Chapter 2. Experimental

2.1. Materials.

2.1.1. Benzoyl peroxide (Aldrich): m.p. 104-106 ^{o}C, FW 242.23

Benzoyl peroxide was used as an initiator for the vinyl ester oligomers and styrene copolymerization. The one hour half-life temperature of benzoyl peroxide is 92 ^{o}C and the 1-min half-life temperature of benzoyl peroxide is 131^{o}C (Benzene)[1] . BPO was used as received.

2.1.2. t-Butylperoxybenzoate (Atochem): b.p. 75-76 ^{o}C/0.2mm, FW 194.23

t-Butylperoxybenzoate was used as an initiator for the vinyl ester oligomers and styrene copolymerization. The one hour half-life temperature of t-butylperoxybenzoate is 125 ^{o}C and the 1-min half-life of t-butylperoxybenzoate is 171^{o}C (dodecane)[1].

t-Butylperoxybenzoate was used as received.

2.1.3. Styrene (Aldrich): m.p. -31 ^{o}C, b.p. 145-146 ^{o}C, FW 104

Styrene was used as a solvent and comonomer for network formation of the vinyl ester resins. It was passed through a neutral alumina column to remove inhibitors before mixing with vinyl ester oligomers.

2.1.4. Methyl ethyl ketone (Fisher): m.p.-87 ^{o}C, b.p. 80 ^{o}C

Methyl ethyl ketone (MEK) was used as an extraction solvent for sol and gel analyses and swelling experiments. MEK was used as received.

2.1.5. Deuterated Chloroform ($CDCl_3$, Cambridge Isotope Laboratories): b.p. 60.9 ^{o}C, m.p.-64 ^{o}C, FW 120.39 .

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[1] J. Sanchez and T. N. Myers in *Polymeric Materials Encyclopedia*, J. C. Salamone ed., CRC Press, 1996, p4927.

$CDCl_3$ was used as an NMR solvent as received.

2.1.6. Methylene Chloride (EM Science): b.p. 39.8-40 ^oC, m.p.-97 ^oC, FW 84.

CH_2Cl_2 was used as a solvent for the reaction of the methacrylate terminated bisphenol A propoxylate. CH_2Cl_2 was stirred over CaH_2 for 24 hours and distilled under a nitrogen atmosphere. Then it was stored in a septum sealed bottle until used.

Methylene chloride was also used as a solvent for swelling experiments . For this purpose , CH_2Cl_2 was used as received.

2.1.7. Triethylamine (Fisher):): b.p. 88.8 ^oC, m.p.-115 ^oC, FW 101.19

Triethylamine was distilled from CaH_2 under nitrogen and was stored in a septum sealed bottle until used. Triethylamine was used both as a dessicant and catalyst for methacrylation reaction.

2.1.8. Propylene oxide (Aldrich): b.p. 35 ^oC, m.p. -112 ^oC, FW 58.08

Propylene oxide was used as received as a reagent for the synthesis of bisphenol A propoxylate or [2,2-bis(4-(2-hydroxyprop-1-oxy)phenyl]propane].

2.1.9. Tetrahydrofuran (EM Science): b.p. 67 ^oC, m.p. -108 ^oC, FW 72.11

Tetrahydrofuran was used as received as a solvent for the synthesis of bisphenol A propoxylate.

2.1.10. Bisphenol A (Dow Chemical):): b.p. 220 ^oC/mm, m.p. 158 ^oC, FW 228.29

Bisphenol-A was used as received as reagent for synthesis of bisphenol A propoxylate.

2.1.11. [2,2-bis(4-(2-hydroxyprop-1-oxy)phenyl] propane or bisphenol A propoxylate (Aldrich, 1 Propylene oxide/phenol group): Average MW=344

The bisphenol A propoxylate was dried under vacuum at 150^oC for 4 hours before methacrylation.

