



Effect of Triphenylphosphine on the Cure Reaction and Thermal Stability of Diglycidyl Ether of Bisphenol A-based Epoxy Resin

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ABSTRACT

A sulphone-nitrogen containing heterocyclic ring, tetraphenylthiophene diamine (TPTDA) was prepared and used as curing agent together with triphenylphosphine (PPh_3) to cure diglycidyl ether of a bisphenol A-based epoxy resin (DGEBA). Activation energies (E_a) for curing DGEBA/TPTDA and DGEBA/TPTDA/ PPh_3 systems by using DSC data and Kissinger equation are 66.6 kJ/mol and 76.6 kJ/mol, respectively. The increase in E_a can be due to polymerization of DGEBA by PPh_3 and formation of larger molecules with reduced mobility before curing with TPTDA to start. E_a of thermal degradation of cured DGEBA/TPTDA and DGEBA/TPTDA/ PPh_3 systems by using TGA data and Horowitz-Metzger equation are 56.0 kJ/mol and 128.0 kJ/mol, respectively. The onset decomposition temperature and the char yield have increased from 230°C to 320°C and from 21.4% to 32.5% for the above systems, respectively. The addition of PPh_3 to the curing mixture enhanced char formation and improved thermal stability of the resin.

Key Words:

epoxy resin;
thermal degradation;
kinetics;
thermal stability;
TGA.

INTRODUCTION

Most cured epoxy resins provide amorphous thermosets with unique combination of properties generally not found in any other plastic material. These superior performance characteristics, coupled with outstanding formulating versatility and reasonable costs, have gained epoxy resins wide acceptance as

materials of choice for growing applications [1]. However, flammability of these resins is a major limitation in areas requiring high flame resistance. There exist two approaches to achieve flame retardancy in polymers generally known as the 'additive' type and the 'reactive' type. Additive type flame

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retardants, which are widely used, are generally incorporated into polymeric materials by physical means. This obviously provides the most economical and expeditious way of promoting flame retardancy for commercial polymers [2]. Halogen-containing monomers such as diglycidyl ether of tetrabromobisphenol-A have been used along with diglycidyl ether of bisphenol-A for imparting flame retardancy to commercial laminates. Under the effects of fire or smoldering they produce a very dense smoke and toxic decomposition products. In addition to these problems, the mechanical properties and thermal stability of these resins are inferior to the corresponding monomers without halogens [3-5].

A growing demand to avoid the generation of such toxic and corrosive gases during thermal degradation has led to the development of non-halogen containing flame retardant polymers. Recently, the polymers or reactive monomers that are inherently flamed retarding contain P in several oxidation states [6-9], Si [10-15], B [16], carboranes [17], N [18], oxazene [19], cyanate esters [20] and other miscellaneous elements [21-22] have been reported. The advantage of phosphorus-containing compounds for imparting flame retardancy to epoxy resins is their high efficiency at low concentrations [3]. Phosphorus-containing fire retardant additives such as triphenylphosphine or phosphate, phosphorus- and halogen-containing tris(2,3-dibromopropyl) phosphate and tris(2,3-dichloropropyl) phosphate, and also epoxy monomers and hardeners containing phosphorus are commonly used to increase thermal stability of epoxy resins [23-30]. A predominantly condensed-phase mechanism was considered for these additives [24,25]. On the basis of the selective action of phosphorus in oxygen-containing polymers, it was speculated that phosphorus may work by promoting dehydration reactions in polymers containing oxygen in the backbone.

In this study, we report the kinetics of cure reaction of epoxy resin DGEBA with tetraphenylthiophene diamine (TPTDA) and its combination with triphenylphosphine (PPh_3) by using DSC and FTIR. Kinetics of thermal degradation of cured samples of DGEBA/TPTDA and DGEBA/TPTDA/ PPh_3 systems have also been studied by using TGA. In the literature survey, we have not found any reports on curing DGEBA with TPTDA and its combination with PPh_3

and neither the thermal degradation of these systems.

EXPERIMENTAL

Materials

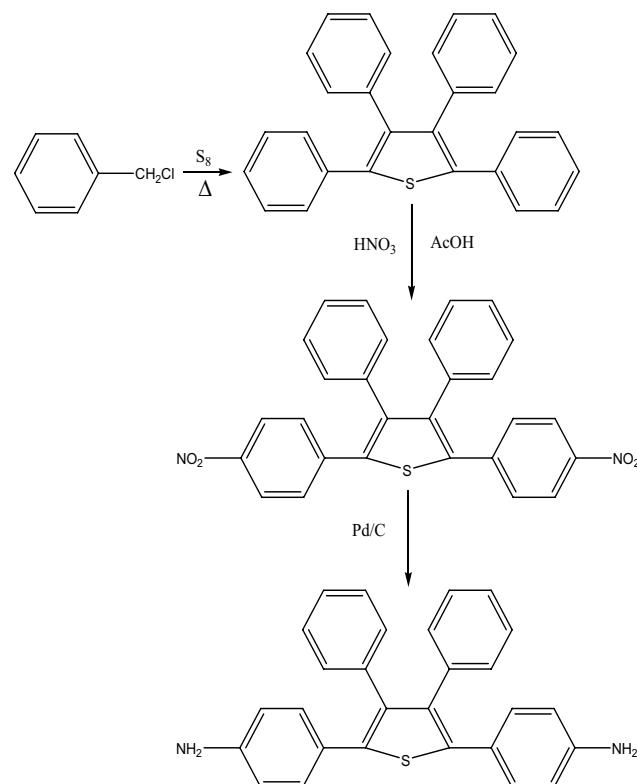
Diglycidyl ether of a bisphenol A-based epoxy (DGEBA), average $M_n \sim 377$, epoxide equivalent 188.5, clear liquid, viscosity (at 25°C) 100-150 poise, density 1.16 g/mL (at 25°C) provided from Sigma-Aldrich Co. All other chemicals were purchased either from Merck or Fluka Co. and used without further purification.

