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Curing and thermal behaviour of DGEBA using mixture of biuret and 4,4′-diaminodiphenylsulfone

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Abstract Curing behaviour of DGEBA was investigated in the presence of varying molar ratio of biuret and 4,4′-diaminodiphenylsulfone (DDS) by means of Differential scanning calorimetery. The multiple heating rate method (5, 10, 15 and 20 °C min^{-1}) was used to study the curing behaviour of epoxy resins. The peak exotherm temperature was found to be dependent on the heating rates, structure of biuret as well as on the ratios of biuret:DDS used. Ozawa method was used for calculating the activation energy of curing reaction. The thermal stability of the isothermally cured resins was evaluated by recording the thermogravimetric traces in nitrogen atmosphere. All the samples were stable up to 330 °C.

Keywords DGEBA · DDS · Biuret · Curing kinetics · Thermal stability

Introduction

Epoxy resin have been used in many industrial applications such as in surface coatings, adhesives, structural composites, printed circuit boards and insulating materials for electronic devices because of their good chemical resistance, superior mechanical and chemical properties [1, 2]. However, the conventional epoxy resins are inefficient to satisfy the required properties in the field of advanced materials which required high thermal resistance [3]. Several approaches were used in the past to improve thermal stability of the epoxy resins [4, 5]. The properties can be varied by use of the epoxy backbone i.e., either during synthesis or cure using curing agents of different structures.

The curing of epoxy resin has been extensively investigated using amines of varying structures and of varying molecular weight [6–8]. Aromatic primary amines are known to impart high glass transition (T_g) and thermal stability up to ~320 °C to the cured resin [1]. But these aromatic amines are costly and increase the cost of the cured products.

Biuret, a condensation product of urea, is a strong base since the resulting positive charge upon protonation can be delocalized throughout the molecule. It has been widely used as a chelate ligand in coordination chemistry [9].

In this study, the curing and thermal behaviour of DGEBA has been investigated using the very cheaper amines i.e., biuret.

Experimental

Materials

Diglycidyl ether of bisphenol A (DGEBA, Grade LY556, epoxy equivalent 186) procured from Hindustan Ciba Geigy Ltd, 4,4′-Diaminodiphenyl sulfone and Biuret purchased from Aldrich were used as received.

Curing studies

TA 2100 thermal analyzer having 910 DSC module was used for recording DSC traces at heating rates of 5, 10, 15

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and 20 °C min^{-1} in nitrogen atmosphere. 5 ± 2 mg of samples in sealed pan were used in each experiment. For curing studies, the samples were obtained by mixing stoichiometric amount of Biuret and DDS with DGEBA in the varying ratio of 0:1, 0.25:0.75, 0.50:0:50, 0.75:0.25 and 1:0 using minimum amount of dimethylketone. After thorough mixing, solvent was evaporated under vacuum and the freshly prepared sealed samples were used for recording

