Study on the curing kinetics of epoxy resins using diorganotin dichlorides

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Abstract

Curing kinetics of diglycidyl ether of bisphenol–A (DGEBA) in the presence of Phenylmethyltin dichloride (PMTC), Phenylethyltin dichloride (PETC), butylmethyltin dichloride (BMTC) and dimethyltin dichloride (DMTC) were investigated by the dyanamic differential scanning calorimetery.

Keywords: Diglycidyl ether of bisphenol–A (DGEBA), dichlorides, curing kinetics, thermal stability.

Introduction

Epoxy resins have been used in many industrial applications such as in surface coating, adhesive, structural composites, printed circuit boards and insulating materials for electronic devices because of their good chemical resistance and superior mechanical and electrical properties[1,2]. These resins also possess excellent process ability. However, the conventional epoxy resins are inefficient to satisfy the required properties in the field of advanced materials which require higher thermal and flame resistance [3,4]. Several approaches were used in the past to improve the thermal stability and flame retardance of the epoxy resins. Improvement in the thermal properties of the epoxy resin by the incorporation of polynuclear aromatic structures such as naphthalene, biphenyl, anthracene, pyrene etc [5-7]. or phosphorus containing moieties [8-11] has been reported in literature. Another approach used to develop flame resistant epoxy formulation involves the incorporation of additives having flame-retarding elements such as halogens, boron, silicon, tin, arsenic or antimony compounds or their combinations [12-14]. Apart from the structure of curing agents, properties of epoxy formulations can also be varied to a large extent by the choice of curing conditions. Kinetic characterization of thermoset resins is therefore of great importance in understanding the structure-properties-processing relationship in

order to manufacture high performance materials.

In view of the above, it was thought worthwhile to develop flame resistance epoxy resins and to study the curing and thermal behaviour of epoxy resin (DGEBA) in the presence of different dichlorides containing tin.

Experimental

Materials

Diglycidyl ether of bisphenol–A (DGEBA, Grade LY556 having an epoxy equivalent 177) was procured from Hindustan Ciba Geigy Ltd. Methyl ethyl ketone, $PhSnCl_3$, Et_4Sn, Me_4Sn, Me_3SnCl and $BuSnCl_3$ (Aldrich) have been used as such. $PhMeSnCl_2$, $PhEtSnCl_2$, Me_2SnCl_2 and $BuMeSnCl_2$ have been prepared as reported in literature [15].

Curing Studies

TA 2100 thermal analyzer having a 910 DSC module was used to record DSC scans at a heating rate of 5, 10, 15 and 20 0C/min. For curing studies, samples were obtained by mixing DGEBA with stoichiometric amounts of unsymmetrical diorganotin dichlorides dissolved in methyl ethyl ketone. After thorough mixing, the solvent was removed under vacuum and the freshly prepared samples were used for recording DSC traces in static air atmosphere at a programmed heating rate from room temperature to $300^{\circ}C$. 5 ± 2 mg of samples were used in each experiment. The curing mixtures of DGEBA and diorganotin dichlorides (PMTC, PETC, DMTC and BMTC) have been designated as DPMTC, DPETC, DDMTC and DBMTC respectively.

Thermal Stability

Thermal stability of the resins cured isothermally by heating at $100 \pm 20^{\circ}C$ for 2h in an air oven in the presence of various diorganotin dichlorides was evaluated by recording TG / DTG traces in nitrogen atmosphere (flow rate $60cm^3$/min) using a Rheometric Thermal Analyzer. A heating rate of $10^{\circ}C$ min^{-1} and powdered samples of 10 ± 2 mg were used in each experiment

Results and Discussions

In the DSC scans of all the samples, a broad exothermic transition was observed. The curing 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 the curve

T_p = temperature of peak position of exotherm

T_f = temperature of the end of curing exotherm

ΔH = heat of curing, calculated by measuring area under the exothermic transition

A single exotherm was obtained in all samples. The peak exotherm temperature was higher in the case of DBMTC as compared to sample DPMTC, DPETC and DDMTC. The heat of polymerization was decreased as the heating rate was increased.

All the characteristic curing temperatures i.e. T_i, To, T_p and T_f showed the effect of the dichlorides structure. The following trend was observed in the peak exotherm temperatures: DPMTC < DPETC < DDMTC < DBMTC. The curing characteristics were expected to be dependent upon the electrophilicity of the tin and induction of the alkyl or aryl group bonded to tin in the various dichlorides. The alkyl groups have + ve induction (+ I) where as aryl groups (benzene) have a – ve induction (- I). On the basis of the electrophilicity and induction one would have expected the highest curing temperatures with BMTC.

