STUDIES ON METHACRYLIC ACID ESTERS/IMIDE MATRIX RESINS AND GLASS FIBRE-POLYMER INTERFACE

by

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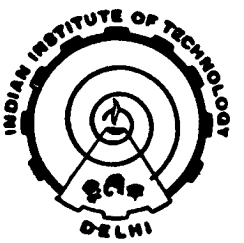

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CERTIFICATE

This is to certify that the thesis entitled **"STUDIES ON METHACRYLIC ACID ESTERS/IMIDE MATRIX RESINS AND GLASS FIBRE-POLYMER INTERFACE"** being submitted by **Ms. Lalita Choudhary** 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. She 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.

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 present thesis reports the results of the investigations on the organic matrix resins and glass fibre/fabric reinforced composites. The study also includes the effect of surface modification of glass fibres on interfacial shear stress and the possible modification of matrix resin in the interphase region.

The thesis has been divided into six chapters. Chapter I deals with a review of the thermosetting matrix resins (vinyl esters, epoxies, bismaleimides, epoxy-bismaleimides etc.) and glass fibres. The role of interface in fibre reinforced organic matrix resins is also discussed. The second chapter gives an outline of the materials and the experimental techniques.

The third chapter deals with glass fabric/fibre reinforced vinyl ester resins. Methacrylic acid esters of diglycidyl ether of bisphenol A (VR) and epoxy novolac resin (VN) containing different weight % (i.e. 30, 40, 50) of reactive diluent (styrene) were used as matrix resins. Interlaminar shear strength of the laminates having 57-62 volume % of resin content was found to be ~20 MPa for VN and 26 MPa for VR based composites. The flexural strength depended upon the concentration of reactive diluent and was in the range of 220-256 MPa and 187-230 MPa for VR and VN composites respectively. A decrease in ILSS was observed when the laminates were immersed in boiling water for 12 h. Further increase in the duration of boiling water treatment up to 36 h only marginally affected ILSS.

Interfacial shear stress (τ) was also determined. In order to increase the interfacial shear strength, glass fibres were treated with γ-methacryloxypropyl

trimethoxysilane (MTS). The tensile strength of untreated and MTS treated glass fibres was found to be 1.66 and 1.76 GPa respectively. The dilution of VN resin with 30-50 wt % of styrene resulted in an increase of τ values, whereas a reverse trend was observed in VR resins. Treatment of glass fibres with MTS resulted in significant improvement of τ (33-70%) in VR resin. A 65% improvement in τ was observed for VN3 samples. A decrease in τ was observed when the samples were treated in an air oven at 100°C for 50 h.

Studies on copolymerisation of N-phenyl maleimide (NPM) and methyl methacrylate (MMA)/(MTS) were carried out in order to investigate the possibility of chemical bond formation between maleimido groups of addition polyimides and the methacryloxy group of coupling agents. These studies form the basis of chapter IV. Bulk copolymerisation of NPM : MMA and solution copolymerisation of NPM:MTS (20% w/v dioxan solution) was carried out using benzoyl peroxide as an initiator at 80°C in nitrogen atmosphere. The rate of copolymerisation of NPM : MTS (percent conversion per unit time) decreased with an increase in NPM content in the feed. Several copolymers of NPM and MMA were prepared by varying the mole fraction of NPM in the initial feed from 0.12 to 0.78. The mole fraction of NPM in the initial feed was varied from 0.3 to 0.7 in NPM:MTS copolymerisation. In the IR spectra of NPM:MMA copolymers, absorption peaks due to imide groups were observed at 1784 and 1720 cm^{-1}, whereas for NPM:MTS copolymers, characteristic peaks of the imide group and alkoxy silane were observed at 1776, 1724 cm^{-1} ($\nu_{C=O}$ imide), 1092 (Si-O-C bending) and 1204 cm^{-1} (C-O-C stretch). The

copolymer composition was determined by ^{1}H-NMR spectroscopy and elemental (C,H,N,Si) analysis.

The glass transition temperature (T_g) of NPM : MMA copolymers (determined by DSC) increased with an increase in NPM content in the backbone. The incorporation of even very low mole fraction of NPM in the PMMA backbone was sufficient to raise the T_g by ~40°C. The intrinsic viscosity of NPM:MMA copolymers decreased with an increase in mole fraction of NPM in the copolymers.

PMMA when subjected to a programmed rate of heating in nitrogen atmosphere showed a three step decomposition, whereas, in PMTS (homopolymer of MTS) a two step decomposition and in PNPM (homopolymer of NPM) a single step decomposition was observed. The copolymers (NPM : MMA and NPM : MTS) exhibited a single step decomposition above 360°C with a char yield of 1-7% and 15-30% respectively.

Chapter V deals with the synthesis and characterisation of 4-maleimidophenyl glycidyl ether resin (MGE). The resin was obtained as a brown compound in three steps with an epoxy equivalent weight of 253 ± 6. In the IR spectrum of the resin, characteristic peaks of different functional groups were observed at 1784, 1717 cm^{-1} ($\nu_{C=O}$ imide), 1464 cm^{-1} (CH_2-O-ϕ symmetric bending), 1240 cm^{-1} (aromatic ether group), 960 cm^{-1} (terminal epoxy group) and 824 cm^{-1} (p-substituted phenyl ring). In the ^{1}H-NMR spectrum of MGE (in $CDCl_3$), the characteristic chemical shifts were at δ = 2.18 ppm (-CH_2- of epoxide ring), 3.11 ppm (-CH- of epoxide ring), 4.2 ppm (-O-CH_2-), 6.82 ppm (2H, -CH=CH-), 7.02 ppm (2H, phenyl) and 7.32 ppm (2H, phenyl). DSC scan of MGE exhibited a broad exotherm in the

temperature range of 250-330°C. In the TG trace of the resin a two step decomposition was observed, whereas cured resin showed a single step decomposition.

The curing of the MGE resin was carried out using different concentrations of amines i.e. 4,4′-diaminodiphenyl methane, 4,4′-diaminodiphenyl ether, 4, 4′ - diaminodiphenyl sulphone and tris (3-aminophenyl) phosphine oxide. A decrease in the curing temperature (~100°C) and initial decomposition temperature (10-30°C) was observed on addition of amines.

Summary and conclusions of the work are given in chapter VI of the thesis. Suggestions for future work are also given. References are given at the end of the thesis.

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