2.1.12. Methacryloyl chloride (ACROS): m.p. -60 ^{o}C, b.p. 95-96 ^{o}C, FW. 104.54

Methacryloyl chloride was distilled under reduced pressure and stabilized with 150 ppm phenothiaine. Methacryloyl chloride was used as a reagent for the synthesis of the methacrylate terminated bisphenol A propoxylate.

2.1.13. Chloroform (Fisher): b.p. 60.5-61.5 ^{o}C, m.p. -63 ^{o}C, FW. 119.38

Chloroform was used as received as a solvent for purification of the bisphenol A propoxylate.

2.1.14. Derakane 441-400 vinyl ester-styrene resin (Dow Chemical)

Derakane 441-400 vinyl ester resins were used as received. Additives such as inhibitors (proprietary to Dow Chemical Co.), which had been added to the resin, were not removed.

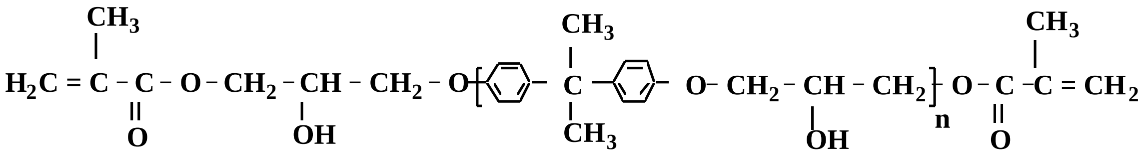

Figure 2.1. The structure of the vinyl ester oligomer in Derakane 441-400

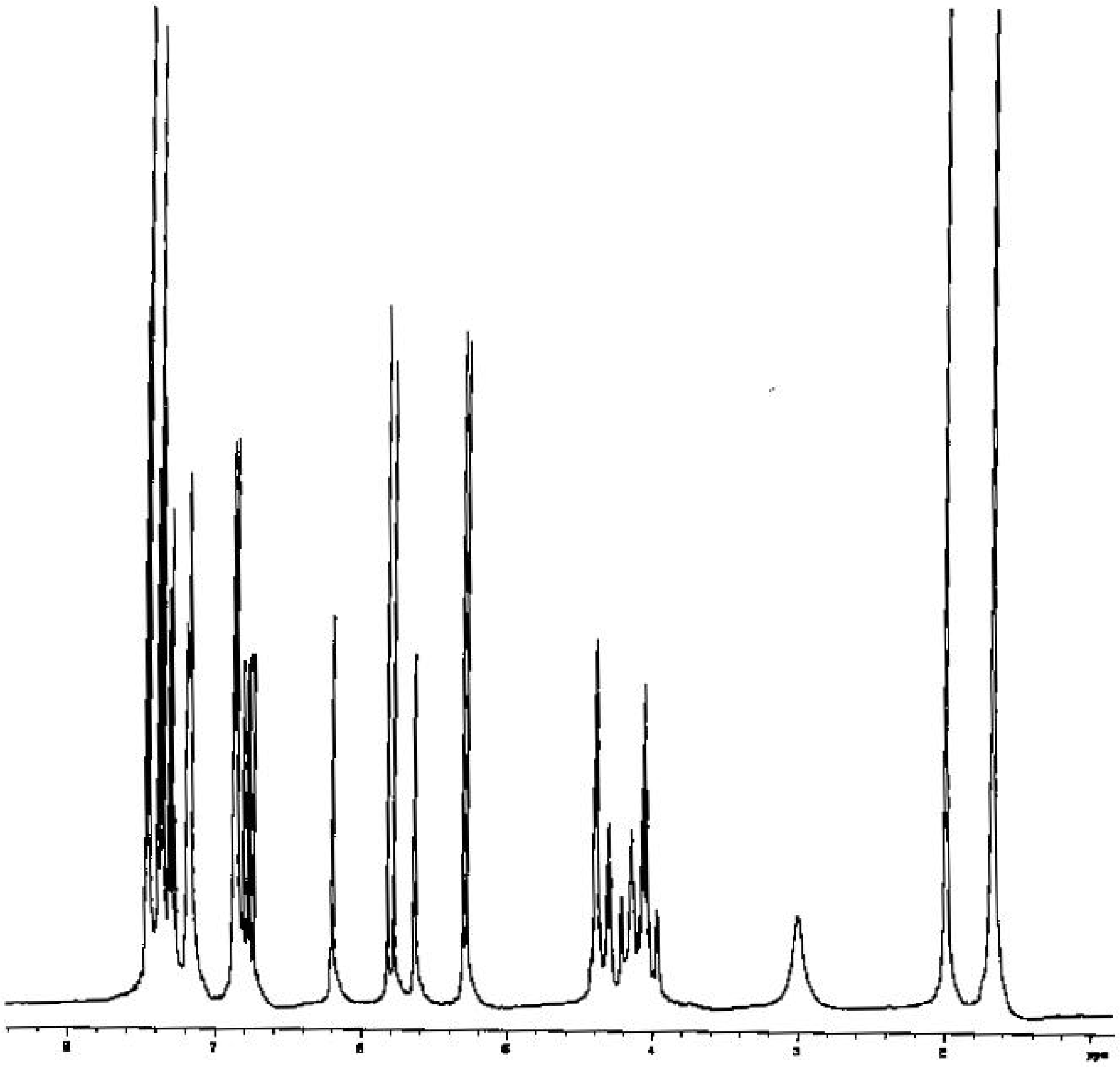

Figure 2.2. ^{1}H-NMR of Derakane 411-400 (Mn = 690 g/mol, 28 % styrene)

The vinyl ester component of the resin is the reaction product of an epoxy terminated polyhydroxyether derived from bisphenol-A and epichlorohydrin endcapped with methacrylic acid to form a material with methacrylate endgroups (Figure 2.1). Proton NMR showed that the number average molecular weight of the vinyl ester component of the Derakane 441-400 resin was about 690 g/mol (Figure 2.2). The integrals of peaks for methyl groups of bisphenol-A (1.65 ppm) and for the methacrylate methyl endgroups (2.0 ppm) were used to calculate the molecular weight of the vinyl ester component. The Derakane 441-400 vinyl ester was diluted with 28 wt. percent styrene monomer (1.28 styrene units per methacrylate unit).

2.1.15. Vinyl ester oligomers (Dow Chemical): viscous liquid, $M_n = 690$ g/mol

The vinyl ester oligomers (same structure in Figure1, n=1.62) were used as received. Additives added by Dow Chemical Co. were not removed.

2.1.16. Vinyl ester oligomers (Dow Chemical): solid, $M_n = 1000$ g/mol

The vinyl ester oligomers (same structure in Figure1, **n=3)** were used as received. Additives added by Dow Chemical Co. were not removed.

2.1.17. NaCl windows for FTIR (International Crystal Laboratories)

NaCl crystal windows were repeatedly used for studying the cure reactions of vinyl ester resins. NaCl crystal windows were placed in an oven at 600 ^{o}C for 6 hours to remove the crosslinked polymer films. Then the NaCl crystal windows were washed with acetone, dried at 90 ^{o}C and stored in a dessicator until used.

2.1.18. Poly(vinylpyrrolidone) (K-17, T_g=178^{o}C) (BASF Corp.)

Poly(vinylpyrrolidone) was used as received to blend with vinyl ester resins to study their phase behavior.

