



Temperature and moisture effects on composite materials for wind turbine blades  
by Mei Li

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
© Copyright by Mei Li (2000)

Abstract:

Temperature and moisture effects on composite materials with E-glass fibers and different potential resins for wind turbine blades have been investigated. The purpose of this study was to identify resins that have good temperature/moisture resistance while providing improved delamination resistance relative to a baseline ortho-polyester resin. The resins included ortho and iso polyesters, vinyl esters and an epoxy. The resins in this study were all appropriate for wind turbine blades in terms of low cost and low viscosity for easy processing by resin transfer molding (RTM). Specimens were conditioned in one of three ways: room temperature dry, 50°C; dry in an oven and 50°C in distilled water. Water absorption was determined at 50°C both for composites and neat resins as a function of time. Mechanical tests performed were 0°tension, 90°tension and 0°Compression with the layup [0/±45/0]<sub>s</sub> and tension with the layup [±45]<sub>3</sub>. Tests were run for both 20°C dry and 50°C wet conditioned specimens, tested at 25°C, 40°C, 55°C and 70°C. A second series of tests involved interlaminar fracture toughness ( $G_{IC}$  and  $G_{IIC}$ ) using DCB and ENF tests at -20°C dry, 50°C dry and 50°C wet conditions. Finally, a series of tests were run to directly measure the fiber / matrix bond strength. The microdebonding test was used with dry and wet conditioned specimens.

Results are presented relative to those for the baseline orthophthalic polyester resin. Epoxy SC-14 and the ortho-polyester are the most sensitive to moisture and temperature. They have relatively high saturation moisture contents and a significant reduction in interfacial bond strength after immersion in distilled water. Iso-polyester has superior environmental resistance, with no mechanical properties affected significantly in the hot-wet conditioning. However, both polyesters are relatively brittle, with low interlaminar fracture toughness, compared with the vinyl esters and epoxy. Vinyl esters provide very good delamination resistance and also good environmental resistance. In general, fiber dominated properties (0°tension) are insensitive to temperature and moisture while matrix dominated properties (±45 °and 90°tension) are more sensitive. The compressive strength in the 0°direction, also a matrix dominated property, showed significant reductions under hot/wet conditions.

TEMPERATURE AND MOISTURE EFFECTS ON COMPOSITE MATERIALS FOR  
WIND TURBINE BLADES

by

Mei Li

A thesis submitted in partial fulfillment  
of the requirements for the degree

of

Master of Science

in

Chemical Engineering

MONTANA STATE UNIVERSITY-BOZEMAN  
Bozeman, Montana

March 2000

N378  
26129

APPROVAL

of a thesis submitted by

Mei Li

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Dr. John Mandell

*J. Mandell*                      3/10/00  
Chairperson, Graduate Committee                      Date

Approved for the Department of Chemical Engineering

Dr. John Sears

*John T. Sears*                      3/11/00  
Department Head                      Date

Approved for the College of Graduate Studies

Dr. Bruce R. McLeod

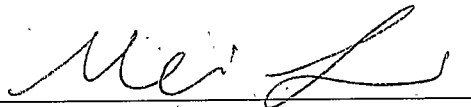
*Bruce R. McLeod*                      3-20-00  
Graduate Dean                      Date

## STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University-Bozeman, I agree that the Library shall make it available to borrowers under rules of the Library.

If I have indicated my intention to copyright this thesis by including a copyright notice page, copying is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for permission for extended quotation from or reproduction of this thesis in whole or in parts may be granted only by the copyright holder.

Signature



Date

3 / 10 / 2000

## ACKNOWLEDGMENTS

I gratefully appreciate the guidance of Dr. John Mandell and Dr. Douglas Cairns in this research study. Thanks are directed to Dr. Bonnie Tyler for being my graduate committee member. Daniel Samborsky deserves my appreciation for all of the assistance with experimental testing, manufacturing and photographs in this thesis. Thanks to the other graduate students in the composite materials group for their help and kindness. Finally, thanks to my dear mother Hongsong Li for her endless love and support, which will always encourage me to attain my goal.

