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. Another limitation of the epoxy resins is relative poor thermal stability and flame resistance. Phosphorus and silicon containing compounds have been used in the past to increase the flame resistance and therefore oxidative stability of polymeric materials. Combination of P and N is reported to have a synergistic effect on flame resistance. Therefore, it was considered of interest to study the effect of silicon and a combination of silicon and phosphorus in the cured network on flame retardancy and mechanical properties.

The present thesis deals with the curing of DGEBA with silicon containing amide-amines of varying structure and molecular weight (ranging from 660-910 g/mole). Synthesis and characterization of aromatic amide-amines obtained by reacting bis (4-chlorobenzoyl) dimethyl silane with aromatic amines such as 4,4'-diamo diphenyl ether, 4,4'-diamo diphenyl methane, 4,4'-diamo diphenyl sulphone, 3,3'-diamo diphenyl sulphone, bis (3-aminophenyl) methyl phosphine oxide and tris (3-aminophenyl) phosphine oxide using dimethyl acetamide as solvent was carried out. The diamine bis (3-aminophenyl) methyl phosphine oxide (BAP) and triamine tris (3-aminophenyl) phosphine oxide (TAP) were synthesised in laboratory by reducing their dinitro and trinitro compounds using hydrazine hydrate in the presence of Pd/C in ethanol solution. Structural characterisation of amide-amines was done using FT-IR, $^1$H-NMR spectroscopic techniques, elemental analysis and amine equivalent weight.
The curing behaviour of diglycidyl ether of bisphenol-A (DGEBA) in presence of stoichiometric amounts of silicon containing aromatic amide-amines (E, M, mS, pS, B and T) was monitored by differential scanning calorimetry. A broad exothermic transition due to curing was observed in all the DSC scans. With amide-amines the exotherm was observed in the temperature range of 200-300°C. With amines DDS showed higher curing temperatures as compared to TAP/BAP. EB, EE and ET samples clearly showed two exotherms whereas in EM, EpS and EmS samples only one exotherm was observed and the samples start degrading immediately after the completion of the exotherm. The curing exotherm was characterised by noting T_b, T_onset, T_p and T_f. The characteristic curing temperatures was dependent on the nucleophilicity of the amines.

The presence of electron withdrawing sulphone (-SO2) group in the amide-amines mS and pS reduced the nucleophilicity of amino group. The peak exotherm temperature (T_p) were comparable when T, B and mS were used for curing DGEBA. Higher T_p was observed for M (272°C) and E (279°C). The heat of curing (ΔH) was in the range of 90-196 J/g. Mixture of amide-amines : 4,4'-DDS in the ratio of 0.25: 0.75, 0.5:0.5, 0.75:0.25 was also used to investigate the effect of silicon content on the curing and thermal behaviour of DGEBA. Activation energy of curing (E_a) determined by using multiple heating rates and was found to be in the range 51-103 kJ/mol for systems based on amide-amines. Activation energy was lowest (50 kJ/mol) when an amide-amine EE was used as hardener and was highest (103.9 KJ/mol) with EM.

The curing behaviour of diglycidyl ether of bisphenol-A (DGEBA) using bis (4-carboxy phenyl) dimethyl silane (CPA) in the ratio of 1:1 as a crosslinking agent and imidazole as catalyst was also investigated by differential scanning calorimetry. Two exotherms were observed in the absence of catalyst in the temperature range of 166-328°C. A significant decrease in the curing
temperature was observed when 0.1% imidazole was used as catalyst. Further increase in the concentration of imidazole resulted in a decrease in the peak exotherm temperature. The effect of stoichiometry of functional group on curing behaviour of DGEBA was investigated by taking varying moles of CPA ranging from 1 to 2.5 keeping the concentration of imidazole as 0.1% w/w. Heat of polymerization ($\Delta H$) was found to be maximum at a molar ratio of 1:1.75 (DGEBA:CPA). Mixture of CPA:DDS in the ratio of 0.25:0.75, 0.5:0.5 and 0.75:0.25 was also used to investigate the effect of silicon content on the thermal behaviour of DGEBA. A significant decrease in curing temperature of DGEBA/DDS was observed on partially replacing DDS with CPA.

Thermal stability of epoxy resin cured isothermally (at 250°C for 2h in an air oven) was evaluated by recording TG/DTG traces in nitrogen atmosphere. Thermogravimetric analysis of DGEBA cured with stoichiometric amounts of aromatic amide-amines showed single step decomposition. All samples were stable upto 300°C and significant weight loss occurred only beyond this temperature. The relative thermal stability of the cured network was compared by comparing IDT, $T_{max}$ and FDT and percent char yield at 800°C. DGEBA cured with DDS, BAP and TAP had % char of 19, 30 and 36% respectively. DGEBA cured with amide-amine E, mS, M and pS had a char yield of 30 $\pm$ 3%. A significant improvement ($\geq$60% compared to DGEBA network with conventional amine DDS) in the percent char was observed in case of DGEBA cured using T or B having phosphorus and silicon atoms in the backbone. Introduction of thermally stable amide linkages did not have much effect on the thermal stability. Percent char yield was highest for sample cured using 1.75 mole of CPA.

Glass fabric epoxy laminates were prepared using amide-amine M, E, mS, pS, B and T. Flexural strength and modulus of the laminates were in the range 115-409 MPa and 11-26 GPa
respectively. The interlaminar shear strength (ILSS) of the laminates cured by amide-amine was in the range of 7-21 MPa. The difference in flexural strength and flexural modulus of the composites can be attributed to the structure of epoxy network. Storage modulus (G') of all the composites calculated at 200°C was in the range 5 x 10⁸ to 33 x 10⁸ Pa and glass transition temperature (T_g) calculated from tan δ curve was in the range 139 - 154°C.

The smoke density decreased with an increase in the char yield, laminate having both phosphorus and silicon has highest LOI (71.7 for CT) whereas all other samples have LOI value in the range of 52 ± 15.

The moisture absorbed by glass fabric/epoxy laminates after immersing for seven days in water was in the range of 1 to 3%.