Monomer Synthesis

A three-step reported strategy was used for the preparation of TPTDA [31]. The reaction states and conditions are given in Scheme I.

Synthesis of Tetraphenylthiophene (TPT)

Into a 250-mL three-necked kettle equipped with a mechanical stirrer, an efficient reflux condenser, and a thermometer, a mixture of 63.3 g (0.5 mol) of benzyl



Scheme I. Synthetic routes for preparation of TPTDA.

chloride and 0.9 g (0.3 mol) of powdered sulphur was added. The content was heated at 180–200°C for 72 h with stirring. The reaction temperature was then raised to approximately 230°C, and was maintained at that temperature for 3 h. The mixture was allowed to cool to 60°C, and 50 mL of ethanol was added. The solidified bitumen-like material was filtered, washed with methanol, and then thoroughly washed with acetone. The obtained crude product was a pink-colour solid, which was recrystallized from dichloromethane-methanol mixture (1:1 v/v) to give pure TPT as white needles; mp 183–185°C. The yield was 37 g (76%). IR (KBr) 3054, 1600, 1492, 1437, 1077, 1030, 764, and 700 cm⁻¹.

Synthesis of 2,5-bis(4-nitrophenyl)-3,4-diphenylthiophene (TPTDN)

Ten grams (25.8 mmol) of TPT and 200 mL of glacial acetic acid were placed in a 500 mL two-necked flask equipped with a magnetic stirrer and a condenser. The mixture was vigorously stirred at 100°C to obtain a suspension. A mixture of glacial acetic acid (20 mL) and concentrated nitric acid (14.5 mL) was added dropwise over a period of 1 h. After stirring at 100°C for an additional 0.5 h, a clear yellow solution was obtained. The solution was allowed to cool to yield a yellow crystalline product. The product was recrystallized from glacial acetic acid to afford bright yellow needles; mp 213–215°C. The yield was 7.8 g (63%). IR (KBr) 3061, 1591, 1515, 1346, 1115, 853, and 700 cm⁻¹.

Synthesis of Tetraphenylthiophene Diamine (TPTDA)

Into a 250-mL round-bottom flask equipped with a reflux condenser and dropping funnel, 2.62 g (5.5 mmol) TPTDN, 48 mL dioxane, 24 mL ethanol and 0.1 g of Pd/C were added and heated for 2 h. Then a solution of 8 mL hydrazine hydrate 85% in 20 mL ethanol was added dropwise in 5 h. The reaction was refluxed for 20 h and the hot solution was filtered. The precipitate was formed during cooling the filtrate which was filtered and washed with methanol. The obtained crude product was recrystallized from dichloromethane-methanol mixture (1:1 v/v) to give pure TPTDA as white needles; mp 270–273°C. The yield was 2.29 g (80%). IR (KBr) 3423, 3338, 1631, 1508, 1292, 1185, 831, 708, and 531 cm⁻¹.

Sample Mixing

The stoichiometric amount of TPTDA (52.25 phr) was dissolved in DGEBA by stirring at room temperature. When TPTDA was used together with PPh₃, TPTDA was dissolved in DGEBA first. PPh₃ was then mixed thoroughly in DGEBA/TPTDA system by vigorous stirring for sufficient time (about 10 min) to give a homogeneous viscous mixture. The mixture was kept in an aluminium dish and stored in a refrigerator to be used later for DSC tests and sample preparation.

DSC Analysis

A Mettler Toledo differential scanning calorimeter (DSC822^e) was used for recording thermograms of cure reaction. 5–6 mg of the uniform viscous mixture was put into a DSC sample pan and covered with an aluminium lid and closed tightly under pressure. The sample pan was placed in the DSC sample cell at ambient temperature and an empty pan was also placed in the DSC reference cell, and it was heated according to the programme of a constant heating rate from room temperature to 300°C. The heating rates were 5, 10, 15, and 20°C/min under nitrogen atmosphere.

TGA Analysis

The thermal decomposition of the cured epoxy systems was carried out at heating rate of 10°C/min under N₂ atmosphere (20 cm³/min) employing a Du Pont Instruments TGA 951 analyzer. The cured samples were prepared by pouring the uniform viscous mixture into an aluminium cell and heating in an oven using programme schedule: at 100°C for 2 h; 130°C for 1 h; and 160°C post cure for 0.5 h. The cured sample was cut into small discs with a certain weight for tests and put into an aluminium cell, placed on detector places and the furnace then heated to 750°C at a heating rate of 10°C/min.