This work was supported by the U.S. Department of Energy and the State of Montana through the Montana DOE EPSCoR Program (Contract # DEFC02-91ER75681) and Sandia National Laboratories (Subcontract BC7159).

## TABLE OF CONTENTS

LIST OF TABLES .....	vii
LIST OF FIGURES .....	viii
ABSTRACT.....	x
1. INTRODUCTION .....	1
2. BACKGROUND .....	4
Environmental Factors .....	4
Temperature .....	4
Moisture .....	6
Chemistry of Composite Components .....	7
Chemistry of Polymer Matrix and Curing .....	7
Polyester Resins .....	7
Vinyl ester Resins .....	9
Epoxy Resins .....	11
Chemistry of Glass Fibers.....	12
Chemistry of Fiber / Matrix Interface.....	13
Environmental Effects on Components of Composites.....	14
Environmental Effects on Glass Fibers.....	15
Environmental Effects on Polymer Matrices.....	16
Environmental Effects on the Fiber / Matrix Interface.....	18
Properties of Composite Materials .....	20
Moisture Diffusion.....	20
Tension and Compression.....	23
Interlaminar Fracture Toughness .....	25
Mode I Interlaminar Fracture Testing .....	26
Mode II Interlaminar Fracture Testing .....	28
Fiber-Matrix Bond Test .....	31
3. EXPERIMENTAL METHODS.....	34
Materials and Processing .....	34
Glass Reinforcement Materials.....	34
Resin Matrix Materials .....	34

**TABLE OF CONTENTS - Continued**

Processing .....	35
Environmental Conditioning.....	36
Apparatus and Testing .....	36
Tension and Compression.....	36
DCB & ENF Test.....	37
Microdebonding Test.....	38
Water Absorption Test.....	42
4. RESULTS AND DISCUSSION .....	44
Introduction.....	44
Water Absorption.....	45
Tension and Compression.....	48
Delamination Resistance.....	59
Microdebonding Test.....	68
5. CONCLUSIONS AND RECOMMENDATIONS .....	70
Conclusions .....	70
Recommendations.....	72
REFERENCES CITED.....	74
APPENDIX.....	78

**LIST OF TABLES**

Table	Page
1. E-glass compositions.....	12
2. Load rate of mechanical testing.....	37
2. Maximum moisture content and diffusivity of composites and neat resins.....	47
4. Composites tested.....	48
5. Summary of experimental data on effects of moisture and temperature on elastic modulus.....	58
6. Summary of experimental data on effects of moisture and temperature on ultimate strength.....	59
7. Results for $G_{IC}$ and $G_{IIC}$ for different conditionings.....	60
8. Test results for interfacial strength, dry and wet (tested at RT).....	68



## LIST OF FIGURES

Figure	Page
1. Unsaturated polyester showing (a) reactive carbon-carbon double bond and (b) crosslinking reaction.....	9
2. Bysphenol A vinylester.....	10
3. Typical epoxy and epoxy reaction.....	12
4. Glass transition temperature as a function of the moisture.....	17
5. Weight gain of neat resins as a function of square root of time.....	21
6. Typical stress - strain curves for 90° loaded $[0/\pm 45/0]_s$ composites.....	24
7. Three fundamental interlaminar failure modes.....	26
8. Geometry and loading for a DCB specimen.....	27
9. Typical load-displacement curve for a DCB specimen.....	28
10. Geometry and loading of ENF specimen.....	29
11. Typical load-displacement curve for a ENF specimen.....	29
12. Loading of micro-debonding test.....	33
13. The testing apparatus of micro-debonding test.....	40
14. SEM picture of the probe tip.....	41
15. SEM picture of a tested fiber.....	41
16. A picture of a debonding fiber (from Dr. Mandell).....	42
17. Price comparison for different resins (40,000 pound base estimation).....	44
18. Weight gain curves for $[0/\pm 45/0]_s$ composites conditioned in 50°C distilled water.....	46

