SYNTHESIS, CHARACTERIZATION AND EVALUATION OF VINYL ESTER RESINS

by

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Submitted

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to the

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Dedicated
To
my parents

CERTIFICATE

This is to certify that the thesis entitled **"Synthesis, Characterization and Evaluation of Vinyl Ester Resins"** submitted by **Ms. Nimisha Agarwal**, to the **Indian Institute of Technology, Delhi** for the award of degree of Doctor of Philosophy, in Polymer Science and Technology is a record of bonafide research work carried out by her. Ms. Nimisha Agarwal 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 are original and have not been submitted in partial or full, to any other university or institute for the award of any degree (or) diploma.

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One's work may be finished some day, but one's education never.

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ABSTRACT

Vinyl ester resins based on epoxy resins such as diglycidyl ether of bisphenol A (DGEBA) and its oligomer or epoxy-novolac resins (VE resins) have been extensively investigated in the past. The presence of aromatic rings in such resins makes them inherently susceptible to UV absorption and subsequent degradation. Photo-oxidation can cause chemical and physical changes in polymers and their networks. This is one of the major shortcomings of such resins especially in outdoor applications (coatings etc.). It is therefore desirable to use VE resins based on aliphatic or cycloaliphatic epoxy resins. Such cycloaliphatic networks show significantly reduced ultraviolet adsorption. Hence it is expected that VE resins based on cycloaliphatic epoxies will show improved durability in outdoor environments relative to their aromatic analogs.

The other shortcomings in these resins are (a) poor toughness of cured resins (b) high viscosity of neat resins (c) evolution of diluents during processing and (d) low elongation at break.

The present thesis addresses some of these problems. It describes synthesis of VE resin based on diglycidyl ester of hexahydrophthalic anhydride (ER). In order to improve toughness and elongation at break of cured network, flexible methylene units were introduced in the backbone. The high viscosity of neat resins is believed to be a consequence of intermolecular hydrogen bonding of pendant –OH groups in VE resins. Partial removal of these groups was done by reacting with isophorone diisocyanate. Such treatment will introduce rigidity in the backbone.

The thesis had been divided into six chapters. Chapter 1 reviews the current status of vinyl ester resins.

The synthesis and characterization of vinyl ester resins is given in chapter 2. VE resins were synthesized by reacting diglycidyl ester of hexahydrophthalic anhydride (ER) and methacrylic (or acrylic) acid using a molar ratio of 1:1 (sample A) & (sample C) and 1:2 (sample B) & (sample D) in the presence of imidazole (catalyst) and hydroquinone (inhibitor) in oxygen atmosphere at 90 ± 5°C.

The oxirane end group of mono methacrylate / acrylate terminated resins (sample A and C) were chain extended by reacting with aliphatic dicarboxylic acids (i.e. glutaric acid, adipic acid and sebacic acid) in a molar ratio of 2:1 (VE: aliphatic dicarboxylic acids) to yield bis methacrylate/ acrylate terminated vinyl ester resins. The resins obtained by reacting methacrylate terminated vinyl ester resin with glutaric acid, adipic acid or sebacic acid have been designated as E, F and G respectively, while the corresponding bisacrylate terminated resins have been designated as E', F' and G' respectively.

The bis (meth) acrylate terminated epoxy resin (VE resin, sample B and D, having 2 hydroxyl groups/ mol) was modified by reacting with low amount of isophorone diisocyanate (resin: IPDI molar ratio 5: 1 or 10: 1) and the samples have been designated as B_2I_5 or B_2I_{10}.

All the vinyl ester resin samples were characterized by acid number determination, FTIR and ^{1}H-NMR spectroscopy.