FTIR Analysis

A Bruker Vector 22 FTIR was used for the characterization of curing agent and also for recording the curing process. The uniform viscous mixture was cured (between two KBR plates) in an oven at a constant temperature (170°C) for various durations and the partially cured samples were scanned by FTIR

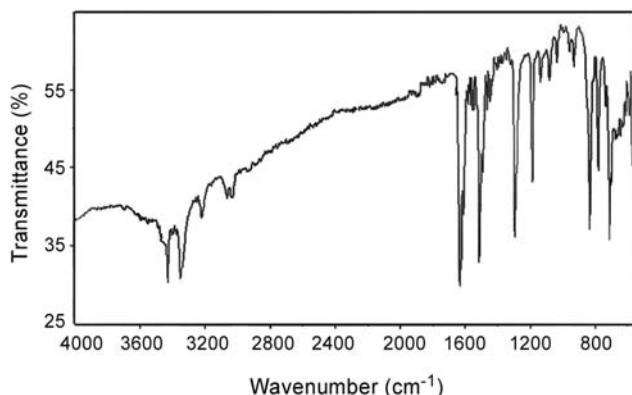


Figure 1. FTIR spectrum of TPTDA.

spectroscopy from 4000 to 700 cm⁻¹. The characteristic band for epoxide group at 916 cm⁻¹ was recorded.

RESULTS AND DISCUSSION

TPTDA was prepared according to reported procedures [31] and used as curing agent. FTIR spectrum in Figure 1 shows the characteristic peaks at 3423–3338 cm⁻¹ (related to N-H stretching) and at 1631–1508 cm⁻¹ (related to C=C aromatic rings). The prepared TPTDA with a melting range of 270–273°C is soluble in DGEBA at room temperature. Figures 2 and 3 display the FTIR absorption spectra obtained before (uncured) and after heat treatment of DGEBA/TPTDA and DGEBA/TPTDA/PPh₃ systems, respectively. A comparison of these spectra reveals that upon curing at 170°C the stretching vibration band of the epoxy ring at 916 cm⁻¹

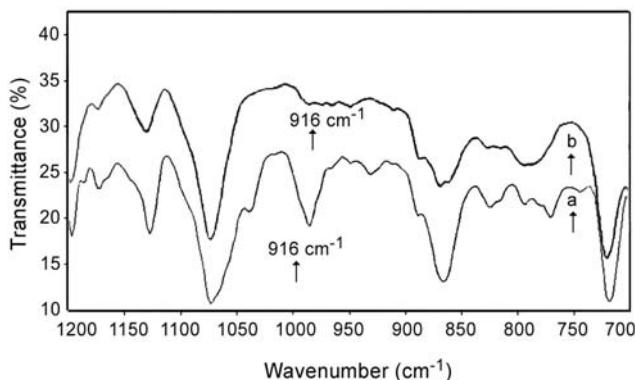


Figure 2. FTIR spectra of DGEBA/TPTDA system: (a) before curing, and (b) after curing at 170°C for 55 min.

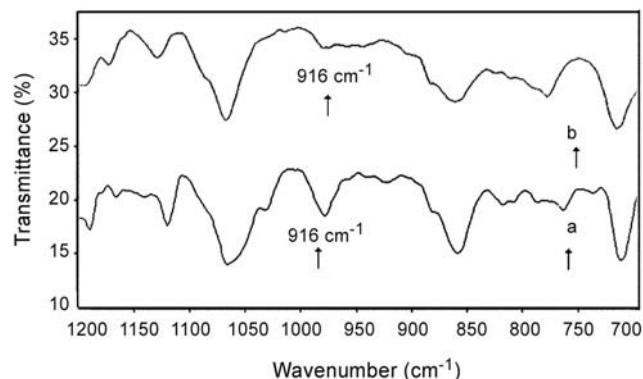


Figure 3. FTIR spectra of DGEBA/TPTDA/PPh₃ system: (a) before curing, and (b) after curing at 170°C for 65 min.

decreases in intensity and shifts downward.

The curing rate of epoxy resin depends on the structure and reactivity of the curing agent. The onset of the curing exotherm depends on the nucleophilicity of the amino group. Aromatic amines containing electron donor substituents start curing the epoxy resin at lower temperatures. The chemical structure of the amine is not the only factor; steric restrictions to the epoxy-amine addition reaction, physical interactions among different functional groups of the constituent components, and the cure extension can also influence the cure kinetics.