19. Weight gain curves for neat resins conditioned in 50°C distilled water .....	46
20. Compression strength in the 0° direction vs. test temperature, dry and wet ([0/±45/0] <sub>s</sub> laminates).....	50
21. Tensile modulus in the 0° direction vs. test temperature, dry and wet ([0/±45/0] <sub>s</sub> laminates).....	51
22. Tensile modulus in the 0° direction vs. test temperature, dry and wet ([0/±45/0] <sub>s</sub> laminates).....	52
23. Failure mode for wet specimens of 8084 and iso-polyester at 40°C.....	52
24. Tensile modulus for ±45 laminates vs. test temperature, dry and wet ([±45] <sub>3</sub> laminates) .....	53
25. Tensile strength for ±45 laminates vs. test temperature, dry and wet ([±45] <sub>3</sub> laminates.....	55
26. Tensile modulus in 90° direction for [0/±45/0] <sub>s</sub> laminates vs. test temperature, dry and wet .....	56
27. Tensile strength in 90° direction for [0/±45/0] <sub>s</sub> laminates vs. test temperature, dry and wet .....	57
28. Moisture effects on initial mode one fracture toughness, tested at 50°C.....	62
29. Moisture effects on mode two fracture toughness, tested at 50°C.....	64
30. Temperature effect on initial mode one fracture toughness, tested at 50°C .....	65
31. Temperature effect on mode two fracture toughness, tested at 50°C .....	66
32. Effect of matrix on initial mode one interlaminar fracture toughness, tested at 50°C dry (0 degree D155).....	67
33. Effect of matrix on mode two interlaminar fracture toughness, tested at 50°C dry (0 degree D155).....	68

## ABSTRACT

Temperature and moisture effects on composite materials with E-glass fibers and different potential resins for wind turbine blades have been investigated. The purpose of this study was to identify resins that have good temperature/moisture resistance while providing improved delamination resistance relative to a baseline ortho-polyester resin. The resins included ortho and iso polyesters, vinyl esters and an epoxy. The resins in this study were all appropriate for wind turbine blades in terms of low cost and low viscosity for easy processing by resin transfer molding (RTM). Specimens were conditioned in one of three ways: room temperature dry, 50°C dry in an oven and 50°C in distilled water. Water absorption was determined at 50°C both for composites and neat resins as a function of time. Mechanical tests performed were 0° tension, 90° tension and 0° compression with the layup  $[0/\pm 45/0]_s$  and tension with the layup  $[\pm 45]_3$ . Tests were run for both 20°C dry and 50°C wet conditioned specimens, tested at 25°C, 40°C, 55°C and 70°C. A second series of tests involved interlaminar fracture toughness ( $G_{Ic}$  and  $G_{IIc}$ ) using DCB and ENF tests at -20°C dry, 50°C dry and 50°C wet conditions. Finally, a series of tests were run to directly measure the fiber / matrix bond strength. The micro-debonding test was used with dry and wet conditioned specimens.

Results are presented relative to those for the baseline orthophthalic polyester resin. Epoxy SC-14 and the ortho-polyester are the most sensitive to moisture and temperature. They have relatively high saturation moisture contents and a significant reduction in interfacial bond strength after immersion in distilled water. Iso-polyester has superior environmental resistance, with no mechanical properties affected significantly in the hot-wet conditioning. However, both polyesters are relatively brittle, with low interlaminar fracture toughness, compared with the vinyl esters and epoxy. Vinyl esters provide very good delamination resistance and also good environmental resistance. In general, fiber dominated properties (0° tension) are insensitive to temperature and moisture while matrix dominated properties ( $\pm 45^\circ$  and 90° tension) are more sensitive. The compressive strength in the 0° direction, also a matrix dominated property, showed significant reductions under hot/wet conditions.

