EFFECT OF STRUCTURE OF AROMATIC DIAMINES ON PROPERTIES OF EPOXY RESINS AND COMPOSITES

by

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CERTIFICATE

This is to certify that the thesis entitled **'EFFECT OF STRUCTURE OF AROMATIC DIAMINES ON PROPERTIES OF EPOXY RESINS AND COMPOSITES'** being submitted by **Mr. Neeraj Gupta** 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 him. Mr. Neeraj Gupta has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The ease of processing and performance of cured products have made epoxy matrix resins as material of choice in advanced fibre reinforced composites. However, the cured resins are brittle in nature due to high cross-link density. An increase in molecular size of curing agent may lead to a reduction in cross-link density. Therefore, in the present work the curing of DGEBA with aromatic diamines of varying molecular size was carried out. The effect of variation of epoxy network on the properties of cured resins and glass/carbon fibre reinforced composites was evaluated.

1,3-bis(4-aminophenoxy)benzene (R), 1,4-bis(4-aminophenoxy)benzene (H), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (B), 1,1-bis[4-(4-aminophenoxy)phenyl]cyclo-hexane (C) and 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide (T) were prepared by synthesising corresponding dinitro compounds followed by reduction using hydrazine hydrate in the presence of Pd/C in methanol/DMAc (2:1 v/v) solution. 4,4'-bis(4-aminophenoxy)benzophenone (P) and bis[4-(4-aminophenoxy)phenyl] sulfone (S) were prepared by the condensation of sodium-4-aminophenate with 4,4'-diflourobenzophenone or 4,4'-dichlorodiphenylsulfone respectively. The dinitro compounds and diamines were characterised by FT-IR and ^{1}H-NMR spectroscopic techniques.

The curing behaviour of DGEBA with diamines was monitored by DSC. An exothermic transition was observed in the temperature range of 80-220°C. The onset temperature of curing (T_i) depended on the nucleophilicity of the diamines and varied in the following manner:

$$B < R \approx T \approx C < H < P < S$$

The presence of electron withdrawing carbonyl (-CO-) and sulfone (-SO_2-) groups in the diamine P and S reduced the nucleophilicity of amino groups. The peak exotherm temperatures (T_p) was comparable when R, H, B, C and T were used for curing DGEBA (175±5°C). Higher T_p was observed for P (186°C) and S (189°C). The heat of curing (ΔH) was in the range 238-369 J/g. Activation energy of curing (E_a) determined

by using multiple heating rates, was found to be 53 ± 1 kJ/mol for systems based on diamines R, H, B, C and T. Higher E_a was observed when diamine P and S (61 kJ/mol) were used for curing. In order to investigate the effect of non-equivalence of functional groups, different concentrations of diamines ranging from 20 to 100 phr (epoxy : amine molar ratio 1 : 0.24 - 1 : 0.71) were used. T_i remained unchanged with concentration of diamine but T_p marginally decreased (~ 15°C) with increase in diamine concentration. There was an increase in heat of curing (ΔH) till the stoichiometric ratio was reached due increase in the extent of cure.

The effect of epoxy network on glass transition temperature (T_g) was determined by DSC. Lowest T_g (139±1°C) was observed when diamines R and H were used for curing DGEBA while a value of 166-172°C was obtained with diamines S and T. T_g also depended on the stoichiometry of the diamine and epoxy resin. A decrease or increase in diamine concentration from the stoichiometric ratio decreased the T_g. An explanation has been given to account for the variation in T_g due to change in structure of diamine and the stoichiometry of the reagents.

Thermogravimetric analysis of DGEBA cured with stoichiometric amount of diamines showed single step decomposition. The temperature of initiation (T_1) (340-360°C), temperature of maximum rate of decomposition (T_{max}) (375-410°C) and final decomposition temperature (T_2) (400-460°C) were similar in all the cases. However, higher char yield at 800°C were obtained with DGEBA cured by diamine P (25%) and T (26%) respectively.

The room temperature tensile properties of DGEBA cured with various diamines were not affected significantly by a change in structure of diamines. The tensile strength, Young's modulus and % elongation at break were in the range of 70-90 MPa, 1.7-2.2 GPa and 7-11%.

The interfacial shear strength (τ) of the single glass/carbon fibre reinforced epoxy resin composites was determined by using embedded interfacial shear method. The

presence of polar carbonyl, sulfone and phthalide groups in diamines P, S and T resulted in higher τ values (22-28 MPa) as compared to other diamines (16 $\pm$ 2 MPa) in glass fibre reinforced composites. However, no significant difference in τ values (10-12 MPa) was observed in case of carbon fibre reinforced epoxy resin composites cured by different aromatic diamines.

Glass fabric/epoxy laminates (V_f = 0.39-0.42) were prepared using diamines H, S, T and diaminodiphenylsulfone (DDS). Tensile strength, Young's modulus and % strain at break were found to be in the range of 355-418 MPa, 21-29 GPa and 2.2-3.0 % respectively. Flexural strength and modulus of the laminates were in the range of 507-630 MPa and 26-39 GPa respectively. The interlaminar shear strength (ILSS) of the laminates cured by diamines S and T was higher ($\sim$42 MPa) as compared to diamine H (36 MPa).

Isothermal aging of these composites was carried out at 200°C for 200 and 500 h and then ILSS was determined. The decrease in ILSS on isothermal aging was in the range of 3-5% after 200 h and 11-13 % after 500 h of exposure at 200°C.

The moisture absorbed by the glass fabric/epoxy laminates after immersing for seven days in water was maximum when diamine H was used (0.51%) while minimum for laminate cured by diamine T (0.11%).

Curing behaviour of DGEBA using a rigid diamine N,N'-bis(4-aminophenyl)-quinonenediimine (Q) (synthesised in laboratory) was also studied by DSC. Higher temperature dependence was observed with this diamine (E_a = 102 kJ/mol). T_g of the cured resin was also high (170°C). Co-curing studies of DGEBA using stoichiometric amount of two diamines i.e. Q and DDS was also carried out. A synergistic effect of diamines on the onset temperature of curing (T_o) was observed. Addition of even 0.1 mole fraction of Q in DDS or DDS in Q lowered the T_o values by 20°C.

CONTENTS

CHAPTER II : MATERIALS AND TECHNIQUES