Figure 4 shows dynamic DSC curves for DGEBA cured with stoichiometric amount of TPTDA at four different heating rates. All the curves show only one

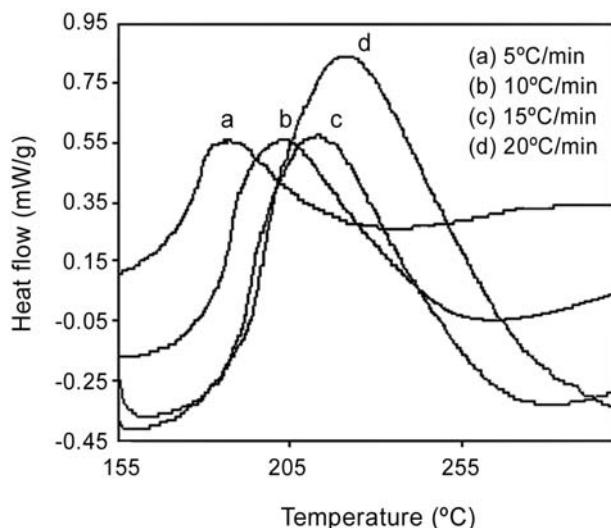


Figure 4. Typical dynamic DSC thermograms of DGEBA/TPTDA.

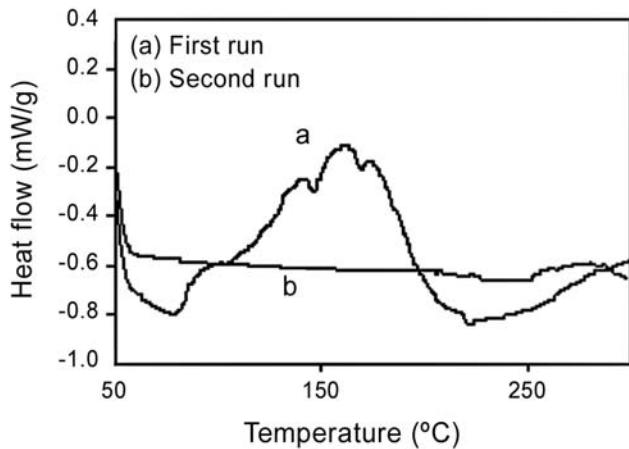
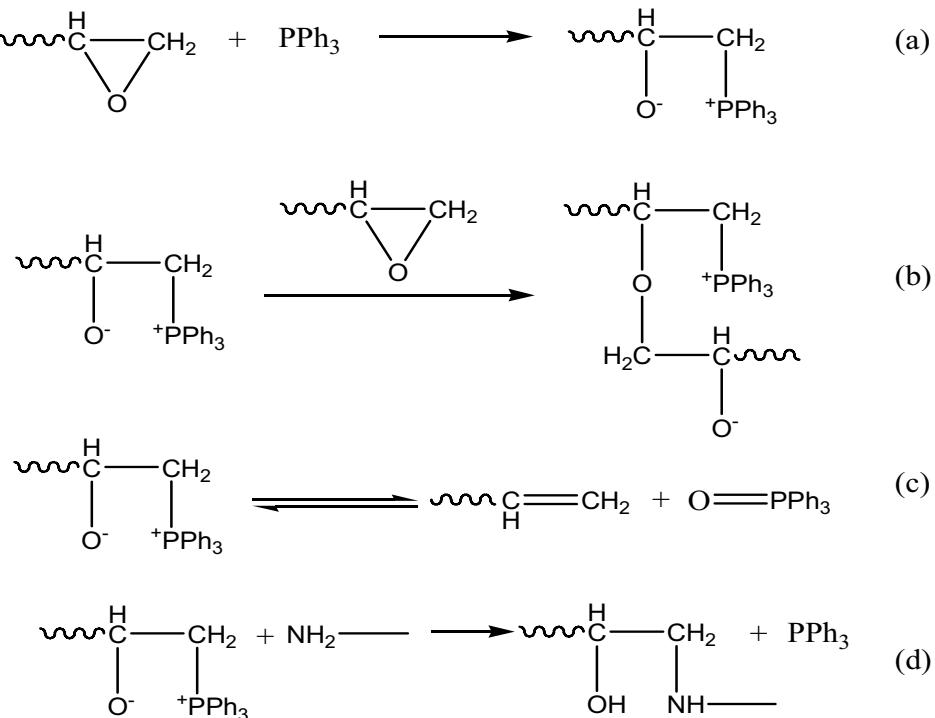


Figure 5. Typical dynamic DSC thermograms of DGEBA/PPh₃.

exothermic peak regardless of the heating rate. The exothermic peaks (T_p) depending on the heating rate became larger and also shifted towards higher temperatures (from 170°C to 220°C) as heating rate increased. Figure 5 shows dynamic DSC thermograms for the reaction of DGEBA with PPh₃ at the heating rate of 10°C/min. The exothermic peak during the first scan shows that PPh₃ is capable to react with DGEBA and T_p appears at 150°C. The mechanism of

curing of DGEBA with PPh₃ should be ionic through coordination by the lone pair electron of phosphorus with less restricted carbon of epoxide groups [1]. The mechanism of formation of oxy anion next to the positive phosphorus is carried out through ring opening reaction of epoxide groups by the nucleophilic attack of triphenylphosphine, producing a betaine which decomposes into a terminal olefin and triphenylphosphine oxide (Scheme IIa-c). It can also be suggested that electrophilic carbon next to the positive phosphorus reacts with the amine groups at the higher temperatures and generating the PPh₃ catalyst (Scheme IId).