## CHAPTER 1

### INTRODUCTION

Composite materials consist of two or more physically distinct and mechanically separable components called reinforcement and matrix. These two components can be mixed in a controlled way to achieve optimum properties, which are superior to the properties of each individual component. Composite materials have been widely used in the wind turbine blade manufacture because of the following advantages: high strength and modulus to weight ratio, low cost and flexibility in material and structure design.

Wind turbine blades should have a service life of 20 to 30 years in a variety of climates, which makes environmental resistance one of the most important factors in the wind turbine blade design. Actually, it has been reported that composite materials can be degraded by environmental attack such as moisture diffusion, thermal spikes, ultraviolet radiation, and thermal oxidation, etc [1-2]. Moisture diffusion, for example, can decrease the strength of composites, degrade the fiber / matrix interface, swell and plasticize the resin to lower its glass transition temperature (the temperature where the resin transforms from the glassy solid state to a visco-elastic state) [3-13]. The relative degree of the degradation process is related to the chemistry of the reinforcement and matrix, as well as the exposure time [7,11,13-15]. Different kinds of composites, however, are also sensitive to different environmental attacks. The combination of two or more individual environmental factors can aggravate the degradation of composite performance. In this

study temperature and moisture are the environmental factors of concern. Materials are soaked in distilled water at 50C to accelerate the environmental conditioning process.

Ortho-polyester is a low cost general purpose resin which has been used in wind turbine blade manufacture. Due to the disadvantages of its low temperature resistance and significant moisture sensitivity found in this study, new resin systems with the advantages of providing temperature and moisture resistance as well as easy processing by resin transfer molding (RTM) are investigated. A study of the same systems relative to matrix toughness has been reported by Orozco [16]. The first objective of this research was to evaluate moisture and temperature effects on polyester, vinyl ester and epoxy resins. Different sets of property data have been derived for wind turbine blade design in hot-wet conditioning and at different use temperatures with different resins. Tests included:

- 0 degree tension, 90 degree tension, 0 degree compression with the layup [0/±45/0]<sub>s</sub> and tension with layup [±45]<sub>3</sub>, for both 20C dry and 50C wet conditioned samples tested temperatures at 25C, 40C, 55C and 70C. Initial modulus and ultimate strength are derived as a function of temperature and moisture. The purpose of these tests was to provide database results for design properties of significance, with a focus on matrix-sensitive properties.
- Interlaminar fracture toughness ( $G_{Ic}$  and  $G_{IIc}$ ) using DCB and ENF tests at -20C dry, 50C dry and 50C wet conditions. The purpose was to provide guidelines for matrix selection in terms of composite structural integrity as expressed through the delamination resistance.

- Micro-debonding test to evaluate fiber-matrix interfacial strength dry and after wet conditioning in distilled water at 50C. These tests were run to determine whether the fiber/matrix bond was important in the environmental degradation process.
- Water absorption at 50C both for composites and neat resins. Duffusivity and maximum amount of water absorption of these candidates are calculated and compared as a basic measure of matrix sensitivity.

The second objective of the study was to identify resins that have good temperature-moisture resistance and improved toughness while providing other properties superior or similar to the baseline ortho-polyester resin. Reasonable cost and easy manufacturing by RTM were also of concern.

## CHAPTER 2

### BACKGROUND

#### Environmental Factors

Environmental effects on composite materials have to be considered in the early stages of design, or the design iterations and failure will cause a waste of time, energy and money. Usually the degree of sensitivity of composites to individual environmental factors is quite different. For wind turbine blade design, temperature and moisture are the most important environmental degradation factors taken into consideration. In the following paragraphs, the effects of these two environmental factors will be specified separately. However, it has been shown that their combination has more aggressive effects on the properties of composites than each alone, and the failure mode can also be changed at high temperatures under moisture conditioning [12,13]. The primary environmental effects are on the matrix phase and possibly the interface, while the fibers are usually relatively insensitive in the range of conditioning for polymer matrix composites. In fact, a primary role of the matrix is to protect the fibers from chemical environments.