In order to reduce the viscosity of these resins, methyl methacrylate was added as reactive diluent. The neat vinyl ester resins i.e. samples A, B, C and D were diluted with 20, 30 or 40 phr of MMA and the samples have been designated by appending a numerical suffix of 2, 3 or 4 after the letter designation of resin sample. For example, sample A diluted with 20, 30 or 40 phr of MMA have been designated as A-2, A-3 and A-4 respectively. Similarly samples B, C and D have been designated. Brookfield viscosity of the samples was determined using a Brookfield synchroelectric viscometer having spindle No. 3 and 7 (RV type at 20 rpm) at room temperature (25 ± 2°C). The viscosity of ER, sample A and sample C was found to be 1025 cps, 3375 cps and 3475 cps respectively. The viscosity of B and D was determined using spindle number 7 and was found to be 22000 cps and 24000 cps respectively. A significant increase in viscosity was observed by introducing (meth) acrylate end caps in epoxy resin. This may be attributed to the increased molecular weight and intermolecular hydrogen bonding of hydroxyl groups generated during the reaction of epoxy with (meth) acrylic acid. The viscosity decreased significantly upon dilution with methyl methacrylate.

The effect of varying content of diluent on curing characteristics of VE resins was evaluated by gel time determination and differential scanning calorimetry (DSC) (chapter 3). Thermal stability of the cured samples was assessed by thermogravimetric analysis (TGA) in nitrogen atmosphere.

Gel time of VE resin (samples A, B, C and D) diluted with varying amounts (20, 30 or 40 phr) of methyl methacrylate was determined at 60°C using AIBN as an initiator. A decrease in gel time was observed with increasing amount of MMA in sample A, C and D, while in sample B dilution had no effect on gel time. The gel time were in the following order D-2 > D-3 > C-2 > C-3 > A-2 > B-2 = B-3 = B-4 > A-3 > D-4.

Curing studies of vinyl ester resin samples were carried out in presence of BPO (2 phr) or AIBN (1 phr) at a heating rate of 10°C/ min in the temperature range of 50 - 300°C in static air. The DSC scans of resins A, B, C and D containing 1 phr of AIBN or 2 phr of benzoyl peroxide (BPO) showed a sharp exotherm above 70°C. An increase in T_{onset} and T_{exo} was observed when di (meth) acrylate resins were cured (B and D) compared to corresponding mono (meth) acrylate resin (A and C).

In the samples cured with BPO, the exothermic peak position were at 88°C (A), 95°C (B), 81°C (C) and 88°C (D) due to the decomposition of BPO and curing reaction of VE resins having methacrylate or acrylate end groups. A second less intense exotherm was observed above 105 ± 5°C in these resin samples with exothermic peak temperature of 129°C (A), 139°C (B) and 126°C (C). In sample D no such well defined peak was observed.

In chain extended VE resins i.e. (E, F & G / E', F' & G'), on curing with 2 phr BPO, a sharp exotherm was observed with exothermic peak position in the temperature range of 95°C - 102°C (E, F and G) and 77°C - 88°C (E', F'and G') followed by a second less intense exotherm above 100 ± 5°C with exothermic peak position at temperature ranging from 125 - 138°C. In acrylate terminated resins, an increase in bridge length also reduced the T_{onset} and T_{exo}. For example T_{onset} for resin D was 82°C while for resin E' it was 79°C. The curing temperature was only marginally affected by dilution with varying amounts of methyl methacrylate but a significant increase in ΔH value was observed.

Thermal stability of isothermally cured VE resins (i.e. samples A, B, C and D cured in presence of 1 phr of AIBN at 60°C in N_2 atmosphere in a water bath for 2 h and then in air oven at 60°C for another 2 h and of chain extended resins A - G, E', F' and G' cured in presence of 2 phr of benzoyl peroxide in N_2 for 2 h at 80°C followed by heating in an air oven at 100°C for 2 h) was investigated by recording TG/DTG traces at a heating rate of 20°C/min. The cured VE resins were stable upto 250°C and started losing weight above this temperature. Most of the samples decomposed in a single step. In most of the resins, a mass loss upto 300°C was 7.5 ± 3% and the major mass loss was observed above 300°C.

In chain extended VE resin, an increase in bridge length resulted in an increase in initial decomposition temperature (T_i) of resin samples. The maximum decomposition temperature and the final decomposition temperature were above 400°C. The initial decomposition (T_i) temperature was higher in acrylate terminated resin than the corresponding methacrylate resins. The thermal stability decreased with increase in the amount of isophorone diisocyanate.

The thermal stability of isothermally cured VE resins (samples A, B, C and D) containing varying amounts of MMA show that all the samples were stable up to 230°C and decomposed in a single step above this temperature. Major mass loss was observed in the temperature range of 300 - 500°C and 85 ± 3 % of the sample was lost in this decomposition step. However in all the samples initial mass loss of ~ 10 ± 3 % was observed between 100 and 300°C.

