

AN ABSTRACT OF THE DISSERTATION OF

Yili Wu for the degree of Doctor of Philosophy in Wood Science and Chemical Engineering presented on June 9, 2016.

Title: Investigation of Styrene-Free Unsaturated Polyester Resins for Fiber-Reinforced Composites

Abstract approved:

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Most of existing commercial unsaturated polyester (UPE) resins are typically composed of a UPE and a high amount of highly volatile, flammable, and toxic styrene. The emission of hazardous styrene in the handling of the UPE resins and the preparation and use of fiber-reinforced UPE composites poses severe hazards to people's health and the working environment. In this study, two non-hazardous chemicals have been investigated for the replacement of styrene in the UPE resins. The first chemical is acrylated epoxidized soybean oil (AESO) that is derived from soybean oil and is not toxic and not volatile. The second chemical is methyl cinnamate that is extensively used as a food additive. Styrene-free UPE resins were prepared through combinations of these styrene replacements and three different UPEs. The styrene-free UPE resins were cured without the reinforcement of fibers and then evaluated and characterized for their properties. Kenaf fibers and glass fibers have been investigated as reinforcing fibers for the styrene-free UPE resins. An efficient process of making the fiber-reinforced UPE

composites was developed. The viscosity and the pot life of the styrene-free UPE resins under different temperature were studied. The curing behavior of the resins under heat was investigated. The viscoelastic properties of the cured UPE resins and the fiber-reinforced UPE composites were characterized with dynamic mechanical analyses. Mechanical properties such as flexural and tensile properties of the composites were measured. It was found that these styrene replacements were comparable or even superior to styrene in terms of the mechanical properties of the composites. The weight ratio between a styrene replacement and a UPE was studied in detail for maximizing mechanical properties. The curing mechanisms of these styrene-free UPE resins are discussed in detail.

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Investigation of Styrene-Free Unsaturated Polyester Resins
for Fiber-Reinforced Composites

by
Yili Wu

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Yili Wu, Author

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CONTRIBUTION OF AUTHORS

Dr. Kaichang Li was involved with all experimental design and revision of the dissertation.

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Investigation of Styrene-Free Unsaturated Polyester Resins for Fiber-Reinforced Composites

Chapter 1 – Introduction to UPE resins and issues related to styrene emission

1.1 General introduction

Unsaturated polyester (UPE) resins are by far the most widely used thermoset resins for fiber-reinforced polymer composites.¹ Glass fiber-reinforced UPE composites have a wide range of applications in numerous industries such as marine industry, automobile industry, construction and building industry, and wind power industry. The widespread applications are due to many advantages of the UPE resins. UPE resins are less expensive than other thermoset resins. For example, UPE resins are about 25% less expensive than vinyl ester resins and about 33-50% less expensive than epoxy resins.¹ UPE resins have a wide range of properties and are generally easier to cure and easier to mold than other thermoset resins.

Commercial UPE resins typically contain a UPE and a crosslinking agent. The UPE is typically synthesized from the polymerization of diols, unsaturated dibasic acids or acid anhydrides, and saturated dibasic acids or acid anhydrides. Because of its low cost and ready availability, maleic anhydride is currently the most commonly used unsaturated acid anhydride for introduction of free radically polymerizable C=C bonds onto the UPEs.

The reaction between the C=C bonds on the UPE chains is difficult, because the UPE chains have low mobility and the C=C bonds have the low tendency of homopolymerization. For turning the UPE into a useful product, the UPE has to be crosslinked with a crosslinking agent that can react with the C=C bonds on the UPE chains. Most UPEs are typically solid at room temperature. For the easy application of a UPE resin onto reinforcing fibers, effective crosslinking agents are typically required to be able to dissolve the UPE to form a liquid resin with low viscosity at room temperature or other use temperatures. Therefore, the crosslinking agents are also called reactive diluents. Styrene is currently the most commonly used reactive diluent because it is inexpensive and can significantly improve stiffness, strengths, water resistance, and thermal stability of the fiber-reinforced UPE composites.¹

However, styrene is highly volatile and of bad odor. It is classified as a hazardous air pollutant and a “reasonably anticipated human carcinogen” by the National Toxicology Program in 2011.² Emissive styrene poses severe health hazard for people who manufacture and use styrene, styrene-containing UPE resins, and fiber-reinforced UPE composites. It has been reported that unreacted styrene could continue to emit during the lifetime of fiber-reinforced UPE composite products.^{3, 4} The toxicity, particularly the potential carcinogenicity, of styrene has raised concerns over its use in the fiber-reinforced UPE composites. Such concerns have prompted the need for development of a safe alternative for styrene in the UPE resins.

1.2 History of UPE resins

UPEs with well-defined polymeric structures and high molecular weights were first prepared in 1929.^{5,6} The UPEs were prepared from ethylene glycol and fumaric acid, and from ethylene glycol and maleic anhydride.^{5,6} It was discovered in 1936-1937 that the curing of a UPE in the presence of a crosslinking agent such as vinyl acetate or styrene was much faster than the curing of the UPE alone.^{7,8} This discovery greatly increased the commercial viability of the UPE resins.

The non-reinforced cured UPE resins were weak and brittle, and found limited applications. The U.S. Rubber Co. first discovered that styrenated UPE resins could be reinforced with glass fibers for the generation of composites with high strength and yet light weight in 1942.⁹ The glass fiber-reinforced UPE composites were also found to have excellent electrical properties, making them highly transmissive to radar waves.⁹ This finding gave birth to the first commercial glass fiber-reinforced UPE composite product: aircraft radomes⁹ (A radome is a structural enclosure that protects a radar antenna from weathering and physical damage. The radome should be made of materials that minimally attenuate the electromagnetic signal transmitted or received by the antenna).

The shortage of natural rubber in the World War II greatly promoted the research and production of synthetic rubbers such as styrene-butadiene rubber. For ensuring the sufficient supply of styrene, several production plants for styrene were built in the U.S. during the World War II, which turned relatively expensive styrene to an inexpensive,

and readily available commodity chemical, and subsequently facilitated the widespread commercial production of the UPE resins.⁹

The growth of petrochemical industry after the World War II introduced a wide range of raw materials for preparations of different UPE resins, which greatly promote the development of UPE resins and fiber-reinforced UPE composites. For example, chlorendic acid was incorporated into UPEs for improving the flame retardance of the cured products (i.e., cured UPE resins and fiber-reinforced UPE composites).¹⁰ Incorporation of 1,6-dicyclohexanol¹¹ or neopentyl glycol¹² into UPEs significantly improved the chemical resistance of cured products. Diallyl phthalate was used as a crosslinking agent for UPEs for the production of molding compounds.¹³ By the late 1950s, efficient productions and numerous applications of the UPE resins and fiber-reinforced UPE composites had been well established.¹⁴

At present, UPE resins are the most commonly used thermoset resins for fiber-reinforced thermoset composites, accounting for more than 80% of all thermoset resins used.¹⁵ The UPE resins and the fiber-reinforced UPE composites are a multi-billion dollar business.⁹ Major producers of the UPE resins include AOC resins (Collierville, TN), Ashland Inc. (Covington, KY), DSM (Heerlen, Netherlands), Polynt Composites (formerly Cook Composites and Polymers) (Kansas City, Missouri), Reichhold (Durham, NC), Scott Bader (Wellingborough, United Kingdom), and TOTAL Cray Valley (Exton, PA).

1.3 Major raw materials for the preparation of UPEs

Commercial UPE resins are typically a mixture of a UPE and a crosslinking agent (predominantly styrene). The UPE is synthesized by polyesterification reactions between diols and dibasic acids (or acid anhydrides) (Figure 1.1). The choices of the diols and the dibasic acids (or acid anhydrides) greatly affect the properties of the resulting UPEs and accordingly their applications.