#### Temperature

Composites for wind turbine blades may be exposed to low temperature conditions (-20C or below) or high temperature conditions (50C or above) in their

30-year service life. Exposure to low temperature of some tough polymers may make them more brittle and the modulus may increase [17].

In recent years, a lot of tests have been carried out to evaluate the response of composite materials to elevated temperature [24]. It has been reported that the temperature effect on the fiber-matrix interface is as strong as those of the fiber treatment and resin properties [19]. Other mechanical properties such as compression strength, ultimate tensile strength, and  $[\pm 45]$  tensile strength (which is matrix dominated) have also been reported to decrease at elevated temperature [9,11,12,20]. Temperature effects on the fracture properties of composites were widely investigated by Marom [21]. The study showed that interlaminar fracture energy decreased 25-30% as the temperature increased from -50 to 100C. The interlaminar fracture surface characteristics of graphite/epoxy were also investigated and pronounced differences were observed in the amounts of fiber/matrix separation and resin-matrix fracture with increasing temperature.

The temperature effect on the mechanical properties of composites derives partly from the internal stresses introduced by the differential thermal coefficients of composite components. Such internal stresses change magnitude with temperature change, in some cases producing matrix cracking at very low temperatures. In practical applications each polymer has its own operating temperature range. Usually a polymer has a maximum use temperature slightly below its glass transition temperature ( $T_g$ ), at which the polymer transfers from rigid state to rubbery state and suffers substantial mechanical property loss. Elevated temperatures combined with



humid environments have been found to exacerbate the problem by further reducing  $T_g$ , among other factors.

### Moisture

Water molecules can diffuse into the network of composites to affect the mechanical properties. Marom [21] reported that the short-term effect of water is to increase the mode I fracture toughness, while in the long run the toughness deteriorates. Shen and Springer [22,23] reported that for 90 degree laminates the ultimate tensile strength and elastic moduli decreased with increasing moisture content. The decrease may be as high as 50-90 percent. When moisture diffuses into composites, it degrades the fiber-matrix interfacial bonding [5], lowers the glass transition temperature [24], swells, plasticizes, hydrolyzes and sometimes microcracks the matrix [3,13]. The ability to predict the diffusion of water and its influences on the resin properties are necessary to predict long term behavior.

The uptake of moisture usually is measured by weight gain and the mechanism of water diffusion is characterized by Fick's law [25]. In 1975, Shen and Springer [25], based on Fick's law, studied the absorption and desorption of water in composite materials and presented expressions for the moisture distribution and moisture content as a function of time for one-dimensional composite materials. Many experimental data support the analytical solution and this expression has been widely accepted to describe the water diffusion behavior in composites.

Water absorption behavior for some composites, however, is far from fitting the Fickian model. Such a non-Fickian mechanism has not been well understood due

to the complication of absorption behavior and variation of the experimental data. Some methods and computing codes are presented trying to reduce the non-Fickian moisture content data to evaluate the diffusivity and moisture profiles across the thickness of laminates [26-28].

## Chemistry of Composite Components

### Chemistry of Polymer Matrix and Curing

A polymer matrix is obtained by converting liquid resins into hard and brittle solids by chemical cross-linking. Polymers can be classified as thermoplastic (capable of being softened and hardened repeatedly by increasing and decreasing temperatures) or thermoset (changing into a substantially infusible and insoluble materials when cured by the application of heat or by chemical means). In wind turbine blade manufacture, thermoset resins, including polyester, vinyl ester and epoxy are of interest. The variety of thermoset resins provides flexibility for designers. Actually, the properties of the polymer resin depend on the molecule units making up of the three-dimensional network and on the length and density of cross-links. The former is determined by the initial chemical reactions and the latter is determined by the control of processing and curing.