2.2. Kinetics Study by FTIR[2, 3, 4]

The initiators were first dissolved into the vinyl ester-styrene resin mixture, and oxygen was removed using a freeze-thaw technique. One drop of the material was placed between two NaCl windows which were then placed in the preheated controlled temperature cell in the FTIR cell, as shown in Figure 2.3. Preheating the cell was desirable to minimize the time lag required for heating to the pre-set temperature. Eight scans were collected for each spectrum every thirty seconds. The absorbancies of the peaks at 943 cm^{-1} and 910 cm^{-1} were plotted as a function of the concentration of styrene and methacrylate functionalized oligomers to confirm that the heights of these peaks followed Beer's Law over the absorbance range of 0-1. A small background absorbance assigned to the vinyl ester backbone overlapped the absorbance at 943 cm^{-1} (about 20 percent of the initial absorbance at 943 cm^{-1}). Therefore all spectra were subtracted by a spectrum where the conversion of methacrylate and styrene were complete. The phenyl peak at 700 cm^{-1} was used as an internal standard. For each reaction, all spectra were normalized such that the height of the peak at 700 cm^{-1} was equal.

Then the spectrum corresponding to the fully reacted material was subtracted from each spectrum recorded during the reaction . Solid state NMR measurements were used to establish that the residual absorbance was indeed due to the network as opposed to residual methacrylate double bonds (see Results and Discussion). Corrections for any changes in sample thickness during polymerization were also made by normalizing the spectra to the 700 cm^{-1} absorbance. The heights of the infrared absorptions at 943 cm^{-1} and 910 cm^{-1} corresponding to methacrylate and styrene double bonds respectively, were monitored quantitatively and used to calculate reaction conversions. Reaction conversion was determined from the changes of the normalized absorptions (equation (1)) after subtraction of

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[2] Y. S. Yang and L. J. Lee, *Macromolecules*, 20, 1490, 1987.

[3] M. Ganem and B. Mortaigne, *J. M. S. Pure Appl. Chem.*, A30, 828, 1993.

[4] J. L. Koenig, *Spectroscopy of Polymers, American Chemical Society*, Washington, DC, 1993.