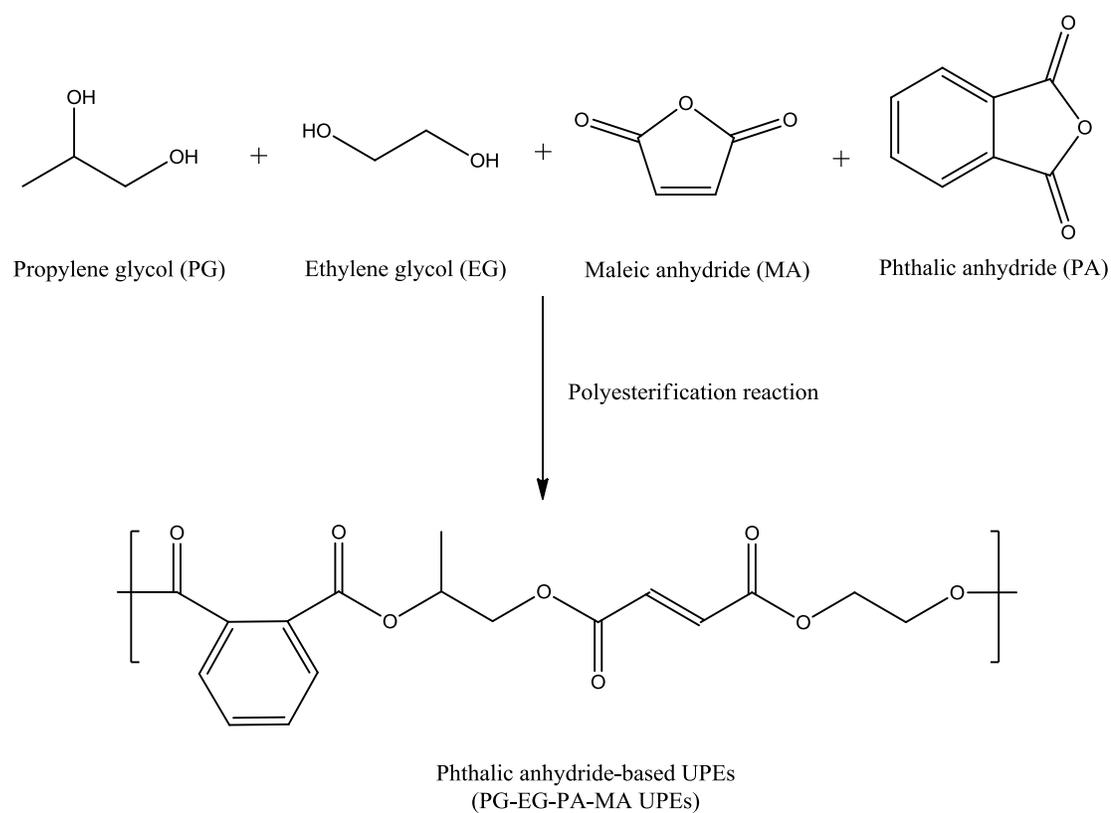


Figure 1.1 A representative synthetic scheme for the preparation of PG-EG-PA-MA UPEs

1.3.1 Diols

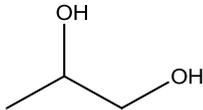
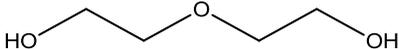
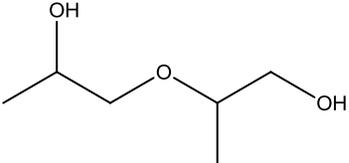
A diol is a chemical that contains two hydroxyl groups on the molecule. Table 1.1 summarizes the diols that are used for the preparation of UPEs in the industry, and features of the diols, the resulting UPEs, and the resulting cured products (including cured resins and composites).

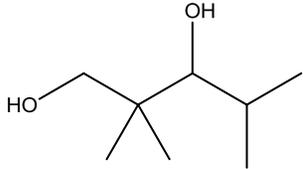
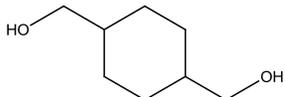
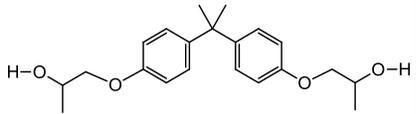
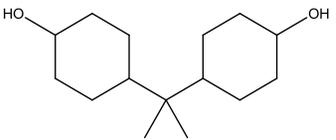
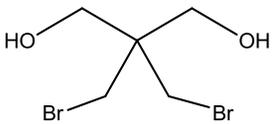
Propylene glycol is the most commonly used diol for UPEs because it is inexpensive and can impart good general properties to UPEs and cured products.^{1, 9} Ethylene glycol is also inexpensive and can impart rigidity to cured products.^{1, 9} Neopentyl glycol can impart good UV, water, and chemical resistances to cured products.^{9, 12}

The flexibility and toughness of the cured UPE resins increase and the rigidity decreases when the chain lengths of aliphatic diols and aliphatic dibasic acids increase.⁹ For example, the cured UPE resins from a shorter chained ethylene glycol have a lower flexibility, a lower toughness, but a higher rigidity than those from longer chained diethylene glycol or dipropylene glycol when dibasic acids used and molecular weights obtained are the same.⁹

Propoxylated bisphenol A is a diol that contains two aromatic rings on its molecule. Use of propoxylated bisphenol A can generally improve the rigidity, the strengths, and the chemical resistances of the cured UPE resins.⁹ Other diols listed in Table 1.1 are less common, but are used for some UPEs that provide some special properties.

Table 1.1. Diols for the preparations of UPEs^{1,9}

Name	Structure	Features		
		Diols	UPEs	Cured products
Propylene glycol		Low cost		High toughness
Ethylene glycol		Low cost		High rigidity
Diethylene glycol			Good flexibility	High toughness
Neopentyl glycol				High UV resistance, water resistance (i.e, hydrolytic stability), and chemical resistance
Dipropylene glycol			Good flexibility	High toughness

Name	Structure	Features		
		Diols	UPEs	Cured products
2,2,4-Trimethyl-1,3-pentanediol				High water and chemical resistance
1,4-Cyclohexanedimethanol				High chemical resistance
Propoxylated bisphenol A				High strength, toughness, water resistance, and chemical resistance
Hydrogenated bisphenol A				High strength, toughness, water resistance, and chemical resistance
Dibromoneopentyl glycol				High flame retardance

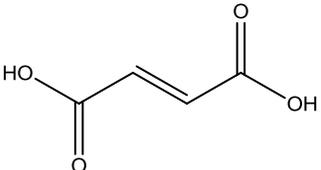
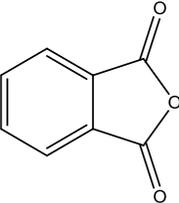
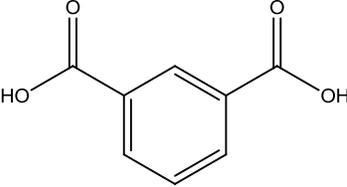
1.3.2 Dibasic acids and acid anhydrides

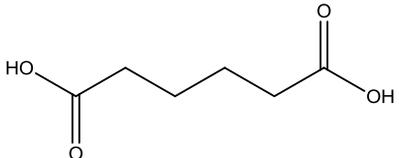
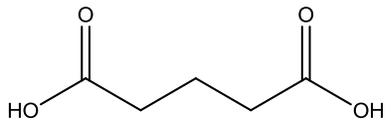
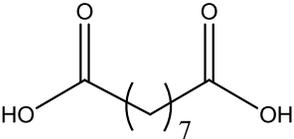
A dibasic acid is a chemical containing two carboxylic acid groups per molecule. Dibasic acids for the synthesis of UPEs can also be in the form of acid anhydrides. Table 1.2 summarizes the dibasic acids and acid anhydrides that are used for the preparation of UPEs in the industry, and features of the dibasic acids and acid anhydrides, the resulting UPEs, and the resulting cured products (including cured resins and composites).

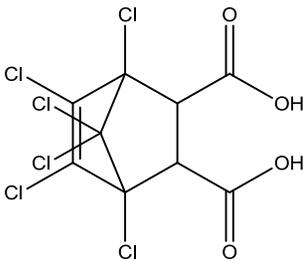
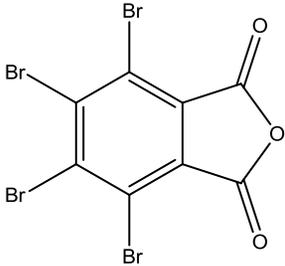
1.3.2.1 Unsaturated dibasic acids

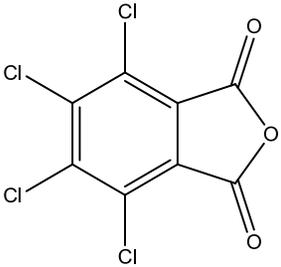
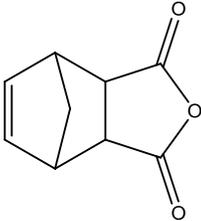
The C=C bonds in UPEs are typically introduced from an unsaturated dibasic acid. Unsaturated dibasic acids that are commonly used for production of UPEs include maleic anhydride and fumaric acid. Maleic anhydride is less expensive than fumaric acid, thus being the most commonly used unsaturated dibasic acid for the preparation of UPEs. The C=C bond of fumaric acid is more reactive to styrene than that of maleic anhydride.