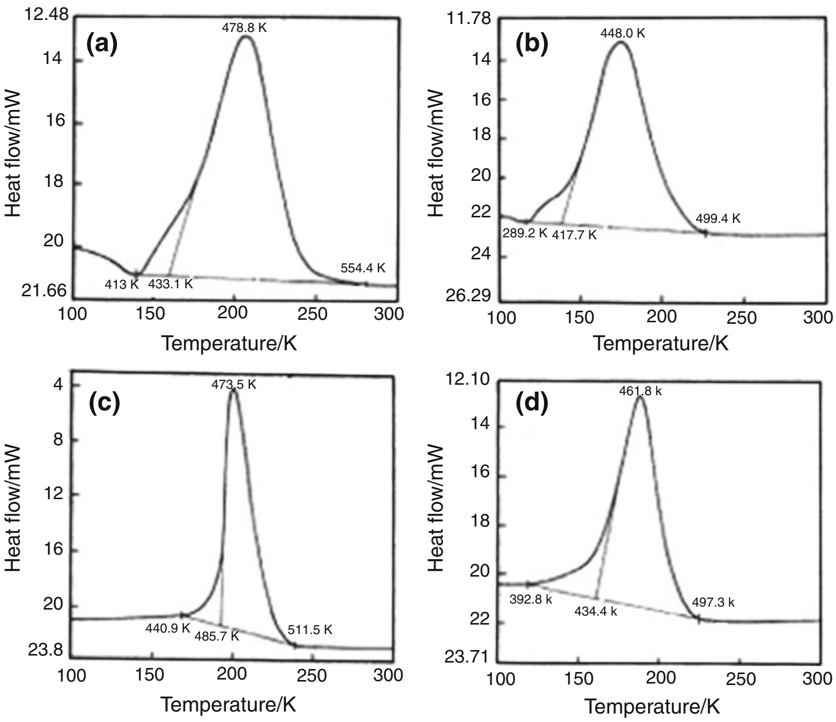

Fig. 1 **a–d** shows DSC scans of epoxy resins (DDB_1, DDB_2, DDB_4 and DDB_5) in the presence of mixtures of biuret and DDS in varying proportions at 10 °C min^{-1}

Table 1 Results of DSC scans of samples at different heating rates

Sample	Molar ratio of DDS:Biuret	Heating Rate/°C min^{-1}	T_i/K	T_{onset}/K	T_p/K	T_f/K	ΔH	E_a/KJ
DDB_1	1:0	5	407.0	423.1	461.3	489.8	476.5	68.3
		10	413.5	433.1	479.0	554.4	472.8	
		15	420.3	444.5	489.9	523.9	479.9	
		20	427.5	451.2	497.9	533.0	473.5	
DDB_2	0.75:0.25	5	378.5	410.6	439.0	546.0	436.5	106.9
		10	389.2	417.7	448.0	499.4	426.6	
		15	394.8	422.1	455.9	509.3	439.1	
		20	399.6	427.3	459.5	518.6	440.7	
DDB_3	0.50:0.50	5	380.1	421.4	440.9	470.6	449.7	127.1
		10	392.8	434.4	461.8	497.3	412.3	
		15	403.4	438.4	466.4	488.9	455.7	
		20	415.0	444.3	469.3	546.0	461.7	
DDB_4	0.25:0.75	5	403.3	428.8	546.6	460.8	406.1	189.4
		10	409.8	437.6	470.9	482.8	407.2	
		15	416.6	444.0	467.9	484.7	417.9	
		20	422.6	447.6	471.8	490.3	424.5	
DDB_5	0:1	5	428.9	456.4	464.3	502.3	388.4	111.9
		10	440.9	465.7	473.4	511.5	379.8	
		15	452.7	474.2	482.5	520.3	384.8	
		20	464.2	484.3	491.4	529.1	383.1	

DSC traces at a programmed heating rate from room temperature up to 300 °C by using nitrogen as the purge gas. The epoxy samples with a mixture of DDS and Biuret have bean designated by adding prefix DDB followed by numerical suffix. For example, epoxy cured using mixture of DDS(D):Biuret(B) in the ratio of 1:0, 0.25:0.75, 0.50:0.50, 0.75:0.25 and 1:0 has been designated as DDB_1, DDB_2, DDB_3, DDB_4, DDB_5.

Thermal stability

Thermal stability of epoxy resin cured isothermally by heating at 200 ± 20 °C for 3 h in air oven in the presence of DDS and Biuret or a mixture of DDS:Biuret in varying molar ratio was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate 60 m^3 min^{-1}) using Rheometric scientific module. A heating rate of 10 °C min^{-1} and samples of 5 ± 2 mg were used in each experiment.

Results and discussion

Curing studies

The curing reaction depends on the nature of the curing agent as well as on the stoichiometry. Figure 1a–d shows the DSC scans of DGEBA with mixtures of biuret and DDS in varying proportions at 10 °C min^{-1}. No exothermic transition was seen in the temperature range of 50–300 °C in the DSC scans of biuret and epoxy alone. In the DSC traces of all the other samples, a broad exothermic transition associated with curing was observed at 105–281 °C. The DSC exotherm was characterized by noting the following temperatures:

T_i = kick-off temperature, where the curing starts.
T_{onset} = temperature where the first detectable heat is released. It was obtained by extrapolation of the steepest portion of curve to the base line.
T_p = temperature of peak position of exotherm.
T_f = temperature of the end of curing exotherm. This was taken as the temperature where the exotherm levels with the base line in the final stage of curve.
ΔH = heat of curing, calculated by measuring the area under the exothermic transition.