Figure 6 shows dynamic DSC curves for DGEBA cured with stoichiometric amount of TPTDA in the presence of 25% of PPh₃ at four different heating rates. DSC thermograms in Figure 6 show two different size exothermic peaks; a small shoulder peak in the temperature range of 150-162°C related to the polymerization reaction of DGEBA with PPh₃, as shown in Figure 5, and a large one in the temperature range of 195-226°C due to the cure reaction of DGEBA with the amine group of TPTDA, as shown in Figure 4. The presence of the large exothermic peak related to the cure reaction of DGEBA with TPTDA indicates that polymerization reaction of DGEBA



Scheme II. Mechanism of epoxide group reaction with PPh₃.

Table 1. DSC data for curing of DGEBA with TPTDA and TPTDA/PPh₃.

Curing system	β (°C/min)	T _i (K)	T _p (K)	1/T _p × 10 ³ (K ⁻¹)	Lnβ	-ln(β/T _p ²)
DGEBA/TPTDA	5	448.80	460.18	2.17	1.60	10.65
	10	453.30	475.05	2.10	2.30	10.02
	15	457.30	486.26	2.05	2.70	9.66
	20	459.03	495.55	2.01	2.99	9.41
DGEBA/TPTDA/PPh ₃	5	450.70	467.21	2.14	1.60	10.68
	10	469.65	480.76	2.08	2.30	10.04
	15	472.16	490.65	2.03	2.70	9.68
	20	477.24	499.14	2.00	2.99	9.43

with PPh₃ was not accomplished. The amine groups of TPTDA are more reactive towards the epoxide groups and a large exothermic peak around 200°C shows extensive network formation. Table 1 lists all the data obtained from the exothermic peak of curing DGEBA with TPTDA. The exothermic transition was characterized by noting the following parameters: T_{onset} (the exotherm onset temperature, obtained by the extrapolation of steepest portion of the initial side of the exotherm) and T_p (the peak position temperature of the exotherm). The exothermic peaks were

attributed to the generation of heat during the cure reaction. DSC method assumes that for a cure process the measured heat flow (dH/dt) is proportional to the conversion rate, dα/dt. This assumption is valid for materials with a single reaction and no other enthalpic events, such as the evaporation of the solvent or volatilization of components, enthalpy relaxation, or significant changes in heat capacity with conversion.

Two multiple-heating rate methods that have been shown to be effective and used in the previous publications [32-36] are Kissinger and Ozawa-Flynn-Wall eqns (1) and (2), respectively:

$$\ln(\beta_i / T_{p,i}^2) = \ln(AR / E_a) - E_a / RT_{p,i} \quad (1)$$

$$\ln(\hat{\alpha}_i) = \text{const.} - 1.052E_a / RT_p \quad (2)$$

where β_i is the heating rate, T_{p,i} is the peak temperature at different heating rates, E_a is the activation

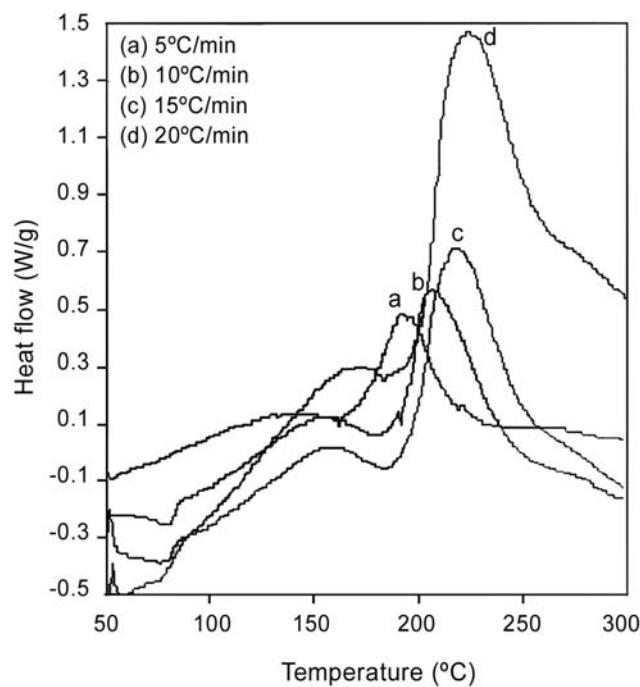


Figure 6. Typical dynamic DSC thermograms of DGEBA/TPTDA/PPh₃.

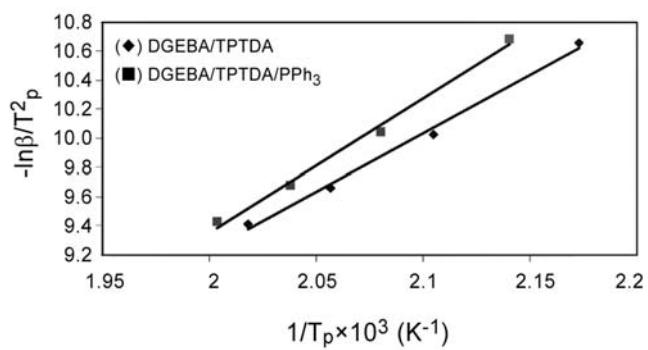


Figure 7. Kissinger plots for the curing of DGEBA/TPTDA/PPh₃ system.