Table 1.2. Dibasic acids and acid anhydrides for the preparations of UPEs^{1,9}

Name	Structure	Features		
		Dibasic acids and acid anhydrides	UPEs	Cured products
Maleic anhydride		Low cost	unsaturation	
Fumaric acid			high reactivity of the C=C bond with styrene	
Phthalic anhydride		Low cost	Increase in the compatibility between UPE and styrene	
Isophthalic acid				High strength, toughness, thermal stability (i.e., high heat distortion/deflection temperature), water resistance, and chemical resistance

Name	Structure	Features		
		Dibasic acids and acid anhydrides	UPEs	Cured products
Terephthalic acid				High thermal stability
Adipic acid			Good flexibility	High toughness and weathering resistance
Glutaric acid			Good flexibility	High toughness and weathering resistance
Dimer acids			Good flexibility	High toughness and weathering resistance
Azelaic acid			Good flexibility	High toughness and weathering resistance

Name	Structure	Features		
		Dibasic acids and acid anhydrides	UPEs	Cured products
Chlorendic acid				High flame retardance and chemical resistance
Tetrabromophthalic anhydride				High flame retardance and chemical resistance

Name	Structure	Features		
		Dibasic acids and acid anhydrides	UPEs	Cured products
Tetrachlorophthalic anhydride				High flame retardance and chemical resistance
Nadic anhydride			Good air drying properties	

1.3.2.2 Maleate-to-fumarate isomerization

The C=C bonds of maleic anhydride and fumaric acid are in *cis*- and *trans*-configuration, respectively. The *trans*-configuration is more linear, less strained, and in lower energy level than the *cis*-configuration.^{16, 17} As a result, some C=C bonds of maleic anhydride isomerize from *cis*- to *trans*-configuration during the synthesis of UPEs (Figure 1.2).^{16, 17}

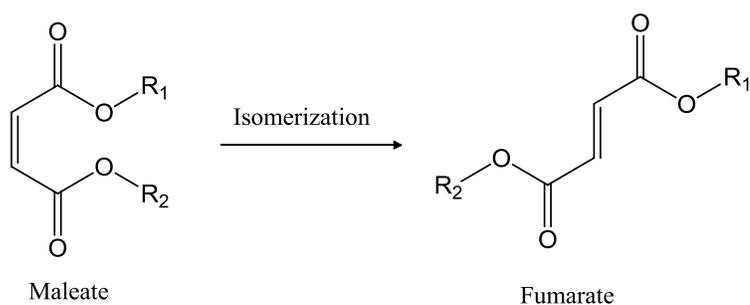


Figure 1.2 Isomerization of maleate to fumarate

The isomerization from maleate to fumarate can significantly increase the reactivity of the UPEs to styrene in the crosslinking reactions because the *trans*-C=C bond of the fumarate is more reactive to styrene than the *cis*-C=C bond of the maleate.⁹ It has been reported that the reactivity of ethyl fumarate to styrene was twenty-one times higher than that of ethyl maleate.¹⁸

The degree of the isomerization is greatly affected by the chain length of the diol used.¹⁷ The diol with a shorter chain length tends to result in a higher degree of the isomerization than that with a longer chain length. It was found that the degree of the

isomerization increased from 36 to 64% in the resulting UPEs when 1,6-hexamethylene glycol was replaced by ethylene glycol in the synthesis of UPEs.¹⁷ The degree of isomerization increased to as high as 96% when propylene glycol was used for replacing ethylene glycol or 1,6-hexamethylene glycol.¹⁷ It was proposed that the C=C bonds of polyesters from propylene glycol and maleic acid were more strained than those of polyesters from ethylene glycol (or 1,6-hexamethylene glycol) and maleic acid.¹⁷ The high strain meant the high energy level that tended to be lowered through the isomerization of the C=C bonds from *cis*- to *trans*-configurations.¹⁷ The isomerization is also facilitated by a high reaction temperature.¹⁷ It was found that the isomerization increased from 34 to 74% when the esterification reaction temperature increased from 105 to 140 °C. Further increase in the reaction temperature from 140 to 180 °C resulted in the 96% isomerization.¹⁷

The degree of the isomerization can be measured by the comparison of the peak area at 6.24 ppm (protons on the C=C bond of maleate) with that at 6.82 ppm (protons on the C=C bond of fumarate) in ¹H NMR spectra of UPEs.¹⁹

The isomerization during the preparation of UPEs works well economically because maleic anhydride is less expensive than fumaric acid and UPEs containing the *trans*-C=C bonds are more reactive to crosslinking agents and easier to cure than those containing the *cis*-C=C bonds. The degree of the isomerization in most commercial UPEs is typically above 80%.²⁰

1.3.2.3 Addition of diols to C=C bonds of maleates (Ordelt reaction)

It was found that C=C bonds of maleates can react with hydroxyl groups on diols via Michel addition at a high temperature, leading to saturation of the C=C bonds and the formation of branches in UPEs (Figure 1.3).^{21, 22} Such a side reaction was first investigated by Ordelt and coworkers; and is now known as Ordelt reaction.^{21, 22} Ordelt reaction is not desirable because it consumes C=C bonds and thus reduces the number of crosslinking sites of the resulting UPEs. It was found that approximately 10–20 % of the C=C bonds in the resulting UPEs had been saturated.^{23, 24} This side reaction also leads to the loss of diols for the polyesterification reaction. The C=C bonds of fumarates, however, usually do not undergo Ordelt reaction.²⁵

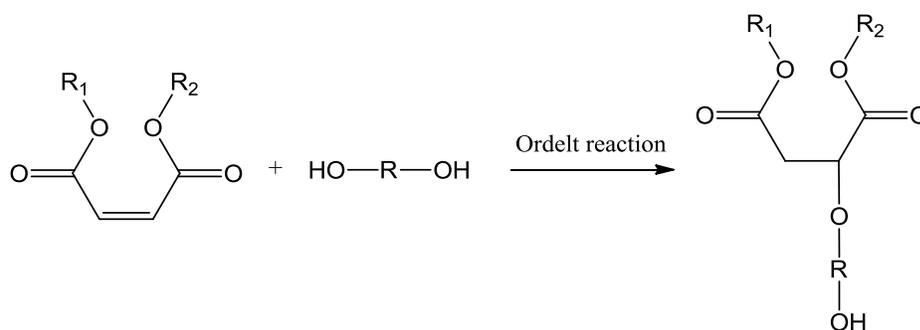


Figure 1.3 The addition of diols on C=C bonds of maleate

1.3.2.4 Saturated dibasic acids

UPEs that are derived from diols and unsaturated dibasic acids only have a high degree of unsaturation. Each C=C bond is a potential site for reactions with a crosslinking agent. The high degree of the unsaturation typically results in a high curing speed and a high crosslinking density. As a result, the cured resins are usually

brittle and often have cracks. It was found that the partial replacement of maleic anhydride with phthalic anhydride significantly reduced the brittleness and completely resolved the cracking issues of the cured UPE resins and the resulting fiber-reinforced UPE composites.²⁶ This created the first commercially useful UPE resins.

Saturated dibasic acids and acid anhydrides that are used for the preparation of UPEs are summarized in Table 1.2. In general, aromatic saturated dibasic acids can improve the stiffness and strength of the UPEs.¹ Phthalic anhydride and isophthalic acid are two most commonly used saturated dibasic acids or acid anhydrides. Phthalic anhydride is relatively inexpensive and makes the resulting UPEs soluble in styrene. Isophthalic acid is about 10% more expensive than phthalic anhydride. The increase in the cost for isophthalic acid is well compensated by significantly improved properties of the UPE resins from isophthalic acid. Cured isophthalic acid-based UPE resins and fiber-reinforced UPE composites generally have higher flexural strength, tensile strength, toughness, heat stability, and resistances to water and chemicals than cured phthalic anhydride-based UPE resins and fiber-reinforced UPE composites.^{27, 28}

Aliphatic saturated dibasic acids such as adipic acid are less rigid than aromatic saturated dibasic acids. Adipic acid can improve the flexibility and toughness, but reduce the strength and hardness of the cured UPE resins. The incorporation of adipic acid in the UPEs also improved resistances of the cured UPE resins to UV light and oxygen.^{1, 9} Other aliphatic saturated dibasic acids such as glutaric acid and dimer

acids have similar effects to adipic acid. However, they are more expensive than adipic acid and thus less commonly used in the industry.

