. The experiments were made in a static air atmosphere.

Analysis of TGA thermograms

The thermograms obtained during the TGA scan were analyzed to give the percentage weight loss as a function of temperature. The weight loss data were processed further to obtain the rate of the thermal decomposition reaction. In order to determine the rate constants, it was assumed that the decomposition reaction of the epoxy resins was first order and that it obeyed

Arrhenius-type kinetics. Estimating the fraction of the number of initial molecules not yet decomposed (y) by eqn. (1) at several temperatures

$$y = (w_t - w)/(w_0 - w) \tag{1}$$

and by using the Broido relation [10] (eqn. (2)), the energy of activation E was calculated

$$\ln(\ln 1/y) = -(E/R)(1/T) + \text{constant} \tag{2}$$

In addition, another relation (eqn. (3)), the modified equation of Dharwadkar and Kharkhanawala [11] was used to evaluate the activation energy

$$\ln\left[\ln(1-\alpha)^{-1}\right] = \frac{E}{RT_1^2} \times \frac{100}{T_2 - T_1} Q + C \tag{3}$$

and the values of the frequency factor ln A were evaluated by using the following relation [12] (eqn. (4))

$$\ln \frac{ART_s^2}{E(\mathrm{RH})} = \frac{E}{RT_s} \tag{4}$$

The terms involved in the above-mentioned relations are as follows: y is the fraction of the number of molecules not yet decomposed; w_t is the weight of the sample at any time t; w_0 is the weight initially; w is the weight of the sample at the completion of the degradation reaction; E is the activation energy; α is the weight loss at a particular temperature T; T is the temperature under consideration; $Q = T - T_s$, where T_s is the maximum decomposition temperature; R is the gas constant; T_1 and T_2 are the initial and final decomposition temperatures; C is a constant; A is the frequency factor and RH is the heating rate.

RESULTS AND DISCUSSION

In order to investigate the effect of the diamine structure on the thermal stability of the cured epoxy resins various diamines such as *m*-phenylene diamine (MPD), benzidine (Bz), *p,p'*-diamino-diphenyl methane (DDM), *p,p'*-diaminodiphenyl ether (DDE) and diaminodiphenyl sulfone (DDS) were used as curing agents. Also one polyamine, diethylene triamine (DETA) was used for some selected resin systems. Selected thermograms obtained under dynamic conditions at a heating rate of 10 ° C min^{-1} are reproduced in Fig. 1. The degradation of the cured epoxy resins proceeds in a single step. An initial slight loss in weight takes place at about 200 ° C, then a sharp break occurs in each of the thermograms, indicating the onset of a decomposition process involving a rapid loss in weight. Finally, the decomposition rate decreases gradually, reaching a constant weight representing the carbonized char.

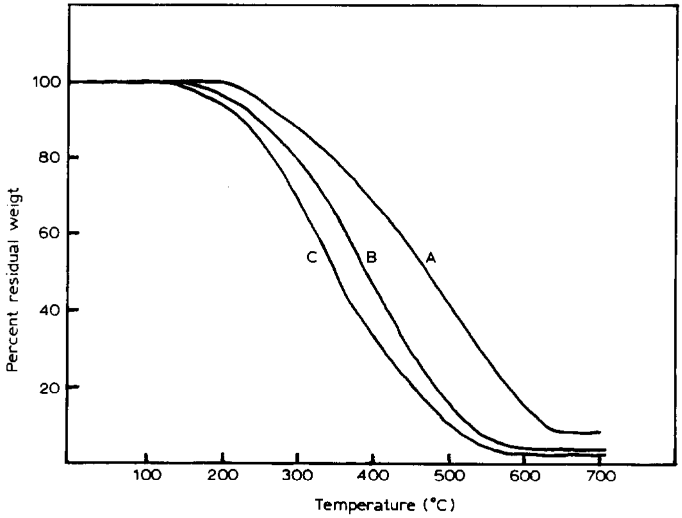

Fig. 1. Typical thermograms of the cured epoxy systems in air at a heating rate of 10 °C min^{-1}: (A) TGAP–DDS; (B) TGAP–DETA; (C) DGEBA–DETA.

The temperature characteristics such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), $T_{\max}$ (temperature of maximum rate of degradation) and T_{50} (half volatilization temperature) as determined from the thermograms are shown in Table 1 along with the integral procedure decomposition temperature (IPDT) values, which were calculated by Doyle's method [13].

T_0 and T_{10} are two of the main criteria of the heat stability of polymers. The higher the values of T_0 and T_{10} the higher the heat stability will be [14].