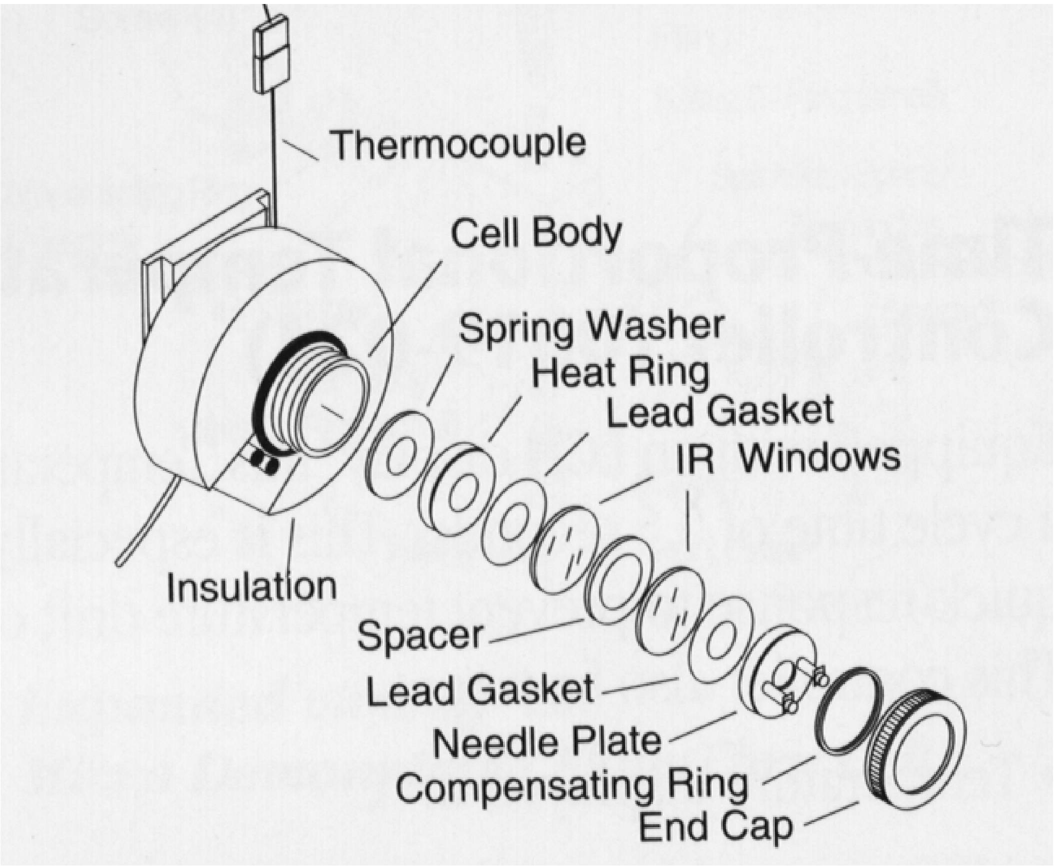

Figure 2.3. Heated IR Cell for Monitoring Cure Reactions

the background where A_o and A_t are normalized absorptions before the reaction and after a reaction time t

$$a = 1 - A_t/A_o \quad (1)$$

2.3. Sol and Gel Analyses [5]

The resin mixture (ca. 10 g) was charged to a series of vials. Each vial was deoxygenated using a freeze-thaw technique and then was sealed with a screw cap and Teflon tape. Each vial was placed in a temperature controlled silicone oil bath (±0.1 °C) for desired periods. The reactions were stopped by plunging the vials into a dewar filled with liquid nitrogen. The samples were then transferred carefully into 25 ml methyl ethyl ketone, and approximately 100 ppm 1,4-benzoquinone inhibitor was added to each sample. The samples were sealed and stored at 5 °C until analyzed. The chemical compositions of the sol fractions were analyzed using FTIR in a liquid cell in methyl ethyl ketone as the solvent. The concentrations of vinyl ester and styrene in the sol in methyl ethyl ketone solution were measured according to the peak heights at 830 cm^{-1} (vinyl ester) and 700 cm^{-1} (styrene). Systematically varied concentrations of vinyl ester-styrene resin were dissolved in methyl ethyl ketone and FTIR absorptions at 830 cm^{-1} and 700 cm^{-1} were calibrated for the concentrations of vinyl ester and styrene. The same liquid cell was used for all measurements. The sol solution was also analyzed by ^1H NMR ($CDCl_3$ as solvent). The insoluble gels were filtered, washed with acetone, dried in a vacuum oven for several weeks at room temperature to remove the solvents, then measured gravimetrically. The gel fractions were calculated as

$$\% \text{ Gel} = g/w \times 100 \quad (2)$$

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[5] R. Mao, Y. Liu, M. B. Huglin, and P. A. Holmes, *Macromolecules*, 28, 6739, 1995.

where g and w were the weights of the gels and initial weights of the vinyl ester resins. The chemical compositions of the gels were analyzed by FTIR using KBr pellets. Systematically varied ratios of styrene to vinyl ester oligomer were analyzed by FTIR to calibrate the compositional ratios using the absorptions at 700 cm^{-1} (phenyl peak from styrene) and 830 cm^{-1} (vinyl ester backbone).

2.4. Syntheis of Vinyl Ester Oligomers[6]

2.4.1. Synthesis of [2,2-bis(4-(2-hydroxyprop-1-oxy)phenyl]propane or Bisphenol A Propoxylate

Bisphenol A (114.1g, 0.5 mol) was dissolved in 1500 ml tetrahydrofuran in a 2-neck round bottom flask equipped with a magnetic stir bar. Sodium hydroxide (8 g, 0.2 mol) dissolved in 100 ml of water was added. The slurry was stirred under N_2 atmosphere until the reaction mixture became homogeneous (otherwise, more water as needed was added into the flask). Propylene oxide (135 ml, 116 g, 4 mol) was added to this mixture via syringe and the reaction vessel was placed in an oil bath at 40 ^{o}C for 24 hours. The tetrahydrofuran solvent was removed by rotary evaporation. The crude product was washed several times with hot water and then dissolved in chloroform. The solution was extracted with dilute sodium hydroxide solution three times and saturated sodium chloride solution three times. The organic layer was separated, dried over magnesium sulfate, filtered, and the chloroform was evaporated. The product was distilled at 150 ^{o}C under vacuum for 5 hours to remove the major side-product of the reaction, propylene glycol. The yields were 80-90%.

