EFFECT OF REACTIVE DILUENTS AND FLAME RETARDANT ADDITIVES ON PROPERTIES OF VINYL ESTER RESINS

by

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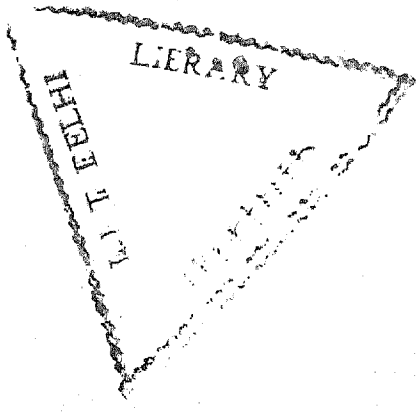

CERTIFICATE

This is to certify that the thesis entitled "**EFFECT OF REACTIVE DILUENTS AND FLAME RETARDANT ADDITIVES ON PROPERTIES OF VINYL ESTER RESINS**" being submitted by **Ms. Mona Malik** 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. Mona Malik 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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Mona

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ABSTRACT

Fiber reinforced organic matrix resins are being used as structural materials in defence, aerospace, transportation, building and construction and other related industries. The organic matrix resins that have been used in such advanced fiber reinforced composites are unsaturated polyester resins, vinyl esters, epoxy resins and addition polyimides. Bismethacryloxy derivatives of diglycidyl ether of bisphenol-A belong to the category of unsaturated polyester resins. The viscosity of neat VE resins is high hence, reactive diluents (generally styrene) are added to reduce the viscosity and improve the processability. The main objective of the present studies was to evaluate the role of glycidyl methacrylate on curing characteristics and thermal behaviour of VE resins, and to develop resin formulations with improved flame resistance.

The thesis deals with the synthesis and characterization of vinyl ester resins obtained by reacting diglycidyl ether of bisphenol-A (DGEBA) and methacrylic acid in stoichiometric (0.5:1, sample A) and non-stoichiometric (0.5:0.85, sample B and 0.5:0.5, sample C) quantities in the presence of imidazole (catalyst) and hydroquinone (inhibitor) in air atmosphere at 100-110°C. Methacryloxy terminated hyperbranched polyester (D2) was also synthesized by reacting pentaerythritol with trimellitic anhydride followed by reaction of this polyfunctional carboxylic acid (eight –COOH groups) with glycidyl methacrylate.

Characterization of these resin samples was done by determination of molecular weight (Vapour Pressure Osmometry), IR and ^{1}H-NMR spectroscopy. Presence of residual oxirane groups in sample B and C was confirmed by these studies.

In order to reduce the viscosity of these resins, reactive diluents i.e methyl methacrylate (MMA), styrene and glycidyl methacrylate (GMA) were added and the effect of these diluents and D2 on curing characteristics and thermal stability of VE resins was evaluated.

Curing of these resins was monitored by gel time determination and differential scanning calorimetry. Gel time of VE resins (sample A, B and C) diluted with reactive diluents was determined using 2% BPO and 0.5% N, N-dimethylaniline. Gel time decreased with increase in the oxirane content either in VE resin (sample C) or in reactive diluents (GMA). For example, resin A and C containing 50% of GMA had a gel time of 120 and 28.0 seconds respectively. The effect of initiator concentration on gel time was also studied and it was found that gel time decreased with increase in initiator concentration.

The curing behaviour of VE resins was evaluated by recording DSC scans in the temperature range of 50-250°C at a heating rate of 10°C/min. 2% benzoyl peroxide was used as an initiator. The characteristic temperatures of curing decreased with increase in oxirane content. A sharp exotherm in the temperature range of 107-150°C was observed for both samples A and B while a broad exotherm (69-169°C) was observed in case of sample C. VE resin (sample A) diluted with styrene and D2 showed two curing exotherms in the temperature range of 70-250°C. The DSC exotherms were only marginally affected by the type of reactive diluent.

The activation energy (E_a) of curing of VE resin was evaluated by using multiple heating rate method. The activation energy of curing was affected by the type of reactive diluent. In sample A diluted with 50% styrene or GMA, E_a was 105.2 and 76.9 kJ/mol

respectively while in sample C containing 50% styrene or GMA, E_a was 102.7 and 71.3 kJ/mol respectively. In VE resins containing mixed reactive reactive diluents, E_a decreased with increase in the amount of GMA.

The thermal stability of cured VE resins was evaluated by recording their TG/DTG traces in nitrogen atmosphere at a heating rate of 20°C/min. VE resin samples containing MMA/GMA as reactive diluents were stable up to 250-260°C while samples containing styrene/GMA were stable up to 380-410°C and started losing weight above this temperature. VE resin (sample A) diluted with styrene/D2 was also stable up to 380-410°C. Samples containing higher amounts of D2 showed higher char yields at 600°C.

The mechanical properties of VE resins containing reactive diluents were evaluated by fabricating neat sheets as well as glass fabric reinforced laminates. The properties of laminates were affected by the type of reactive diluent. Interlaminar shear strength improved by an increase in oxirane content (as in sample C or by using GMA). Limiting oxygen index and smoke density of the laminates were not affected by the type of reactive diluent.

In order to enhance the flame resistance of USP resins, flame retardant additives such as hydrated alumina (ATH), ammonium polyphosphate (APP) tris (2-hydroxyethyl) isocyanurate (THEIC) and azobiscarbonamide (AZCN) in the ratio of 10:6:3:1 were added. Incorporation of additives resulted in deterioration of mechanical properties of laminates. Limiting oxygen index (LOI) of the laminates improved significantly by the incorporation of additives. Sample C contained residual oxirane ring which can react with amino group very easily. Therefore, a laminate was fabricated using sample C containing

50% styrene, flame retardant additives and phosphorus containing amine (tris-3-amino phenyl phosphine oxide). LOI of this laminate was very high (50.2).

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