Halogen-containing saturated dibasic acids or acid anhydrides are used for improving the flame retardance of the cured UPE resins. Chlorendic acid, tetrabromophthalic anhydride, and tetrachlorophthalic anhydride are three most commonly used dibasic acids for the improvement.⁹ Chlorendic acid can also impart chemical resistance to the cured UPE resins.^{29, 30} Nadic anhydride can improve the air drying properties of the UPE resins.⁹

1.3.5 Polyesterification reaction

The polyesterification reaction is generally conducted in an inert atmosphere, so as to minimize oxidative degradation of C=C bonds at high reaction temperatures.³¹ The inert gas (e.g., nitrogen) is usually introduced from the bottom of the reactor, which provides additional benefits of improving the mixing of the materials and increasing the rate of removing the reaction by-product, water.⁹

The molar ratio of diols to dibasic acids can range from 1.05 to 1.20.³¹ Diols are added in excess, for making up their loss due to the Ordel reaction, evaporation, and decomposition at high reaction temperatures. The reaction temperature is usually in the range of 180–220 °C, with a reaction time ranging from 8 to 28 hours.^{9, 20}

An esterification catalyst is often used for increasing the polyesterification rate.⁹ Common esterification catalysts include mineral acids such as sulfuric acid, aryl

sulfonic acids such as *p*-toluenesulfonic acid, tin compounds such as dibutyltin oxide, and titanates such as tetrabutyl titanate.^{9, 14} However, the presence of a catalyst such as sulfuric acid or *p*-toluenesulfonic acid in a UPE can result in side effects such as darkening the UPE.²⁷ As a result, the reaction mixture is usually neutralized at the end of the polyesterification reaction if an acid catalyst is used.²⁷ Tin compounds usually have a good balance between a high efficiency of catalyzing the polyesterification reaction and low side reactions.⁹

The polyesterification reaction is typically monitored through the measurement of the acid number of the reaction mixture. As the dibasic acids are consumed, the acid number of the reaction mixture decreases. The acid number is measured by the titration of the reaction products with potassium hydroxide (KOH) and is expressed as milligrams of KOH required for the neutralization of 1 g of the reaction products. Assuming each polyester chain contains one acid end group, The number-averaged molecular weight (M_n) can be estimated by the following empirical formula³²:

$$M_n = \frac{56000}{\text{Acid number}}$$

A more accurate method for estimating the M_n is through measurements of both the acid number and the hydroxyl number of the reaction products. In this case, the M_n can be estimated by the following empirical formula³²:

$$M_n = \frac{112220}{\text{Acid number} + \text{Hydroxyl number}}$$

ASTM D3644 is a commonly used method for measuring the acid number. ASTM D2849 is a commonly used method for measuring the hydroxyl number.

UPEs generally do not have very high molecular weights, with the M_n ranging from 700 to 3000.²⁰ As a result, UPEs are generally considered to be reactive low-molecular-weight prepolymers, which can be cured by further reactions with a crosslinking agent such as styrene.⁹

1.4 Crosslinking agents and curing reactions

1.4.1 Crosslinking agents

UPEs alone are seldom useful products. The crosslinking reactions among the C=C bonds in the UPEs are difficult. Only a very limited amount crosslinks may be formed after a prolong reaction time at high temperatures.³³⁻³⁵ The cured products typically have very low strengths. It was found that the crosslinking of UPEs was significantly improved by curing the UPEs with a crosslinking agent.⁷

Styrene is by far the most commonly used crosslinking agent for UPEs, mainly because it is relatively inexpensive and readily available, and can impart good general properties to the cured UPE resins and fiber-reinforced UPE composites.

In the industrial production of UPE resins, the UPEs are prepared in a reactor and then cooled down to a molten form before being discharged into a mixing tank that contains styrene. For prevention of UPEs from crosslinking in the mixing tank, a

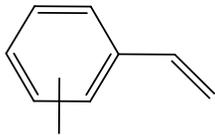
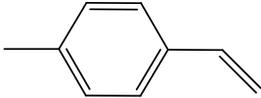
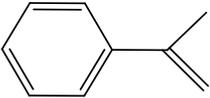
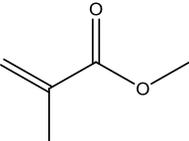
polymerization inhibitor is added to styrene before mixing. Commonly used inhibitors are hydroquinone or substituted hydroquinones such as toluhydroquinone or *tert*-butylhydroquinone.^{9, 20} While a low temperature decreases the efficiency of the mixing, a high temperature increases the risk of crosslinking *in situ*. The optimum mixing temperature is around 82 – 93 °C.⁹ The styrene content generally ranges from 35% to 50 % by weight in commercial UPE resins.^{36,37} For lowering the emission of styrene in the use of UPE resins and fiber-reinforced UPE composites, UPE resins with the styrene content of below 35% have been recently developed.³⁸ The styrene content of some UPE resins has been reported to be as low as 20%.³⁸

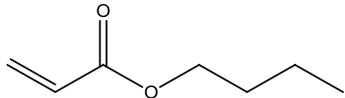
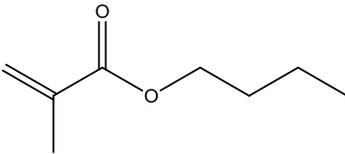
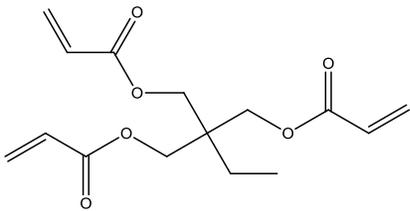
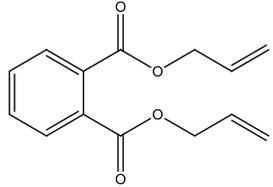
Styrene copolymerizes well with the C=C bonds in UPE resins, thus resulting in superior fiber-reinforced UPE composites. Styrene also has an added advantage of being able to dissolve most UPEs for the formation of a pourable solution. Most composite-manufacturing processes require that UPE resins can be poured at room temperature onto reinforcing fibers. In general, the viscosity of UPE resins decreases as the styrene content increases or as the molecular weight of the UPEs decreases. The viscosity of commercial UPE resins typically ranges from 0.05 Pa·s to 6 Pa·s at room temperature.⁹

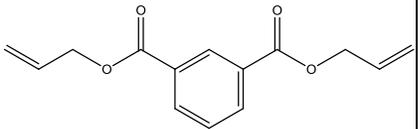
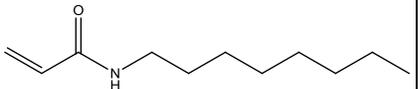
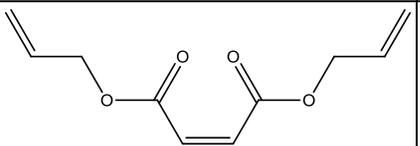
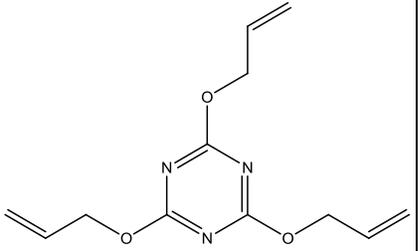
Besides styrene, some other crosslinking agents are also currently used with UPEs in the industry (Table 1.3). They are less commonly used than styrene, but can provide UPE resins and the cured products with some special properties. For example, the

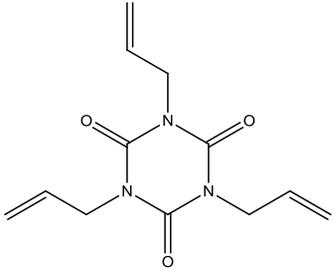
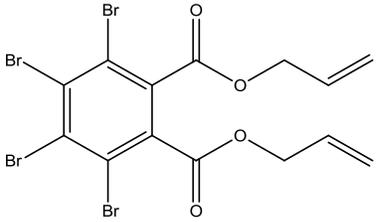
replacement of styrene with methyl methacrylate was found to improve the weathering properties of the resulting composites.