2.4.2. Methacrylation of Bisphenol A Propoxylate

Dry bisphenol A propoxylate (100g, 0.29 mol) was dissolved in CH_2Cl_2 (500ml) in a clean, dry, two neck 1000 ml round-bottomed flask fitted with a dry nitrogen atmosphere and magnetic stirring. Triethylamine (64.4 g, 0.64 mol) was added via syringe.

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[6] S. Kalachandra, D. F. Taylor, C. D. DePorter, H. J. Grubbs, and J. E. McGrath, *Polymer*, 34, 778, 1993.

The reaction flask was then placed in an ice bath. Methacryloyl chloride (66.6 g, 0.64 mol) was added via syringe at a very slow rate such that the temperature of the reaction mixture was maintained at or below room temperature. After addition of all of the methacryloyl chloride, the ice bath was removed and stirring was maintained for an additional 4-5 hours. The esterification reaction proceeded with the salt by-products precipitating from the solution within 10-20 minutes. The progress of the reaction was monitored by FTIR. The hydroxy functional group (at 3400 cm^{-1}) disappeared after 3-4 hours. The reaction mixture was filtered to remove the triethylammonium chloride salt. The solution was first washed several times with a dilute hydrochloric acid solution, then with a sodium bicarbonate solution, and finally with deionized water. The solution was dried over magnesium sulfate, stabilized with 100 ppm hydroquinone and the solvent was evaporated under vacuum at room temperature.

2.5. Preparation of Vinyl Ester Resin Samples

Styrene monomer was mixed with the vinyl ester oligomers in systematically varied ratios. The compositions of these resins were confirmed by ^1H NMR in $CDCl_3$ by ratioing the integrals for the peak resonances for styrene vinyl protons (5.62 + 5.10 ppm) to methacrylate vinyl protons (6.02 + 5.46 ppm).

2.6. Vinyl Ester Resin Blends

Poly(vinylpyrrolidone) (K-17) was first dissolved in the vinyl ester resin (10 wt% and 20 wt% PVP) with stirring until clear solutions were obtained. The initiators were then added and stirring was maintained for 4 hours to ensure that the initiators were dissolved. Curing was carried out at 120°C in a convention oven for 1 hour. Other blends were prepared by the same method. Miscibility of the blends was investigated by DSC (Perkin-Elmer DSC 7).

2.7. Characterization

2.7.1. Nuclear Magnetic Resonance Spectroscopy (^1H NMR)

^{1}H NMR measurements were conducted on a Varian Unity 400 mHz spectrometer. Deuterated solvents such as $CDCl_3$ were used with concentrations typically between 1 and 10% solids.

2.7.2. Differential Scanning Calorimetry (DSC)

DSC was utilized to determine the glass transition temperatures and for monitoring the cure reactions. DSC was conducted on a Perkin Elmer Series 7 thermal analyzer under a nitrogen purge at a heating rate of 10^{o}C/min. All reported data are from second heating scans.

2.7.3. Dynamic Mechanical Analysis (DMA)

DMA was used to determine mechanical properties and glass transition temperatures of vinyl ester networks. The curves of the storage and loss modulus and the loss tangent as functions of temperature were obtained. The temperature of the maximum in the loss tangent peak was taken as the glass transition temperature. The storage modulus above T_g was also used to estimate the crosslink density of the vinyl ester networks. The DMA instrument was a Perkin Elmer DMA-7e. The heating rate was 5 ^{o}C/min. and frequency was 1Hz under amplitude control. The amplitude was set at between 7-10 mm depending on the thickness of the samples. The sample sizes were a thickness of 2.5-3 mm, width 5.9-6.2 mm, and length 18-20 mm.