Table 2. Kinetic parameters of curing DGEBA resin with TPTDA and TPTDA/PPh₃.

Curing systems	E _a (kJ/mol) ^a	E _a (kJ/mol) ^b	A (s ⁻¹)	k (s ⁻¹) ^c
DGEBA/TPTDA	66.6	70.8	7.103×10 ⁶	0.40
DGEBA/TPTDA/PPh ₃	76.6	80.4	7.96×10 ⁷	0.37

(^a) Kissinger's method; (^b) Ozawa's method; (^c) Arrhenius rate constant at 480 K.

energy, and A is the frequency factor.

The dynamic DSC data in Table 1, the temperature at which the instant conversion rate was maximum (T_p) and the heating rate (β) were used for calculation of kinetic parameters by using Kissinger, eqn (1), and Ozawa-Flynn-Wall, eqn (2).

The data of the fifth and seventh columns, in Table 1, are introduced to the Kissinger equation and $-\ln(\beta/T_p^2)$ versus $(1/T_p) \times 1000$ is plotted in Figure 7. The E_a values were calculated from the slope of linear plots and the pre-exponential factors from the y intercept, and these values are listed in Table 2.

The data of fifth and sixth columns in Table 1 were also introduced into the Ozawa-Flynn-Wall equation and plot of $\ln(\beta)$ versus $(1/T_p) \times 1000$ gave straight lines, as shown in Figure 8, with a slope of 1.052 E_a/R. The calculated values of E_a are given in Table 2.

The E_a values for DGEBA/TPTDA/PPh₃ system as shown in Table 2 are higher than those obtained for DGEBA/TPTDA system. The increase of E_a in the cure reaction of DGEBA with TPTDA can be due to the fact that reaction between DGEBA with PPh₃ produces higher molecular weight oligomers with reduced molecular mobility. This makes the next

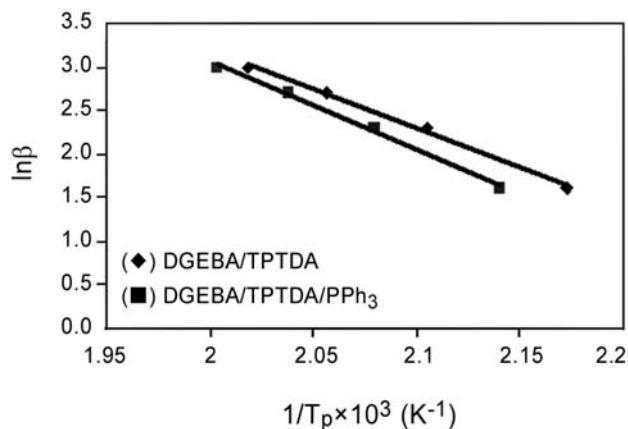


Figure 8. Ozawa plots for the curing of DGEBA/TPTDA/PPh₃ system.

reaction which is between epoxide and amine functional groups more difficult. To compare the cure rate for the two systems, A and E_a values were introduced to the following Arrhenius equation to calculate rate constants at a selected temperature:

$$k = A \exp(-E_a / RT) \quad (3)$$

where k is the rate constant, and T is a selected temperature (480 K). The calculated rate constants for the two systems are shown in Table 2. This also shows that the rate of cure reaction of DGEBA with TPTDA in the presence of PPh₃ decreases to some extent.

TGA traces of the cured epoxy samples provide their thermal stability and thermal degradation behaviours. Figure 9 shows TGA curves of the cured DGEBA/TPTDA and DGEBA/TPTDA/PPh₃ systems under nitrogen atmosphere. The relative thermal stability of the cured samples was compared by noting the initial decomposition temperature (IDT), the final decomposition temperature (FDT), the temperature of maximum rate of weight loss (T_{max}), and the percent of char yield (Ch. Y.). The results are summarized in

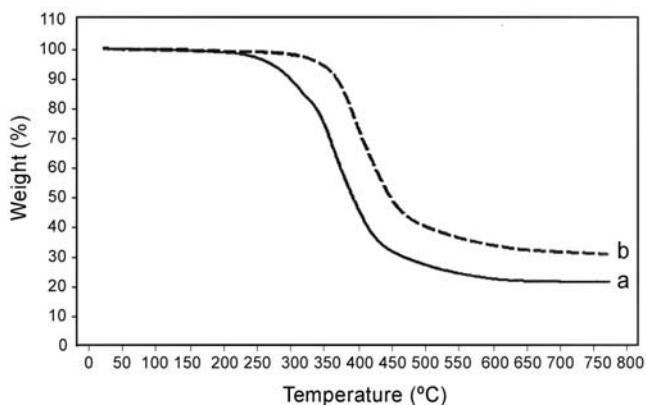


Figure 9. TGA thermograms for the cured samples of: (a) DGEBA/TPTDA and (b) DGEBA/TPTDA/PPh₃ under nitrogen atmosphere.

Table 3. Thermal degradation data.