Table 1.3. Non-styrene crosslinking agents used with UPEs

Name	Structure	Features (compared to styrene or styrene-containing products)	
		Crosslinking agents	Cured products
Vinyl toluene		Lower volatility, higher flash point	
4-Methyl styrene		Lower volatility, higher flash point	
α -Methyl styrene		Generating lower reaction heat (less exothermic; cooler cure)	Reduced physical properties
Methyl methacrylate			Improved weather resistance

Butyl acrylate			Improved weather resistance
Butyl methacrylate			Improved weather resistance
Trimethylolpropane triacrylate		Can be cured by UV light or electron beams	Improved weather resistance
Diallyl phthalate		Very low volatility (used for molding compounds)	

Diallyl isophthalate		Very low volatility (used for molding compounds)	
Octyl acrylamide		Solid monomer (used for molding compounds)	
Diallyl maleate			High thermal stability
Triallyl cyanurate			High thermal stability

Triallyl isocyanurate	 <p>The structure shows a central 1,3,5-triazin-2,4,6-trione ring. Each of the three nitrogen atoms in the ring is bonded to a prop-2-en-1-yl (allyl) group. The allyl groups are attached to the nitrogens at the 2, 4, and 6 positions of the triazine ring.</p>		High thermal stability
Diallyl tetrabromophthalate	 <p>The structure shows a central benzene ring with four bromine atoms (Br) at the 1, 2, 4, and 5 positions. At the 3 and 6 positions, there are two ester groups, each with a prop-2-en-1-yl (allyl) group attached to the oxygen atom. The allyl groups are attached to the oxygens at the 3 and 6 positions of the benzene ring.</p>		High Flame retardance

1.4.2 Initiators

Organic peroxides are commonly used as initiators for the curing of commercial UPE resins. They can be divided into eight classes³⁹: ketone peroxides such as methyl ethyl ketone peroxide (MEKP), hydroperoxides such as cumene hydroperoxide (CHP), diacyl peroxides such as dibenzoyl peroxide (BPO), dialkyl peroxides such as di-*tert*-butyl peroxide (TBP), peroxyesters such as *tert*-butyl peroxybenzoate (TBPB), peroxyketal such as 1,1-bis(*tert*-amylperoxy)cyclohexane (BTAPCH), peroxydicarbonates such as di(4-*tert*-butylcyclohexyl) peroxydicarbonate (TBCHPDC), and peroxy monocarbonates such as *tert*-butylperoxy 2-ethylhexyl carbonate (TBPEHC) (Figure 1.4). MEKP, CHP, and BPO are three most commonly used peroxide initiators.

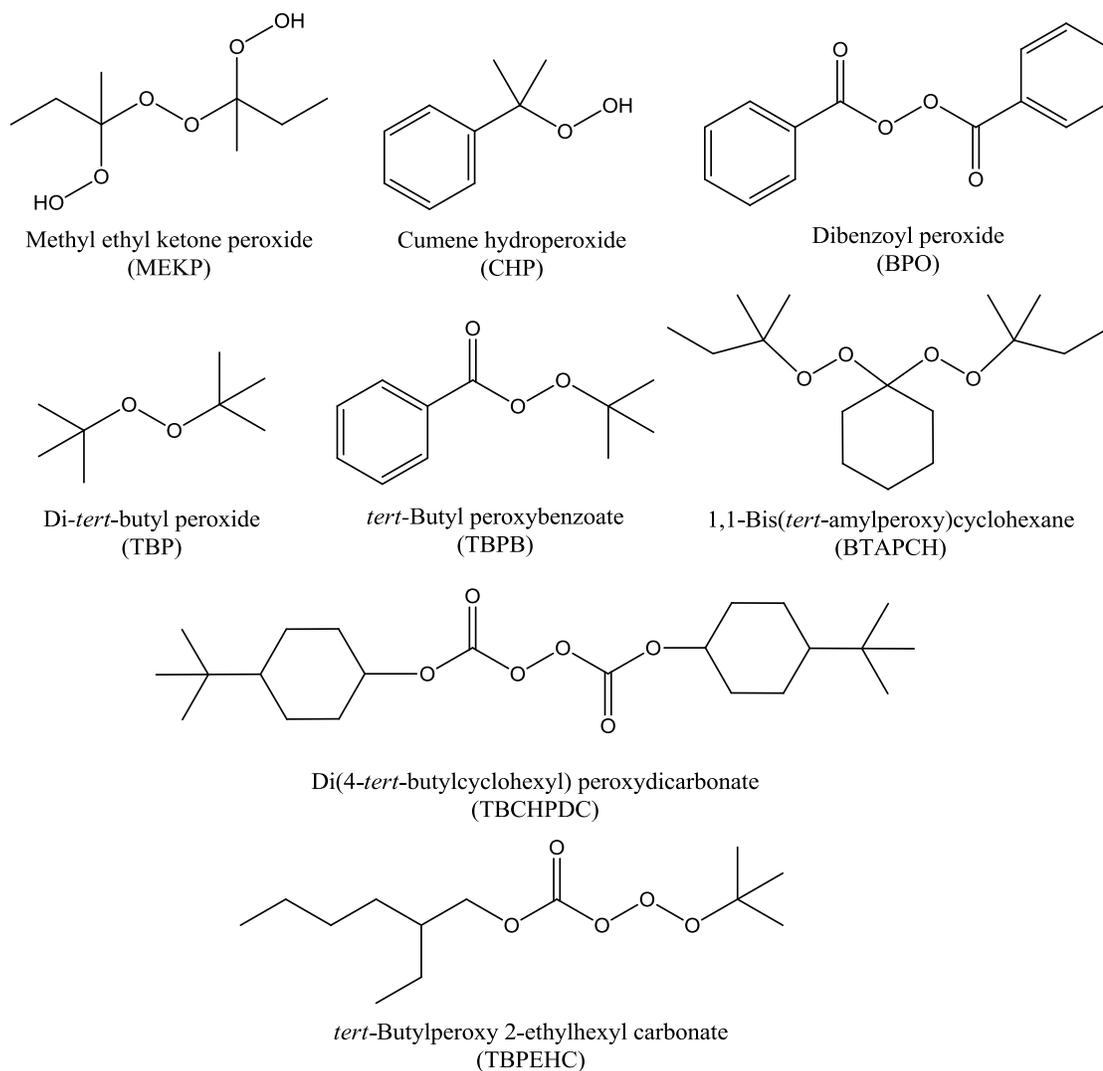


Figure 1.4 Eight classes of organic peroxide initiators

All peroxides are thermally unstable and can decompose into free radicals at an elevated temperature (Figure 1.5). The decomposition rate of a peroxide initiator is manifested by its half-life. Table 1.4 summarizes the temperatures at which half-lives of peroxide initiators are 0.1, 1, or 10 h.^{40,41} The usage of an initiator is usually about 1.5–2% of the resin weight.¹

a –ROOH group, generating a free radical.^{1, 30} Co^{3+} is not stable and can be easily reduced to Co^{2+} by another –ROOH group.^{1, 30} Because Co^{2+} can be regenerated, only a very small amount of cobalt salt is needed for promoting the decomposition of the organic peroxide, usually less than 0.5% of the resin weight.^{1, 30} An excessive amount of a cobalt compound can be detrimental to the curing reaction as the cobalt ions can destroy free radicals by converting them into ions (Figure 1.7).³⁰

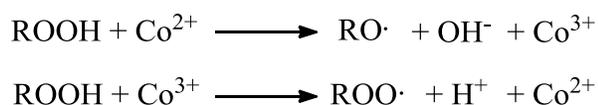


Figure 1.6 Decomposition of a hydroperoxide by cobalt ions



Figure 1.7 Conversion of a free radical to an ion by excessive cobalt ions

A secondary promoter is often used together with a cobalt compound for further improvement of the curing rate. Commonly used secondary promoters include tertiary amines such as N,N-dimethyl aniline and N,N-diethyl aniline, acetamides such as N,N-dimethylacetoacetamide, acetoacetates such as methyl acetoacetate, and quaternary salts such as triphenylsulfonium chloride.⁹