2.7.4. Thermogravimetric Analysis (TGA)

TGA was used to examine the thermal and thermo-oxidative stability of cured vinyl ester networks. TGA was performed on a Perkin-Elmer Series 7 thermal analyzer with an air purge at a heating rate of 10 ^{o}C per minute. The weight loss of the sample was measured as a function of temperature. The temperature corresponding to 5% weight loss was reported.

2.7.5. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were collected using a Nicolet Impact Model 400 instrument equipped with a controlled temperature cell (Model HT-32 heated demountable cell used with an Omega 9000-A temperature controller).

2.7.6. ^{13}C- Solid State Nuclear Magnetic Resonance Spectroscopy

Solid state NMR spectra were collected using a Bruker MSL 300 instrument in the magic angle spinning (MAS) mode operating at a ^{13}C NMR frequency of 75.47 Mhz. About 0.25 g cured resin was packed in a 7 mm diameter cylindrical Zirconia rotor and retained with a Kel-F cap. The rotor was spun at 6.26 kHz using a block decay method. A 90° pulse (4.5 msec) was followed by a 30 millisecond acquisition time. A relaxation delay of 30 s was used between scans. Approximately 1500 scans were collected for each acquisition.

2.7.7. Viscosity Measurements

A Brookfield Digital Viscometer (model DV-2) was used to measure the viscosities of vinyl ester resins at 25, 35, 50 and 75 ^{o}C. The zero shear viscosity (η_o) was determined by extrapolation of low-shear data from the plot of viscosity vs. shear rate.

2.7.8. Density Measurements

The densities of uncured vinyl ester/styrene resin compositions were measured using a 10 ml volumetric density bottle. The volume of the density bottle was calibrated by using water. The densities of crosslinked samples were determined by using a balance (AG Mettle Toledo) with the aid of a density determination kit (Figure 2.4). The weight of each sample (ca. 1 g) was measured in air (A) and in water (B) to the nearest ±0.001 g.

The density was calculated as:

$$\rho = \left(\frac{A}{A - B}\right)\rho_o \qquad (3)$$

ρ_o is the density of water at measuring temperature. An average of three samples was measured for each resin composition.

Volume shrinkage upon cure was calculated as follows:

$$\%\text{shrinkage} = 100 \times \frac{\left(\frac{1}{\rho_{\text{uncured}}} - \frac{1}{\rho_{\text{cured}}}\right)}{\frac{1}{\rho_{\text{uncured}}}} \tag{4}$$

2.7.9. Fracture Toughness

ASTM Standard D 5045-91 test methods were utilized to characterize the toughness of vinyl ester resins in terms of the critical-stress intensity factor K_{1c}. The specimens

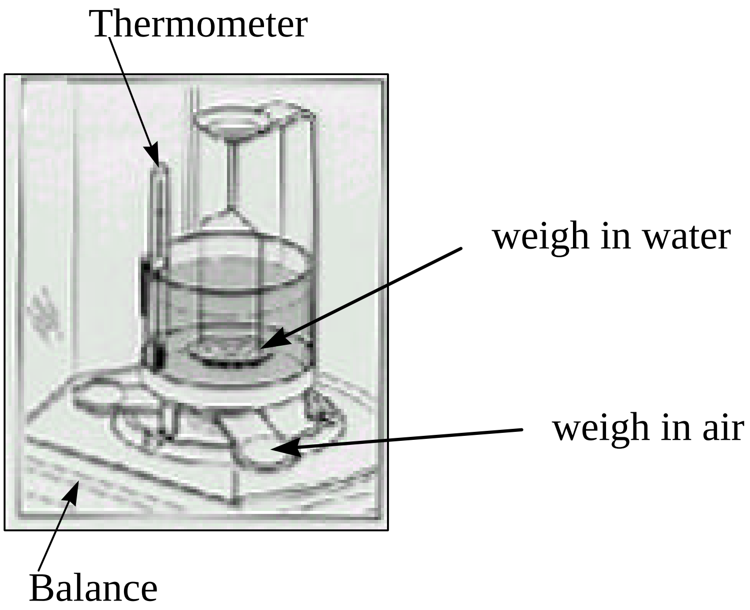

Figure 2.4. Density determination kit.