Cured systems	IDT ^a (°C)	T ^b (°C)	T ^c (°C)	FDT ^d (°C)	T _{max} ^e (°C)	E _a (kJ/mol)	Ch.Y. (%) ^f at 700°C
DGEBA/TPTDA	230	282	300	600	360	56.0	21.4
DGEBA/TPTDA/PPh ₃	320	370	386	700	420	128.0	32.5

(a) IDT, initial decomposition temperature; (b) T, temperature for 5% weight loss; (c) T, temperature for 10% weight loss;

(d) FDT, final decomposition temperature; (e) T_{max}, temperature of maximum weight loss; (f) Ch. Y.% percentage of char yield.

Table 3. IDT for the cured sample of DGEBA/TPTDA is about 230°C and increased to about 320°C when sample contained 25% of PPh₃. IDT indicates the apparent thermal stability of the epoxy resins, i.e., the failure temperatures of the resins in processing and moulding. In TGA thermogram of DGEBA/TPTDA/PPh₃ cured system, no changes in mass were recorded up to 320°C. This result, which agrees with the fact that there was no notable mass loss in the thermogravimetric investigation before 320°C, reveals that the resin is thermally stable below 320°C. About 70% of weight is lost in a temperature interval of 250-400°C for the cured sample of DGEBA/TPTDA system and for the cured sample of DGEBA/TPTDA/PPh₃ system, about 50% of weight is lost in the temperature interval of 320-430°C and 20% of weight is lost in a wider temperature range of 420-600°C. Also, thermostable solid residue or char yield is 21.4% and 32.5% for DGEBA/TPTDA and DGEBA/TPTDA/PPh₃ systems, respectively. Similar and higher percentage of char yields were also reported by other researchers [2,3,27,29,30] for thermal degradation of epoxide resins containing phosphorus fire retardants.

Thermal decomposition of cured epoxy resin proceeds in two or more steps depending on the structure. Evolution of water is believed to take place in the first step (~300°C). Acetone, carbon dioxide, hydrogen cyanide, aliphatic hydrocarbons, etc., are evolved at higher temperatures. The thermal decomposition of secondary alcohol groups (generated during curing) with elimination of water (dehydration) is the first step of degradation of the epoxy network, which precedes chain scission. Dehydration is the source of water that is the major gas evolved on heating epoxy formulations [27]. In fact, a decrease in the alcohol functionalities was detected by FTIR in the first step

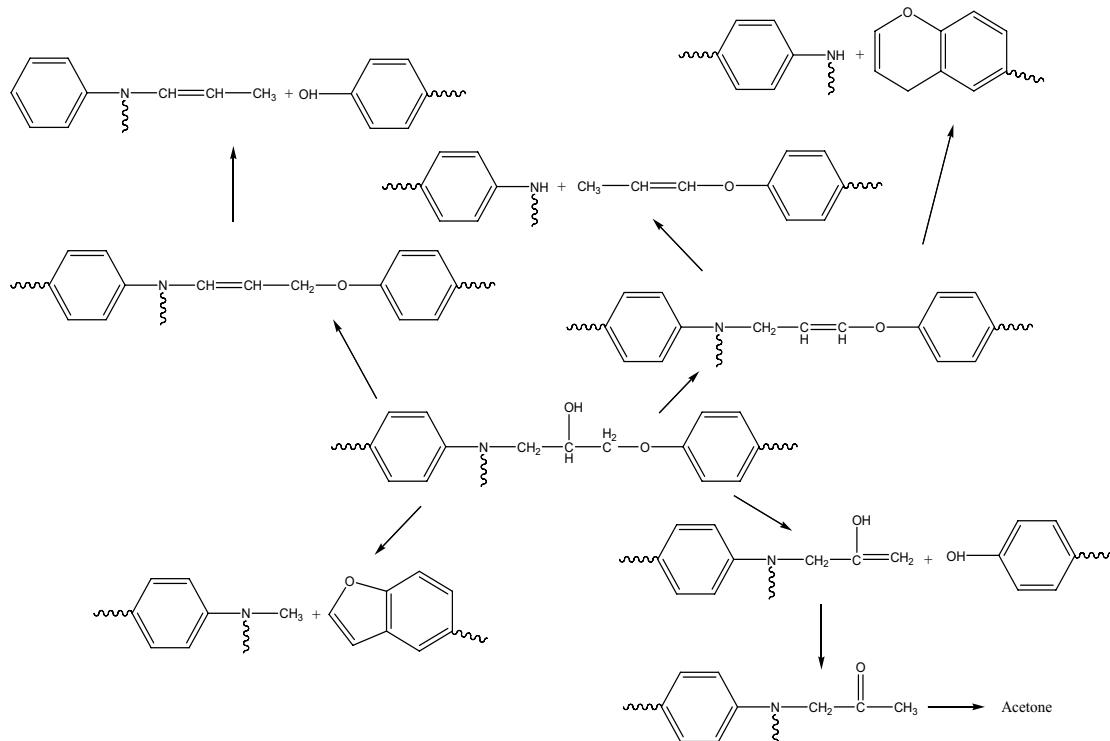
of thermal decomposition of both the flame-retarded and non-flame retarded formulations; further decomposition of the material depends on the nature of the dehydrated structure. The presence of such unsaturations was indicated by the appearance of a 1650 cm⁻¹ band in the IR spectra [37, 38]. The unsaturations weaken the aliphatic C-O or C-N bonds in the b position. It is estimated that the energy of allylic bonds is 290 and 270 kJ/mol, respectively, which is lower than the energy of other bonds in the cured epoxy network. Phenolic chain ends are formed by thermal decomposition of the weakened C-O bonds, whereas secondary amine terminal functions result from the scission of the C-N bonds. Cyclic chain-end structures may also be formed simultaneously, and such cyclization reactions should be favoured because of the reduced mobility of macroradicals in the solid matrix. A more complex process has been suggested for DGEBA units. It involves simultaneous dehydration and C-C bond scission, leading to benzofuran instead of benzopyran chain ends. Organic products such as acetone are also formed if scission of C-O and/or C-N bonds occurs before dehydration of secondary alcohols (Scheme III) [27].