TABLE 1
Temperature characteristics of cured epoxy resins

Resin	Curing agent	T_0 (°C)	T_{10} (°C)	$T_{\max}$ (°C)	T_{50} (°C)	IPDT (°C)	Char yield %
TGAP	DDS	225	285	465	488	507	8.3
TGAP	DDM	220	270	448	480	500	7.9
TGAP	Bz	212	280	425	480	493	5.8
TGAP	DDE	205	265	410	480	488	4.5
TGAP	MPD	200	248	402	475	465	4.8
TGAP	DETA	180	240	375	400	458	3.8
DGEBA	DETA	125	228	320	340	448	3.5
DGEBA–TGAP [a]	DETA	180	235	325	365	456	3.7
DGEBA–TGAP [b]	DETA	175	230	310	370	450	3.0
DGEBA–TGAP [c]	DETA	180	235	322	366	458	3.2

[a] DGEBA, 80 wt.%; TGAP, 20 wt.%. [b] DGEBA, 80 wt.%; TGAP, 20 wt.%; PGEHA, 20 wt.%. [c] DGEBA, 80 wt.%; TGAP, 20 wt.%; VCDHA, 20 wt.%.

However T_0, T_{10} and T_{max} are single features of the TGA curves. To obtain the quantitative picture of the relative stability, IPDT values can be regarded of significant importance, since they represent the overall nature of the TGA curves.

The nature of the thermograms obtained for all the epoxy resin–curing agent compositions were observed to be similar in general shape. However, the characteristic temperatures varied with the curing agent used. Since materials having higher values of T_0, T_{50} and IPDT can be regarded as thermally more stable, the following trend of thermal stability for the amine cured epoxy resins may be revealed from Table 1: TGAP–DDS > TGAP–DDM > TGAP–Bz > TGAP–DDE > TGAP–MPD > TGAP–DETA.

A similar trend can be seen from the values of the residue remaining after complete levelling out of the thermograms beyond 650 °C.

The curing agents DDM and DDS gave relatively more stable cured resins because of the thermally stable linkages present within the aromatic nuclei [15,16]. The greater stability of the DDS cured resin may be ascribed to a greater heat resistance character of the sulphur links compared with those of carbon [16]. The lowest stability observed in the case of TGAP–DETA is due to a purely aliphatic structure of DETA in the cured product. The thermal stabilities of the products obtained by curing TGAP with benzidine, DDE and MPD are better than that of TGAP–DETA due to the aromatic nature of the chains. The lower stability of TGAP–DDE compared with that of TGAP–Bz may be due to the presence of a weak ether link between the phenyl rings in the chains.

The trend in the thermal stabilities of the cured resins can also be deduced from the values of the activation energy, E and the frequency factor, $\ln A$. The values of E and $\ln A$ are higher for the resin systems having higher thermal stability.

During analysis of the thermograms in order to estimate the kinetic parameters for the thermal degradation, it was assumed that the reaction was of first order and the appropriate plots representing the relations eqns. (2) and (3) were made. Selected plots are shown in Figs. 2 and 3. If the assumption that the reaction is first order is in error, deviations from linearity would be observed. In the present case the plots were observed to be linear over the conversion range of about 0.1–0.9 supporting the assumption of a first-order reaction. The values of the activation energy and the frequency factor varied in the compensating manner indicating that the mechanism of the rate-determining step of the thermal degradation is similar. Even though the kinetic parameters refer to the conditions under which they were determined, the usefulness of the kinetic data using TGA is highly satisfactory in the comparative studies in the present case.

The comparative data of the systems involving DGEBA for the values of the temperature characteristics and the values of the activation energy and

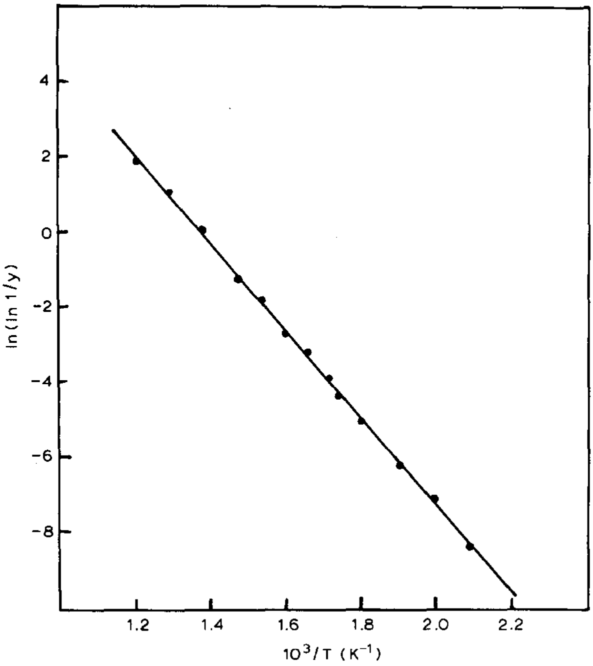

Fig. 2. Plot of ln(ln $1/y$) vs. $1/T$ using the Broido equation for a resin TGAP cured with DETA.