had thicknesses of 3.12 mm, widths of 6.28 mm, notch depths of 2.2 mm and notch widths of 0.8 mm. The single-edge notch bending method was used.

First, a sharp notch was prepared in the sample by sawing. A natural crack was initiated by inserting a fresh razor blade (after being immersed in liquid nitrogen) and tapping. The depth of the natural crack generated by tapping was approximately twice the width of the sawed-in notch. In order to obtain a minimum value of toughness, the crack should be sufficiently sharp. The pre-cracked notched specimen was loaded crack down, into a three-point bend fixture and tested using the Instron 4204. The single edge notch bending rig had moving rollers to avoid excess plastic indention. The three-point bend fixture was set up so that the line of action of applied load passed midway between the support roll centers within 1% of the distance between these centers. The crosshead speed was 10 mm-min^{-1} , and all the tests was carried out at room temperature.

2.7.10. Scanning Electron Microscopy (SEM)

SEM was utilized to qualitatively examine the microstructure of cured vinyl ester resins. The samples were gold coated and examined using a Philips 420T scanning transmission electron microscope with a secondary electron detector, operating at 60 kv in the SEM mode.

2.7.11. Sizing/resin Miscibility Measurements[8]

PVP(K-90, $T_g = 178\ ^oC$) was first dissolved in the vinyl ester resin with stirring until a clear mixture was obtained. The initiators were added and stirring was maintained at room temperature for 4 hours to ensure that the initiators were dissolved. Curing was carried out at 120°C in a convection oven for one hour. Other blends were prepared in the same manner. Miscibility of the blends was investigated by DSC (Perkin-Elmer DSC 7). Non-hydrogen bonded solubility parameters were estimated by group contribution methods using the MG&PC software [8] according to the equation $\delta = \rho\Sigma F_i / M$, where F_i is the molar

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[8] *Miscibility Guide and Phase Calculator Software*. J. F. Graf, Programmer, M. M. Coleman and P. C. Painter, Technomic Publishing Co., copyright 1991.

attraction constant of the group being considered, ρ is the density of the polymer, and M is the molar mass of the polymer (repeat unit). The summation was carried over all structural features in the molecule.

2.7.12. Swelling Experiments[9,10]

Swelling measurements were carried out in water, CH_2Cl_2 and methyl ethyl ketone at room temperature. The samples of vinyl ester networks were small blocks (3x3x5mm). The vinyl ester networks were immersed in each liquid for more than two weeks. The swelling equilibrium was determined when the weights of the swelling gels were constant. The networks were first weighed in the swollen state. Then the swollen gels were washed with fresh solvent and dried under vacuum at 150 ^{o}C for three days until constant weight. The swelling index was defined as follows;

$$\text{Swelling Index} = \frac{\text{Volume of gel in swollen state}}{\text{Volume of gel in dry state}} \qquad (5)$$

$$= 1 + \frac{(W_{sw} - W_d)\rho_g}{W_d \rho_s}$$

Where W_{sw} is weight of gel in the swollen state, W_d is weight of gel in dry state, ρ_s is density of solvent, and ρ_g is the density of the gel. The gel fraction was determined as the weight ratio of gels after drying and before swelling.

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[9] J. E. Mark and B. Erman, *Rubberlike Elasticity*, John Wiley & Sons, New York, 1988.

[10] L. E. Nielsen, *J. Macromol. Sci, Revs. Macromol. Chem.*, C3(1), 69, 1969.