Cobalt compounds, however, is not effective for promoting the decomposition of diacyl peroxides such as BPO. The decomposition of the BPO can be effectively promoted by tertiary amines. N,N-dimethyl aniline and N,N-diethyl aniline are two commonly used tertiary amines for BPO. As shown in Figure 1.8, an unstable cationic

intermediate is first formed and then decomposes to generate a radical cation and a benzoyloxy radical.⁴² It was found that polymers prepared by such initiator systems did not contain nitrogen atoms, indicating that the radical cation did not participate in the curing reactions.⁴²

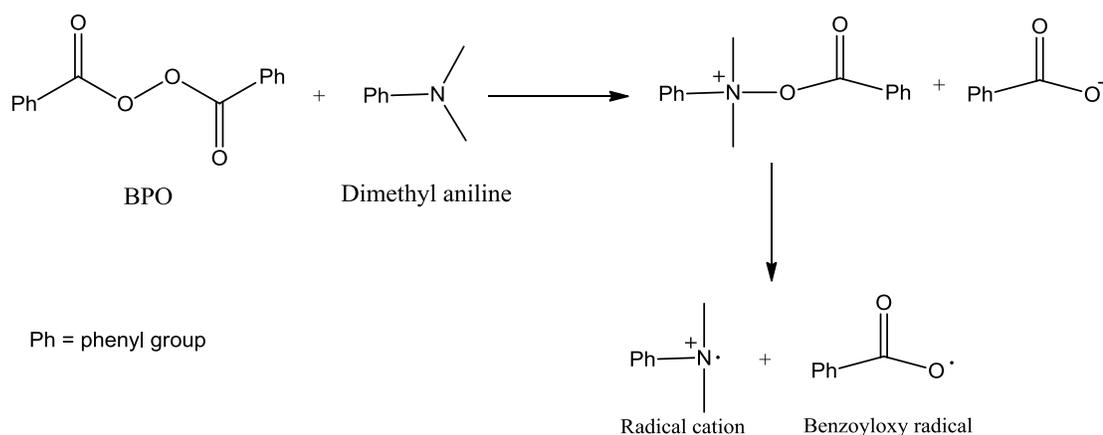


Figure 1.8 Decomposition of dibenzoyl peroxide (BPO) promoted by N,N-dimethyl aniline

The reaction between a promoter and an initiator is very fast at room temperature. Direct mixing of these two chemicals can result in very violent reaction with the risk of fire or even explosion. Therefore, a promoter and an initiator should be added into UPE resins separately. Many commercial UPE resins already contain a promoter such as a cobalt compound.⁹ A peroxide initiator such as MEKP or CHP is typically added to a UPE resin right before the UPE resin is used for production of fiber-reinforced UPE composites.

With some particular initiator/promoter systems, the curing of UPE resins can be accomplished at room temperature without any external heat. The room temperature curing technique is especially useful for some manufacturing processes where a very large part is produced and a long production time is not a problem. For example, boat hulls are made with glass fiber-reinforced UPE composites that are usually cured at room temperature by a MEKP/cobalt initiator system. The curing of UPE resins is typically an exothermic reaction; the heat generated from the curing reaction further facilitates the curing reaction.

1.4.3 Stages of curing reactions

The curing of a UPE resin typically goes through three stages.⁴³ The first stage is called gelation. In this stage, the UPE resin changes from a pourable liquid to a soft gel as UPE chains begin to be crosslinked. The time needed for the gelation to occur is called gel time. The gelation usually occurs when less than 5 mol% of C=C bonds are crosslinked.⁴⁴

The second stage is called hardening. In this stage, more crosslinks among UPE chains are established and the resin changes from a soft gel to a rigid solid. The surface of the cured resins becomes dry and not tacky. The hardening is usually achieved when the consumption of the C=C bonds in UPE resins for the crosslinking is about 50%.⁴⁴

The third stage is called maturing, which is also known as post-cure. The maturing is a slow process which can last for several days or even several weeks if it is carried out at room temperature. The maturing can also be carried out at elevated temperatures, which can significantly shorten the maturing time to several hours. The maturing process is typically monitored by measuring the hardness (e.g., Barcol hardness) of the cured products. As the maturing proceeds, the hardness of the cured products increases. The cured products acquires their full properties at the end of the maturing process when more than 90 mol% of the C=C bonds are usually consumed.⁹

1.4.4 Chemical structure of styrene-crosslinked UPE resins

A representative scheme of styrene-crosslinked UPE resins is shown in Figure 1.9. There are three possible linkages in the crosslinked networks. Linkage I is formed by copolymerization of styrene and UPEs. Linkage II is formed by homopolymerization of styrene. Linkage III is formed by homopolymerization of UPEs.

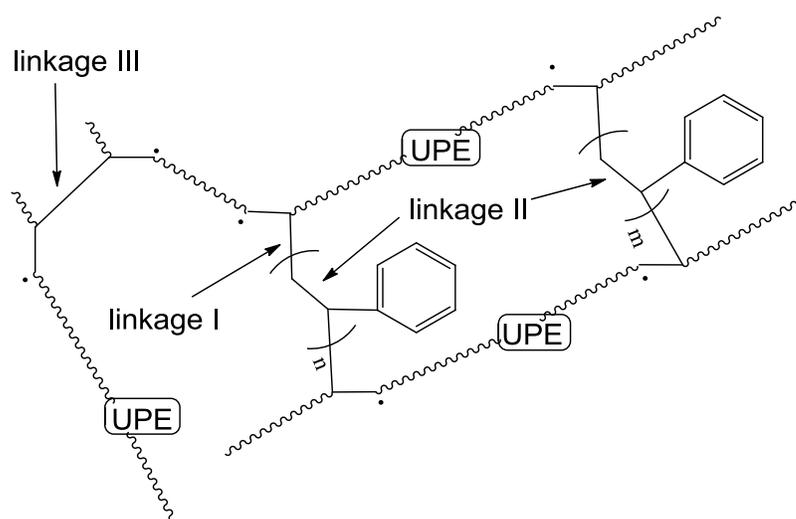


Figure 1.9 Representative scheme of styrene-crosslinked UPE resins

1.5 Types of commercial UPE resins

Commercial UPE resins can be broadly grouped into two types based on their costs and performances: general purpose resins and specialty resins (also called high-performance resins). General purpose resins offer acceptable properties for most general applications. For general purpose resins, users' primary concern is the cost of the resins. Specialty resins are more expensive than general purpose resins; but can offer significantly enhanced product properties such as high mechanical strengths, high resistance to corrosion, and/or high fire retardance.

1.5.1 General purpose resins

1.5.1.1 Phthalic anhydride-based UPE resins

Commercial phthalic anhydride-based UPE resins, more commonly known to the industry as *ortho* resins, general purpose resins, or GP resins, are typically mixtures of phthalic anhydride-based UPEs and styrene. The phthalic anhydride-based UPEs are reaction products of maleic anhydride (MA), phthalic anhydride (PA), and inexpensive diols such as propylene glycol (PG) and ethylene glycol (EG). A representative synthetic scheme for the preparation of the UPEs from PG, EG, PA, and MA is shown in Figure 1.1.