The results of DSC scans are summarized in Table 1. The curing temperatures were dependent upon the structure and ratio of the curing agents. Comparing the curing behaviour the following trend of T_i, T_{onset} and T_p was observed as:

$$DDB_1 > DDB_2 < DDB_3 < DDB_4 < DDB_5$$

DDS is generally used as hardener for curing of epoxies. Biuret decomposes at temperature above 200 °C. But it is interesting to note that decomposition was not seen up to nearly 300 °C in all the samples. It may be due to the fact that all the biuret molecules reacted to produce cured network and this led to change in its property. The incorporation of Biuret along with DDS was expected to affect the curing behaviour and the thermal stability of the cured network. Therefore, Biuret and DDS mixtures in varying ratio were used to cure DGEBA. In all the samples, a single curing exotherm was observed, this showed that these two amines are acting as co-curing agent.

Addition of 0.25 mol fraction of Biuret to DDS decreased Ti significantly which further increases with the increase of mole fraction of biuret. In biuret, amine group is directly involved in the delocalization of electron further presence of more electronegative oxygen atom relatively decreases the electron density on the nitrogen atom of

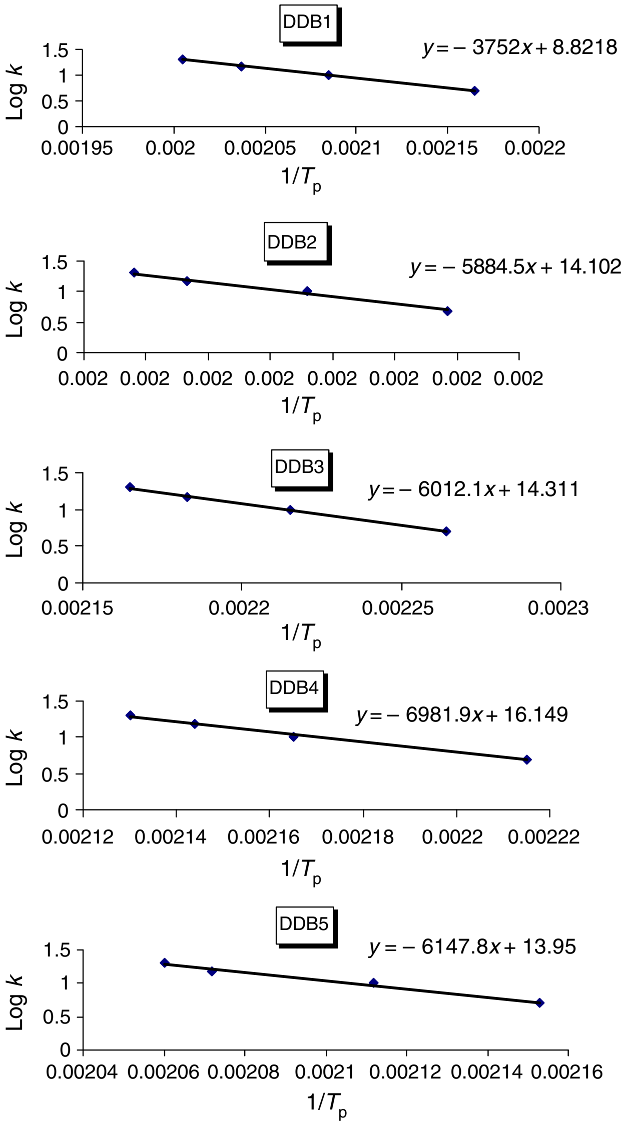

Fig. 2 **a–e** shows plots of log Ø versus $1/T_p$

amine group thereby decreasing its reactivity. The decrease in T_i is difficult to explain, however, it may be due to the reaction of DDS and biuret to form a single product which reacts easily with DGEBA to form cured network. However, when 0.75% of the biuret was used, the 50% of the biuret reacted with DGEBA and the other 50% of the cured product was obtained by the reaction of DGEBA with the product obtained by reaction of remaining 25% of biuret with DDS. Thus, a sudden rise in T_i is obtained when 0.75 and 1% of the biuret was used. This is because biuret alone is a weak nucleophilic agent with respect to DDS.

Curing kinetic

Kinetic parameter of the curing reaction can be obtained from dynamic DSC scans or isothermal experiments.

The dynamic method was used in this study and the DSC scans of samples were recorded at different heating rates. The characteristic curing temperatures for the DGEBA at different heating rates in the presence of Biuret, DDS and mixture of DDS:Biuret are summarized in the Table 1. As expected in all the samples, peak at curing temperature increased with the increasing heating rates. The activation energy of the curing reaction was calculated using Ozawa's method [10] assuming that:

1. The peak exothermic temperature T_p represents a point of constant conversion.
2. The reaction follows the first order kinetics.
3. The temperature dependence of the reaction rate constant obeys Arrhenius equation.