The char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the cured resin without phosphorus element in accordance with Van Krevelen and Hoflyzer, eqn (4) [39], or with the eqn (5) [3] which was suggested for the cured resin with phosphorus containing curing agent:

$$LOI = 17.5 + 0.4 \text{ Ch.Y.} \quad (4)$$

$$LOI = 1.0118 \text{ Ch.Y.} - 6.3467 \quad (5)$$

where Ch.Y. is char yield. The calculated values of the LOI according to the above equations are given in



Scheme III. Representative scheme for thermal decomposition of epoxy resins [27].

Table 4. Sample of DGEBA/TPTDA/ PPh_3 has a value of 30.5 for LOI which is higher than 28.0. On the basis of LOI values, this material can be classified as self-extinguishing resin.

Calculation of E_a for decomposition of the cured epoxy resin can be carried out from the data of TGA curves, through the integral method based on the Horowitz-Metzger equation [40]:

$$\ln[\ln(1-\alpha)^{-1}] = E_a \theta / RT^2_{\max} \quad (6)$$

where α is the decomposition ratio, θ is the difference between T and T_{\max} , T_{\max} is the temperature of maximum rate weight loss, and R is the ideal gas constant. E_a is given by the straight line corresponding to the

Table 4. LOI values for the cured epoxy resin.

Cured systems	LOI	
	eqn (7)	eqn (8)
DGEBA/TPTDA	26.0	15.3
DGEBA/TPTDA/ PPh_3	30.5	26.5

plot of $\ln[\ln(1-\alpha)^{-1}]$ versus θ . The plots of $\ln[\ln(1-\alpha)^{-1}]$ vs. θ are shown in Figure 10. The E_a values of both systems were calculated from the slope of the straight lines and the values are listed in Table 3. The E_a values of thermal degradation of DGEBA/TPTDA and DGEBA/TPTDA/ PPh_3 systems under nitrogen atmosphere are 56 and 128 kJ/mol, respectively. The higher value of E_a indicates the higher thermal stability of DGEBA/TPTDA/ PPh_3 system which can be attributed to the formation of stable and higher char

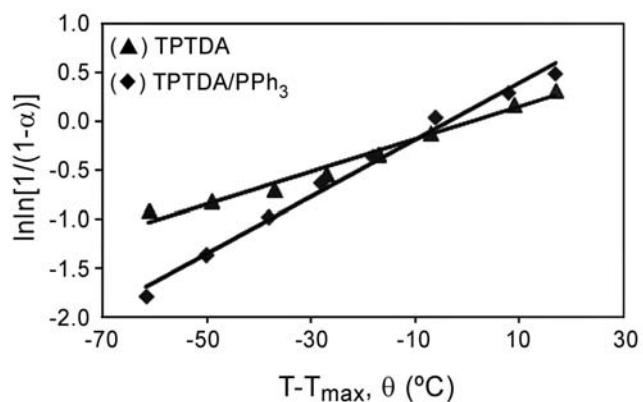


Figure 10. Plots of eqn (5), $\ln[\ln(1-\alpha)^{-1}]$ vs. θ , for DGEBA/TPTDA and DGEBA/TPTDA/ PPh_3 systems.

yield. As shown in Table 3, the char yields at 700°C increased from 21.4% to 32.5% with the addition of PPh₃ to the curing mixture of DGEBA/TPTDA system. The relative high char yield of DGEBA/TPTDA/PPh₃ system can be attributed to the presence of phosphorus.

CONCLUSION

An aromatic diamine curing agent, sulphone-nitrogen containing heterocyclic compound, was prepared and used together with triphenylphosphine (PPh₃) to cure DGEBA resin. The presence of PPh₃ in the curing mixture influenced the curing condition of DGEBA with TPTDA by increasing E_a from 66.6 kJ/mol to 76.6 kJ/mol. This increase was suggested to be due to initial polymerization of DGEBA with PPh₃ and formation of larger molecules which restrict the molecular mobility. The presence of PPh₃ in the cured sample of DGEBA/TPTDA system induced significant effect on the thermal stability of the product: the E_a value of thermal degradation of the cured sample increased from 56 kJ/mol to 128 kJ/mol; the IDT increased from 230°C to 320°C and the char yield increased from 21.4% to 32.5%. This improvement is as a result of the formation of stable and higher amount of solid residue in thermal degradation of DGEBA/TPTDA/PPh₃ system in comparison with DGEBA/TPTDA system.

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