The phthalic anhydride-based UPE resins are generally of low-cost and have adequate mechanical properties. They are used in applications which do not require high mechanical properties, high heat stability, or high chemical resistance.⁹

Phthalic anhydride-based UPEs generally cannot be synthesized to high molecular weights. The M_n is typically around 900 g/mol, the M_w (weight-averaged molecular weight) is around 2400 g/mol, and the polydispersity is about 2.7 (M_w/M_n).⁹ The low molecular weight is due to the decarboxylation of phthalic anhydride at the high reaction temperatures required for the effective polycondensation reactions.⁹ Phthalic anhydride-based UPE resins typically contain 35–45% of styrene by weight.³⁷

1.5.1.2 Dicyclopentadiene-modified UPE resins

Commercial dicyclopentadiene-modified UPE resins, commonly called DCPD resins, are typically mixtures of styrene and dicyclopentadiene-modified UPEs that are reaction products of maleic anhydride, inexpensive diols such as propylene glycol, ethylene glycol and diethylene glycol, dicyclopentadiene, and optionally saturated dibasic acids or acid anhydrides. Dicyclopentadiene can be easily obtained from cyclopentadiene, an inexpensive and readily available petrochemical.⁴⁵ Cyclopentadiene can dimerize to form dicyclopentadiene at room temperature.⁴⁵ However, dicyclopentadiene can go back to cyclopentadiene via a retro-Diels-Alder reaction above 150 °C.⁴⁵ Dicyclopentadiene is less expensive than phthalic anhydride, which encourages the substitution of phthalic anhydride with dicyclopentadiene in the

Figure 1.10 Representative synthetic scheme for the preparation of EG-DEG-MA-NA UPEs by the Diels-Alder reaction method

Cyclopentadiene may be directly added to the mixture of maleic anhydride, diols and a saturated bibasic acid followed by the polyesterification reaction. Cyclopentadiene may be added to the UPE after the polyesterification reaction is already finished. There are some drawbacks for the dicyclopentadiene-modified UPE resins from this Diels-Alder reaction method, including the darkened color of the resins, bad odor from residual dicyclopentadiene, and the reduced reactivity of the resins due to the consumption of reactive C=C bonds on the UPEs.⁴⁷

1.5.1.2.2 Hydrolysis method

As shown in Figure 1.11, mixtures of maleic anhydride, water, dicyclopentadiene are stirred in a reactor, which would result in partial hydrolysis of maleic anhydride to form maleic acid.⁴⁸ Because water is used as a starting material, this hydrolysis method is also called the “water process.”²⁰

The resulting maleic acid would react with dicyclopentadiene for formation of dicyclopentadiene-maleic acid adducts (i.e., dicyclopentadiene-capped maleic acid).⁴⁹ Dicyclopentadiene has a norbornene ring and a cyclopentene ring in its molecule. The C=C bond on the norbornene ring has higher reactivity than the C=C bond on the cyclopentene ring due to the high strain of the norbornene ring, and can react with a H^+ to form a carbon cation intermediate for the addition reaction with $RCOO^-$.⁴⁷ The addition to the C=C bond on the cyclopentene ring could also occur, but is not

common during the synthesis of UPEs, because the reaction requires harsh conditions such as the use of a very strong acid as a catalyst (e.g., perchloric acid).⁴⁷ The reaction temperature is carefully controlled not to exceed 140 °C so that the undesirable decomposition of dicyclopentadiene to cyclopentadiene is minimized.⁴⁷

The resulting dicyclopentadiene-capped maleic acid is polymerized with maleic anhydride, glycols such as ethylene glycol and diethylene glycol, and optionally a saturated dibasic acid/acid anhydride at 200 °C to generate the UPEs with their chain ends being capped with the dicyclopentadiene-maleic acid adducts.

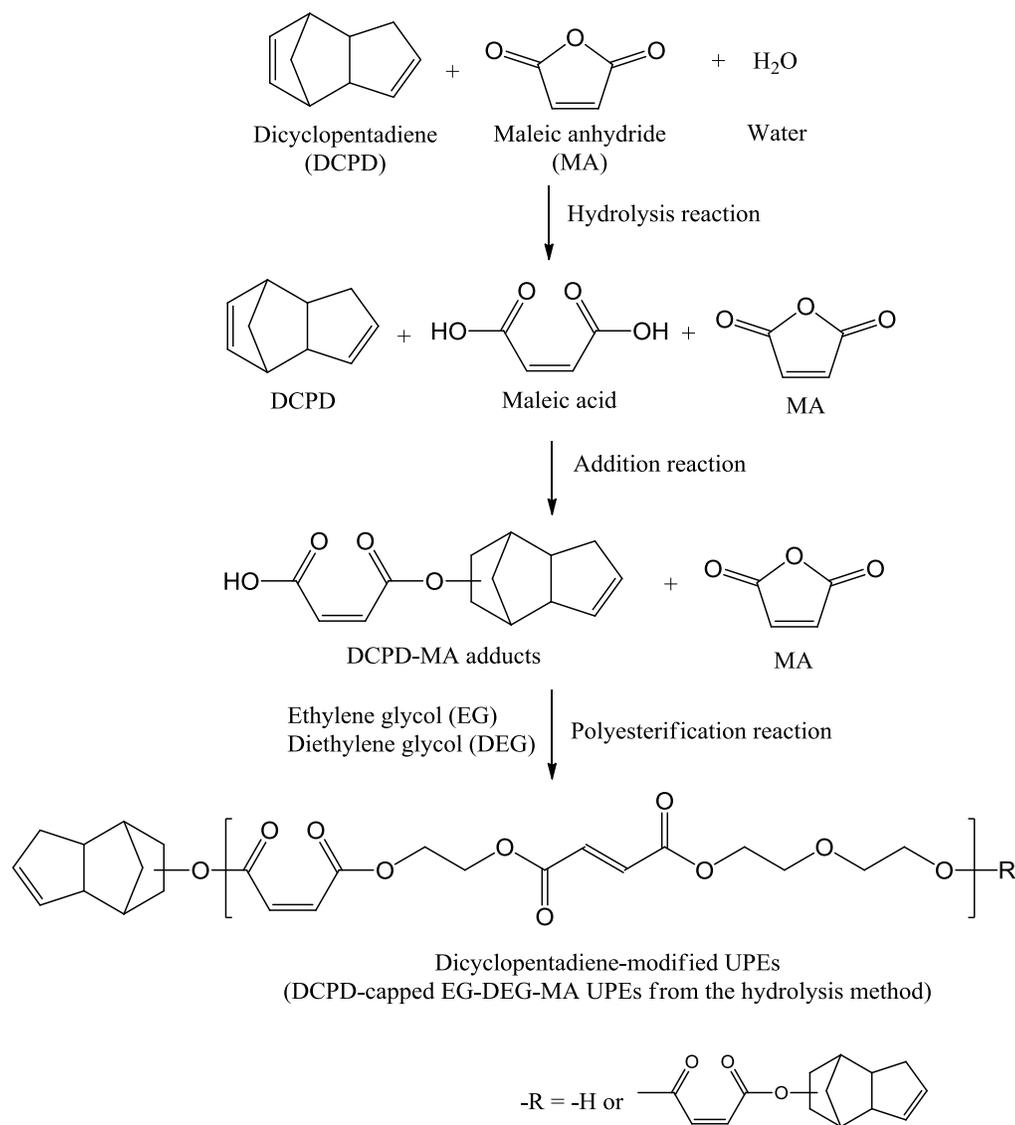


Figure 1.11 Representative synthetic scheme for the preparation of DCPD-capped EG-DEG-MA UPEs by the hydrolysis method

1.5.1.2.3 Direct addition methods

A so called “end” method of capping UPE chain ends with dicyclopentadiene is shown in Figure 1.12.⁵⁰ Ethylene glycol, diethylene glycol, and maleic anhydride are

polymerized at 200 °C to form UPEs with the desired molecular weight, and the reaction temperature is then lowered to 120–140 °C, followed by addition of dicyclopentadiene. Dicyclopentadiene reacts with the carboxylic acid groups⁴⁹ and the hydroxyl groups⁵¹ on the polyester chain ends, usually in the presence of an acid catalyst such as sulfuric acid to form dicyclopentadiene-capped UPEs.