DGEBA was cured isothermally in the presence of different dichlorides by heating in an air oven (100 $20^{\circ}C$ for 2 h) to determine the glass transition temperature. In the DSC scans of isothermally cured samples, no exothermic transition was seen thereby indicating the complete cross-linking reaction. The glass transition temperature is dependent on the rigidity of polymer backbone as well as on the cross link density. Highest value of Tg was obtained for cured resin DPETC.

Curing Kinetics

Kinetic parameters of the curing reaction can be obtained from dynamic DSC scans of isothermal experiments. The dynamic method was used in

the present study and the DSC scans were recorded at different heating rates for the samples. The characteristic curing temperature for the DGEBA at different heating rates in the presence of different dichlorides are

activation energy was calculated from the slope of the graphs obtained and results are summarized in Table 1.

Activation energy of curing was lowest in case of

Sample Designation	Molar ratio of DGEBA: $R^1R^2SnCl_2$	Heating Rate (^{0}C)/min	T_i (^{0}C)	T_{onset} (^{0}C)	T_p (^{0}C)	T_f (^{0}C)	ΔH (J/g)	Ea (KJ/mol)	Tg (^{0}C)
DPMTC	1:1	5	42.3	48.9	81.1	160.5	93.7	34.6	159.1
		10	47.2	62.4	98.8	173.3	65.2		
		15	57.6	75.6	112.2	177.5	55.1		
		20	72.4	89.7	129.5	185.9	44.8		
DPETC	1:1	5	49.3	60.5	98.8	163.8	94.8	41.7	168.4
		10	51.8	61.9	103.8	184.5	93.8		
		15	61.8	83.5	127.2	189.5	38.8		
		20	63.8	84.4	133.0	194.1	41.8		
DDMTC	1:1	5	42.2	45.9	126.6	168.8	73.3	44.9	124.9
		10	62.2	65.1	139.3	180.4	59.4		
		15	64.6	66.3	157.6	188.8	52.2		
		20	73.1	87.4	171.2	191.1	42.3		
DBMTC	1:1	5	103.1	106.6	130.5	136.5	44.7	46.4	113.6
		10	104.6	116.3	145.9	150.9	42.2		
		15	119.8	131.3	160.1	166.7	23.4		
		20	129.8	132.1	174.6	191.1	22.5		

summarized in Table 1.

The activation energy of the curing reaction was calculated using Ozawa's method [16-17] assuming that:

1. The peak exothermic temperature (Tp) 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:

$$ Ea = \frac{R \Delta \log K}{0.4567 \Delta (1/T_p)} $$

Where K is the heating rate, Ea the activation energy, R the gas constant. Assuming a constant conversion at the peak exotherm temperature, plots of log K vs. 1/Tp were obtained for all the resin samples and are shown in Fig. 3. The

(DPMTC) and was highest in case of (DBMTC). Thus the activation energy of curing showed the following trends in the presence of various diorganotin dichlorides.

DBMTC >DDMTC>DPETC >DPMTC

Thermal Stability

The relative thermal stability of the cured resins was evaluated by comparing initial decomposition temperature (IDT), temperature of maximum rate of mass loss (Tmax), final decomposition temperature (FDT) and per cent char yield at 800°C. The results are summarized in Table 2. All the samples were stable up to 235°C. A single step degradation was observed in all the samples. The char yield was lowest in case of resin cured with DMTC and highest in case of resin cured with PETC. Thus the following trend was observed in char yield of the cured resins:

DPETC>DPMTC> DBMTC>DDMTC

Char yield can be used as a criteria for evaluating limiting oxygen index (LOI) of the resins in accordance with Van Krevelen and Hoftyzer equation [18].

Table 2: Results of thermal stability of isothermal cured epoxy resins

(DGEBA: R1R2SnCl2) at 100C heating rate in nitrogen atmosphere

Sample Designation	IDT (^{0}C)	T_{max} (^{0}C)	FDT (^{0}C)	Char yield at 800^{0}C	LOI (%)
DDMTC	239.1	266.8	276.6	27.8	28.6
DBMTC	242.2	279.1	291.5	28.9	29.06
DPMTC	246.8	293.5	318.2	30.1	29.5
DPETC	263.4	306.3	333.7	32.3	30.4

$$LOI = 17.5 + 0.4 \, CR$$

Where CR = char yield

All the samples had LOI values calculated based on their char yield higher than 28. These results thus clearly showed that flame resistant DGEBA resin can be obtained by using curing agents having a combination of tin and chlorine as flame retarding elements.

Conclusions

Thermal stability of the cured resin was found to be dependant on the structure of the network. Curing agents having Sn and Cl elements showed the effect of structure on the curing kinetics as well as on the thermal stability and have increased the flame retardancy of the epoxy resins.

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