the frequency factor listed in Table 1 and Table 2 reveal that TGAP is more heat resistant than DGEBA. This is also evident from the results of the system DGEBA–TGAP (80/20 w/w). The high heat resistance of TGAP is attributed to the increased functionality compared with DGEBA. The

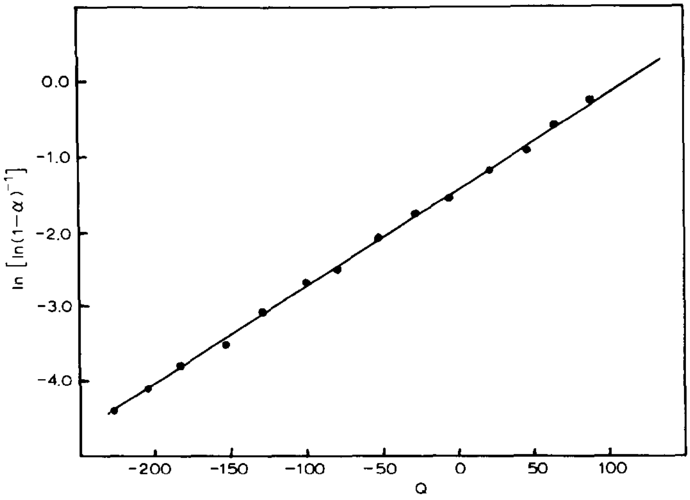

Fig. 3. Plot of $\ln[\ln(1-\alpha)^{-1}]$ vs. Q for a resin TGAP cured with DETA.

TABLE 2

Kinetic parameters for the degradation of cured epoxy resins

Resin	Curing agent	$E \pm 2$ [a] (kJ mol^{-1})	$E \pm 2$ [b] (kJ mol^{-1})	ln $A \pm 0.5$ (s^{-1})
TGAP	DDS	122.0	121.2	17.8
TGAP	DDM	117.7	118.0	16.5
TGAP	Bz	111.5	108.2	15.8
TGAP	DDE	107.2	106.0	15.2
TGAP	MPD	105.2	103.5	14.5
TGAP	DETA	97.5	98.2	13.9
DGEBA	DETA	90.2	91.0	12.8
DGEBA–TGAP [c]	DETA	94.7	95.0	13.5
DGEBA–TGAP [d]	DETA	90.0	93.7	13.0
DGEBA–TGAP [e]	DETA	95.2	96.5	13.8

[a] Evaluated using eqn. (2). [b] Evaluated using eqn. (3). [c] DGEBA, 80 wt.%; TGAP, 20 wt.%. [d] DGEBA, 80 wt.%; TGAP, 20 wt.%; PGEHA, 20 wt.%. [e] DGEBA, 80 wt.%; TGAP, 20 wt.%; VCDHA, 20 wt.%.

incorporation of the fortifiers PGEHA or VCDHA as 20 PHR (20 parts per hundred grams of fortifier on the basis of DGEBA resin) to the blend DGEBA–TGAP lowers the heat resistance. However, the effect of VCDHA is much less than PGEHA. The lowering of the thermal stability by the fortifier is due to the early loss of the chemically unbonded material to some extent. The VCDHA-based cured resin has a lower degree of unbonded material compared with that of the PGEHA-based resin. This may be due to the increased functionality in the VCDHA-based resin. McLean and co-workers [17] observed a similar type of behaviour when using the fortifiers. The fortifiers were found to diminish the glass transition temperature. In our previous papers we observed the important implications of using fortifiers in the epoxy–amine systems. The incorporation of the epoxy fortifiers in the epoxy–amine systems was found to lower the cure temperature, speed up the curing reaction and improve the mechanical properties [8,18]. Thus even though the use of epoxy fortifiers has the disadvantage of lowering the thermal stability, an improvement in certain properties can be achieved.

CONCLUSION

The dynamic thermogravimetric study of various cured epoxy systems reveals that the thermal stability depends upon the structure of the curing agent used. The degradation reactions follow Arrhenius-type kinetics having an activation energy in the range 90–122 kJ mol^{-1} and are of first order. The char yield of the epoxies (in the range 3–8%) at 650 °C in air shows that they are fairly good heat resistant polymers.

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