STUDIES ON PHOSPHORUS CONTAINING AMINE HARDENERS FOR EPOXY RESINS

by

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CERTIFICATE

This is to certify that the thesis entitled "**STUDIES ON PHOSPHORUS CONTAINING AMINE HARDENERS FOR EPOXY RESINS**" being submitted by **Ms. Preeti Jain** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Ms. Preeti Jain has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

This work has not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ABSTRACT

Polymer matrix composites have been successfully used in a wide range of applications spanning from electronic products such as printed circuit boards to advanced aerospace structures and reusable launch vehicles. Many thermoset resins have been synthesised to meet the demands of defence, aerospace and electronic industries. Epoxy resins particularly, diglycidyl ether of bisphenol-A (DGEBA) is one of the most commonly used matrix resin in structural applications such as laminates and composites. This is primarily due to its fluidity, low shrinkage during cure and ease of processing. The cured resins have good mechanical properties (i.e. ultimate tensile strength, modulus, elongation at break, toughness and fatigue resistance), low moisture absorption and excellent resistance to solvents and chemicals. Their main limitation is relatively poor thermal stability and flame resistance.

Phosphorus containing compounds have been used in the past to increase the flame resistance of polymeric materials. Synergistic combination of phosphorus and nitrogen is reported to lead to a significant improvement in flame resistance. Therefore, it was considered of interest to study the effect of incorporation of phosphorus in cured epoxy network on flame retardancy and mechanical properties. The present thesis deals with the curing of DGEBA with phosphine oxide containing aromatic amines of varying structure (molecular mass in the range of 246-2622 g/mol) and phosphorus content.

The amines synthesized in the laboratory by reduction of corresponding nitro compound using Pd/C (10%) and hydrazine hydrate as reducing agent and ethanol as a solvent, include bis(3-aminophenyl)methyl phosphine oxide (B), tris(3-aminophenyl)phosphine oxide (T), amide amines i.e. bis[3(3'-aminobenzamido phenyl)]methyl phosphine oxide (MB), bis[3(4'-aminobenzamido phenyl)]methyl

phosphine oxide (PB), tris[3(3'-aminobenzamido phenyl)] phosphine oxide (MT) and tris[3(4'-aminobenzamido phenyl)] phosphine oxide (PT). Amide-acid amines were prepared by reacting amine B or T with 1,2,4,5-benzenetetracarboxylic acid anhydride (P) / 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (Z) / 4,4'-(hexafluoroisopropylidene)diphthalic acid anhydride (F). The amines based on B were designated as BP, BZ, BF and those based on T as TP, TZ and TF respectively. The structural characterisation of amines was done by elemental analysis, DSC, TGA, ^{1}H-NMR and FTIR. Amine equivalent weight was determined by acetylation method.

The curing behaviour of diglycidyl ether of bisphenol-A (DGEBA) in the presence of stoichiometric amounts of aromatic amines was monitored by differential scanning calorimetry. In order to study the effect of phosphorus content of amines on the curing and thermal behaviour of DGEBA, mixture of phosphorylated amines and conventionally used amine i.e. 4,4'-diamino diphenyl sulfone (D), were used as curing agent. Four categories of resin formulation could be made based on the phr of amines used for curing DGEBA (a) amines D, T and B where the phr was 33 ± 2 (b) Amide-amines where phr needed was 65 ± 1.5 (c) amide-acid amines (phr = 91-132) (d) mixed amines.

Higher curing temperatures were observed when DGEBA was cured with amine D as compared to amines B and T. D contains a strong electron-withdrawing sulfone group ($-SO_2-$), which is in direct conjugation with amino group compared to phosphine oxide group (present at m-position), thereby leading to a significant reduction in the nucleophilicity of the amine D.

In case of phosphorus containing amide-amines curing exotherm appeared at a lower temperature with amines MB and MT as compared to PB and PT. In amines MB and MT, the amino group is at m- position with respect to electron withdrawing carbonyl group (amide) while in PB and PT it is at p- position. Therefore, only inductive effect (-I) will be significant in MB and MT while in PB and PT both resonance and inductive effects will affect the nucleophilic character. Thus, curing behaviour of DGEBA in presence of these amines can be correlated with nucleophilicity of the amines. The presence of m-linkages increases the flexibility of the amine, which may help in diffusion of amines to reaction sites and reduction in the curing temperatures. Curing exotherm was relatively sharper and narrower in amide-acid amines. Curing of DGEBA with amide-acid amines is a complex process. It involves endothermic cyclodehydration of amide-acid to imides as well as exothermic curing reaction in the same temperature range. The phr of amines used was significantly different from each other because of variation in the molecular masses. This basically reduces the epoxy content per gram of resin with increase in the molecular weight of the amine. Therefore the factors affecting the curing process are not only the nucleophilicity of the amine but also diffusion processes as well as reduced oxirane content.