In chapter 4, the performance of bisacrylate terminated cycloaliphatic epoxy resin (having flexibilising units of varying length in the backbone) in UV curable coating formulations was evaluated in terms of gloss, stain/solvent resistance, hardness, scratch, adhesion, abrasion resistance and weatherability on variety of substrates such as metal, wood, board and glass. Fifteen resin formulations were used to evaluate the coating performance. Nano silica and nano ZnO were used as additives in few formulations for stabilizing transparent coated metallic substrates.

Higher gloss was observed in case of flexible coatings having longer bridge length. Mild steel panels had very good gloss which was higher than the aluminium panels. With increase in the amount of nano fillers in the coatings, a decrease in gloss was observed. All the coating formulations on metal panels were found to have very good adhesion. With wood and paper board, the adhesion depended on the rigidity of the resin as well as on the type of cut (vertical or horizontal in wood) or whether anchor coat was present or absent (in paper board). Mild steel panels coated with formulations having varying amounts of nano filler showed no effect on adhesion. All the coating formulations on metal panels were found to pass the zero T-bend tests and showed good impact resistance.

Thermal stability of the UV cured coatings was also assessed and found that all the resins were stable up to 300°C and decomposed in a single step in most of the resins. Significant decrease was observed in the T_{onset} and T_{max} with the addition of nano ZnO while reduction was marginal by addition of nano silica. The weathering studies of UV cured coated panels was done by exposing the samples for 100 h to accelerated weathering in a Ci 35A weather-o-meter equipped with Xenon arc lamp and the temperature of the black panel was 60 ± 2°C and relative humidity was 65 %. The cycle conditions used were 3.5 h light cycle followed by 1 h dark cycle. This type of artificial weathering is considered to reproduce satisfactorily natural weathering conditions. The data obtained from aging tests showed that these coatings are fairly resistant to environmental degradation. No significant yellowing was observed in most of the coating formulations.

The mechanical properties of the glass fibre reinforced VE resin are given in chapter 5. The laminates were fabricated by vacuum assisted resin transfer moulding (VARTM) technique. The Brookfield viscosity and gel time of the resin formulation was in the range of 350 cps - 475 cps and in the range of 20 - 22 minutes respectively. The density of the cured resin samples was in the range of 1.17 - 1.27 g/cm^3. The mechanical properties of the neat sheets and glass fabric reinforced laminates depended on the resin structure. The resin content of all the laminates is in the range of 50 ± 5 %. There was a significant reduction in the tensile strength and increase in elongation at break by introduction of the flexible units between the crosslinks.

Samples ES, FS and GS were very flexible and it was difficult to measure the flexural strength and modulus of these samples. There was a marginal effect on impact strength with the change in backbone structure.

The hygrothermal aging of the samples at 80 % RH and 100 % RH was also carried out. The RH of 80 % was obtained by keeping the samples over a plate in a dessicator containing water and RH of 100 % was obtained by immersing them directly in water. ILSS of the samples was also determined after isothermal aging at 150°C for 240 h and 500 h and at 180°C after 24 h and 125 h.

A decrease in ILSS was observed on hygrothermal aging of the laminates. In almost all the cases, an increase in ILSS was observed on isothermal aging of laminates. LOI of all the laminates was comparable i.e. 21.8 ± 0.5. Results from thermogravimetric analysis of these room temperature cured samples show single step decomposition. All the resins were stable up to 340°C and final decomposition temperature was above 390°C. In chain extended VE resin, an increase in bridge length resulted in an increase in T_{onset}.

General discussion and summary are given in chapter 6 of the thesis.

Bibliography is given at the end.

A procedure describing the synthesis and characterization of products obtained by reacting IPDI with hydroxyl group of low molecular weight compounds (such as phenol and 2 - hydroxyethyl methacrylate) (IPH) is appended at the end. Homopolymerization and copolymerization of IPH with varying amounts of methyl methacrylate (MMA) was carried out with an aim to study the effect of copolymer composition on the thermal behavior of copolymers.

CONTENTS

Appendix