Polyester Resins. Generally polyester resins can be made by a dibasic organic acid and a dihydric alcohol. They can be classified as saturated polyester, such as polyethylene terephthalate, and unsaturated polyester. To form the network of the composite matrix, the unsaturated group or double bond needs to exist in a portion of

the dibasic acid. By varying the acid and alcohol, a range of polyester resins can be made. Orthophthalic polyesters are made by phthalic anhydride with either maleic anhydride or fumaric acid. Isophthalic polyesters, however, are made from isophthalic acid or terephthalic acid. The polyester resin is usually dissolved in monomer (styrene is the most widely used), which will copolymerize with it and contribute to the final properties of the cured resin. The addition of catalyst will cause the resin to cure. The most frequently used catalyst is methyl ethyl ketone peroxide (MEKP) or benzoyl peroxide (BPO) and the amount varies from 1-2%. The catalyst will decompose in the presence of the polyester resin to form free radicals, which will attack the unsaturated groups (like C=C) to initiate the polymerization.

The processing temperature and the amount of the catalyst can control the rate of polymerization, the higher temperature or the more the catalyst, the faster the reaction. After the resin turned from liquid to brittle solid, post cure at higher temperature may need to be done. The purpose of the post cure is to increase  $T_g$  of the resin by complete cross-linking. The properties of the polyester resin are affected by the type and amount of reactant, catalyst and monomers as well as the curing temperature. The higher the molecular weight of polyester and the more points of unsaturation in molecules, the higher is the strength of the cured resins.

Orthophthalic polyesters are environmentally sensitive and have limited mechanical properties. They have been replaced in some applications by isophthalic polyesters due to the excellent environment resistance and improved mechanical properties of the latter. The crosslinking reaction of polyester resin is shown in figure 2.1.

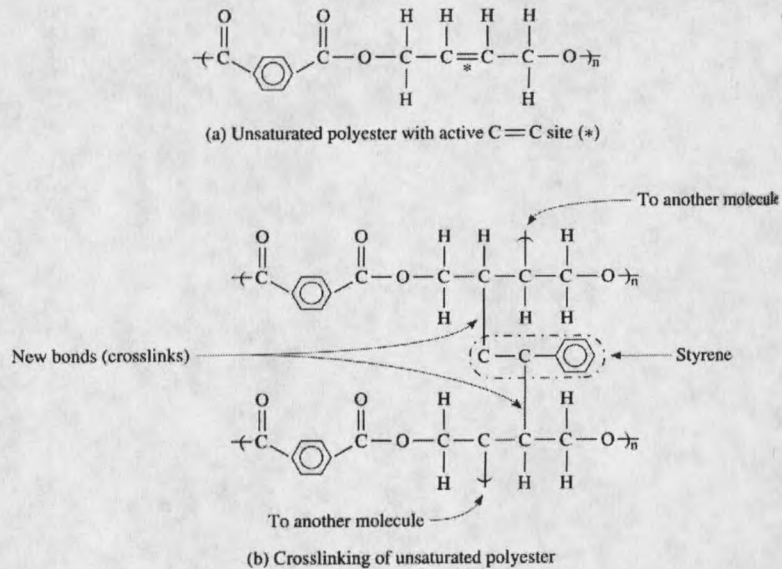


Figure 2.1 Unsaturated Polyester Showing (a) Reactive Carbon-Carbon Double Bond and (b) Crosslinking Reaction (from reference 29).