Activation energy for curing reaction of DGEBA was similar with amines D, B and T and mixed amines BD2 and TD2 (64.5 ± 1.5 kJ mol^{-1}) and was comparable in amine PB and MB (62 ± 2 kJ mol^{-1}) while with PT it was much higher (84.6 kJ mol^{-1}) as compared to MT (56.6 kJ mol^{-1}). The activation energy of curing of DGEBA with amide-acid amines was higher than other amines. Highest E_a (128 kJ mol^{-1}) was observed when amide-acid amine BP was used for curing.

An increase in the curing temperatures was observed when D was added to T/B or amide-amines for curing DGEBA. An increase in phosphorylated amide-acid amines in such mixed amine formulations increased the T_0 and T_p. Our studies indicate that curing of DGEBA depended on three main factors (i) nucleophilicity of the amine (ii) phr of the amines used for curing DGEBA and (iii) side reactions during curing such as cyclodehydration reaction.

Thermal stability of cured resins was evaluated by thermogravimetric analysis in nitrogen atmosphere. Since the amines used for curing of DGBEA differ in their backbone structure and molecular masses, therefore mass loss and char yield depended on amines used for curing, molar mass of amine, aromaticity of amines and phosphorus content.

DGEBA cured with D showed a one step mass loss. Replacement of D by phosphorus containing amine B did not change the thermal stability of the resin. The characteristic decomposition temperatures were similar in DGEBA /D and DGEBA /B systems and the char yield at 800^{0}C was 16± 0.5%. The phosphorus content of epoxy resin cured with B was higher than that cured with T yet the char yield (CY) at 800^{0}C was 27.4% with T. Similarly, phosphorus content of the cured resin network was higher when MB or PB (CY= 22%) were used as curing agent yet the char yield was 30% in MT or PT system. This may be due to the fact that in amines B, MB and PB a methyl group was present while in T, MT or PT a thermally stable phenyl group is present.

In amide-acid amines, the char residue was 0.25-0.44 times higher than that of DGEBA cured with T. This may be due to the presence of thermally stable imide linkages and higher aromatic character of amide-acid amines, which may lead to an increase in char residue.

In general with phosphorylated amines, decomposition started at lower temperatures as compared to DGEBA cured with amine D. Phosphine oxide group first decomposes to form phosphorus rich char, which prevents further degradation of cured resin network and increases the char yield.

In order to correlate the char residue with phosphorus content of the cured resin, DGEBA was cured with mixed amines (D and phosphorylated amines). Amine structure was kept constant and phosphorus content was varied by the addition of D. Char yield increased linearly with phosphorus content. With T based amines char yield was higher as compared to B based amines with same phosphorus content. Char yield was highest with amide-acid amines followed by amide-amines and then amines B or T.

Glass fabric/epoxy resin laminates were fabricated using epoxy compatible E-glass fibre woven mat. Resin content of the laminates was determined by conc. nitric acid method and was found to be in the range of 32 ± 3 %.

Mechanical properties of the composites based on amines D, B, T and amide-amines MB, MT, PB, PT (flexural strength in the range 212-334 MPa, flexural modulus in the range 17-24 GPa and ILSS in the range 17-25 MPa) were higher than the composites prepared by using amide-acid amines (flexural strength in the range 178-270 MPa, flexural modulus in the range 15-22 GPa and ILSS in the range 14-21 MPa) as higher phr of the amide-acid amines was used for curing of DGEBA, which was responsible for a decrease in the epoxy content of the cured resin.

Composites based on phosphorylated amines showed better flame resistance than commercial amine D. Epoxy resin cured with MB, PB, MT and PT had lower flame resistance compared to B and T cured systems. This may be due to the decrease in the phosphorus content from B and T to MB, PB and MT, PT. Composites based on amide-acid amines showed highest flame resistance and highest LOI value of 78.6% and lowest smoke density value of 30% was shown by the composites in which amide-acid amines TP or TB were used as curing agents. Higher aromatic character of these amines may be responsible for better flame properties.

An increase in ILSS was observed on isothermal aging of laminates at 180°C for 200 and 500h. Hygrothermal aging for 7 days resulted in a decrease in ILSS.. Amide-acid amines are highly polar and their composites showed maximum moisture absorption of 1.0-2.5% compared to other composites in which 0.02-0.62% moisture absorption was observed.

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