The data from dynamic DSC measurements are analyzed in accordance with the following equation:

$$\mathrm{E_a} = R\Delta \log k / 0.4567\Delta(1/T_\mathrm{p})$$

where $k(\varnothing)$ is the heating rate, E_a is the activation energy, R is the gas constant.

Assuming a constant conversion at the peak exotherm temperature, plots of log k versus $1/T_p$ were obtained and are shown in the Fig. 2. From the slop of these lines, activation energy was calculated for the exotherm and results are shown in Table 1. The activation energy was highest for DDB_4 and lowest for DDB_1.

Thermal stability

Figure 3a–d shows TG/DTG traces of samples; DDB_2, DDB_3 DDB_4 and DDB_5. The relative thermal stability of the cured resins was evaluated by comparing initial decomposition temperature (IDT, where the first detectable heat is released), temperature of maximum rate of mass loss (T_{max}), final decomposition temperature (FDT). The results of TG/DTG scans are summarized in the Table 2. A single step decomposition was observed in all the samples. All the samples were stable up to 330 ± 20 °C and started loosing weight above this temperature. The decomposition temperature was dependent on the structure of the network.

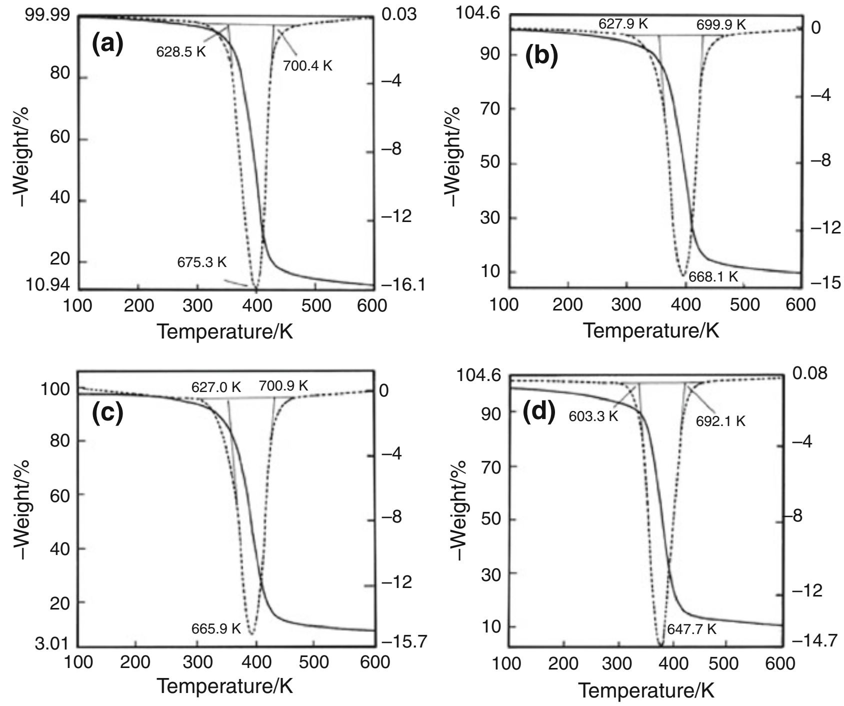

Fig. 3 **a–d** shows TG scans of cured epoxy resins (DDB_2, DDB_3, DDB_4 and DDB_5

Table 2 Results of thermal stability of isothermal cured epoxy resins at 10 °C min^{-1} heating rate

Sample	Mole ratio of Biuret:DDS	IDT/K	T_{max}/K	FDT/K
DDB_1	1:0	667.9	692.9	739.0
DDB_2	0.75:0.25	628.4	675.3	700.4
DDB_3	0.50:0.50	627.4	668.1	699.9
DDB_4	0.25:0.75	627.0	665.9	700.9
DDB_5	0:1	606.2	647.7	692.1

The IDT, FDT and T_{max} were highest in DDB_1 and lowest in DDB_5.

Conclusions

The curing behaviour of epoxy resin depends upon the structure and nucleophilicity of amines. The peak exotherm temperature was highest for DDB_1 and least in DDB_2. The decomposition temperatures were highest in DDB_1 and DDB_2 and lowest in DDB_5.

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