Vinyl ester Resins. Vinyl ester resins consist of a polymer backbone with an acrylate ( $R = H$ ) or methacrylate ( $R = CH_3$ ) termination  $R-[-O-CO-CR=C]$  (shown in figure 2.2). The backbone of vinyl ester can be derived from epoxy resin, polyester resin, urethane resin and so on. Among them epoxy resin as the backbone is of significant commercial interests. At present, epoxide backbones of various molecular weight are used in vinyl esters. Higher molecular weight produces higher toughness and resiliency, lower solvent resistance and lower heat resistance [30]. The source vinyl termination (methacrylate or acrylate) determines the ability to corrosion resistance. The styrenated methacrylate vinyl ester resins exhibit excellent resistance to acids, base and solvents. The acrylate vinyl ester resins, on the other hand, are

more susceptible to hydrolysis. In polymerization the unsaturated C=C termination provides the reactive site to cross-link and in this study, 1-2% volume Trigonox was mixed in the resin as the catalyst to provide free radicals. The free radicals react with the C=C to form a new bond and another free radical, and this free radical reacts with another C=C and so on to make the network. For the resins to cure at the room temperature, Cobalt Naphthalene is also added to the resin from 0.2 to 0.4% by weight as a promoter. Vinyl esters possess a lower ester content and a lower vinyl functionality than polyesters, which result in a greater resistance to hydrolysis. Vinyl esters also have higher elongation to break than polyesters, which also makes them tougher [31].

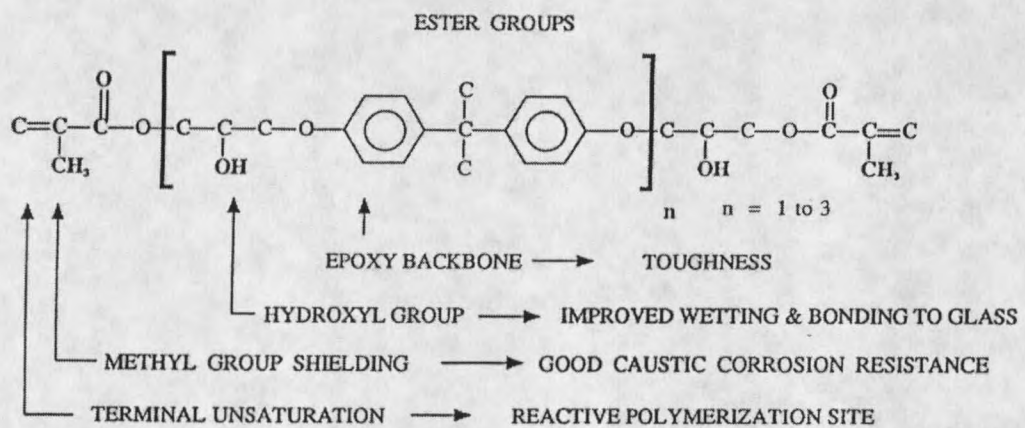


Figure 2.2 Bisphenol A Vinylester (from reference 16).

Epoxy Resins. An epoxy resin is a polymer containing two or more epoxy group rings. Such groups can be terminal, internal or cyclic structures. They can bond with other molecules, forming a large three-dimensional network (figure 2.3). The most used hardeners are aromatic and aliphatic amine as well as anhydride hardeners. All should be added into the epoxy resin with adequate weight ratio to provide cross-linking. The reaction between aliphatic amines and epoxy groups will usually proceed at room temperature. However, heat is required when rigid aromatic amines or anhydride hardeners are used. The properties of epoxy resins are related to the chemical structure of the cured resin. A greater number of aromatic rings results in higher thermal stability and chemical resistance. A lower crosslink density can improve toughness by permitting greater elongation before break. A higher crosslink density can give a higher glass transition temperature and improved resistance to chemical attack. The anhydride-cured system breaks down in strong bases and organic solvents. The Boron Trifluoride-Monoethylene Amine ( $\text{BF}_3\text{MEA}$ ) -catalyzed system is seriously affected by the organic solvent and long exposure to moisture. Recently, rubber toughened epoxy resins have gained significantly in interest. Small rubber particles scattered in the epoxy resin are believed to improve the fracture toughness of the neat resin [30].



















































































































































































































