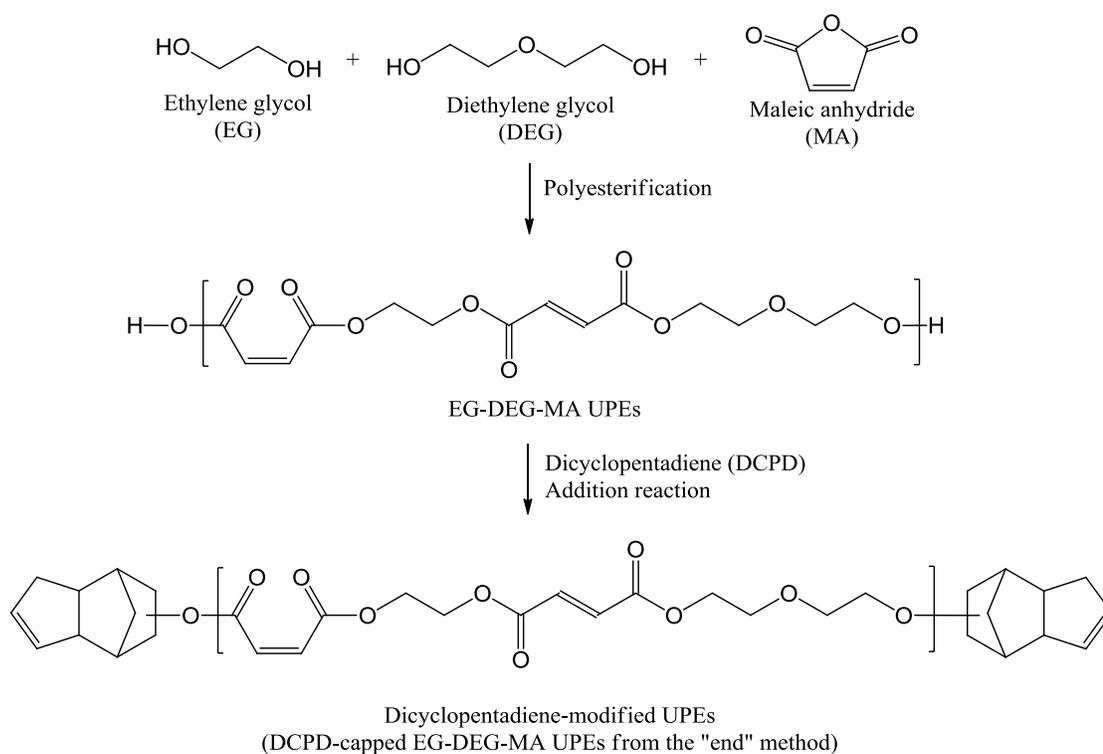


Figure 1.12 Representative synthetic scheme for the preparation of DCPD-capped EG-DEG-MA UPEs by the “end” method

A so called “beginning” method for the preparation of dicyclopentadiene-capped UPEs is shown in Figure 1.13.⁵² Dicyclopentadiene is added to the mixture of glycols such as ethylene glycol and maleic anhydride in a reactor at the beginning of the

polyesterification reaction.⁵² The polyesterification reaction is first carried out at 120–140 °C and then at 200 °C. The additions of dicyclopentadiene to ethylene glycol or ethylene glycol-maleate form dicyclopentadiene-capped adducts, including ethylene glycol-dicyclopentadiene adducts and ethylene glycol-maleate-dicyclopentadiene adducts. Subsequently, the reaction temperature is increased to 200 °C. The polyesterification reaction of these adducts with remaining ethylene glycol, maleic anhydride, and ethylene glycol-maleate form dicyclopentadiene-capped UPEs.

The “beginning” method typically generates dicyclopentadiene-capped UPEs with lower molecular weight and broader molecular weight distribution than the “end” method.⁴⁷ The “beginning” method is easier to conduct and is more economical than other methods.⁴⁷ Dicyclopentadiene-modified UPEs prepared with the “beginning” method or the hydrolysis method typically have low molecular weights (the M_n is less than 1000 g/mol) because the dicyclopentadiene-capped adducts terminates the chain growth and results in reduced chain length.²⁰ The low molecular weight allows a low styrene content (typically around 35%) in the dicyclopentadiene-modified UPE resins for achieving a good processing viscosity.³⁰ Some dicyclopentadiene-modified UPE resins can have a styrene content of as low as 20%. Such resins with reduced styrene contents are useful for lowering styrene emission in the workplace.

Compared to the phthalic anhydride-based UPE resins, the dicyclopentadiene-modified UPE resins typically improve the following properties of the cured resins

and the resulting fiber-reinforced composites: thermal stability, stiffness, shrinkage, air drying properties and resistances to UV, chemicals and water.^{1, 12, 47, 53}

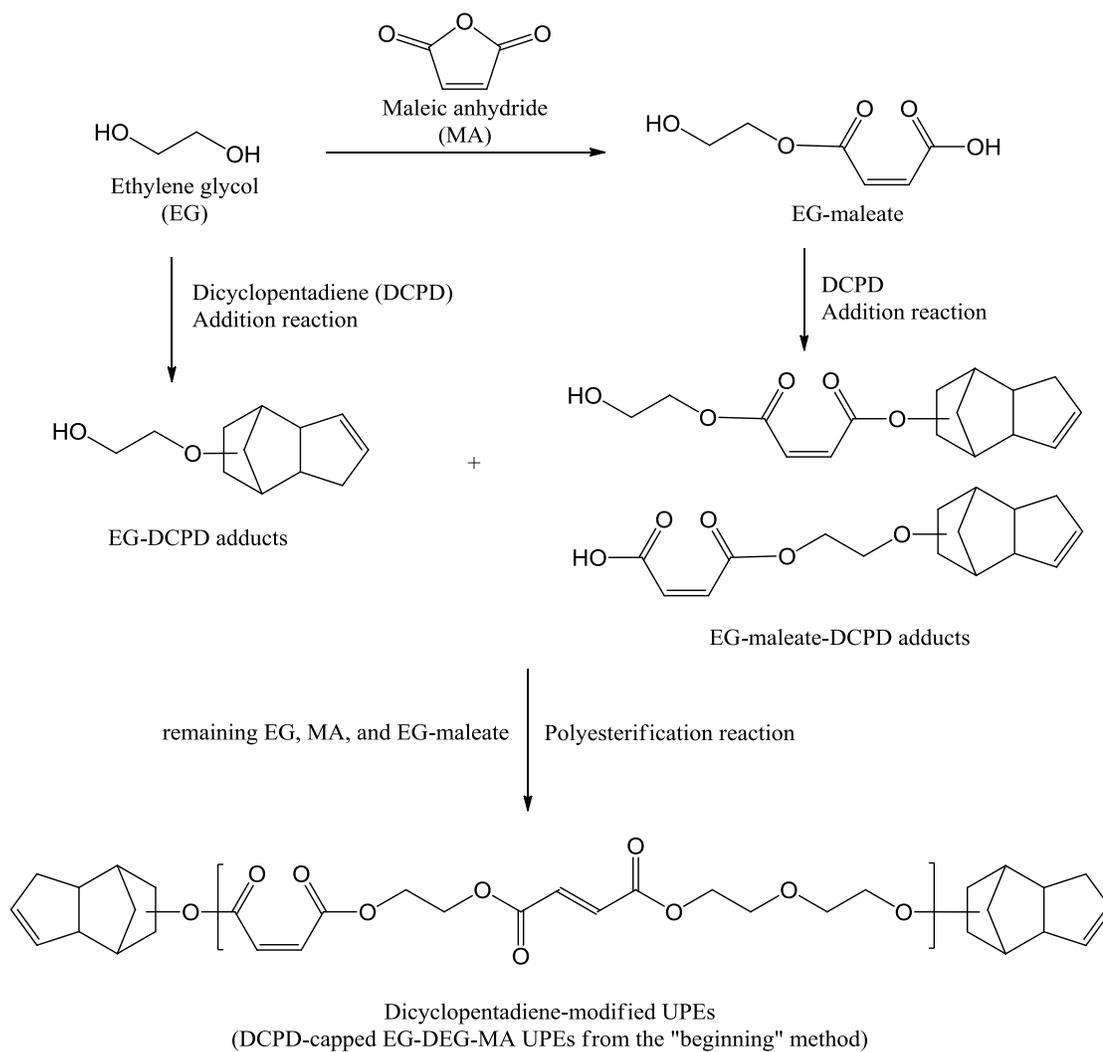


Figure 1.13 Representative synthetic scheme for the preparation of DCPD-capped EG-DEG-MA UPEs by the “beginning” method

1.5.2 Specialty resins

There are three major types of specialty resins: isophthalic acid-based UPE resins, propoxylated bisphenol A-fumaric acid UPE resins, and chlorendic acid-based UPE resins.

1.5.2.1 Isophthalic acid-based UPE resins

Commercial isophthalic acid-based UPE resins, commonly known to the industry as iso resins, are typically mixtures of styrene and isophthalic acid-based UPEs that are reaction products of maleic anhydride, isophthalic acid, and diols such as propylene glycol.

The melting point of isophthalic acid (340 °C) is considerably higher than that of phthalic anhydride (132 °C). Isophthalic acid is also sparsely soluble in organic solvents.²⁰ These two factors make it difficult to use isophthalic acid for the preparation of UPEs. If propylene glycol, isophthalic acid, and maleic anhydride are charged in a reactor at the same time, excessive reactions between propylene glycol and maleic anhydride will occur with little incorporation of isophthalic acid into the resulting UPEs.²⁰ Therefore, the preparation of isophthalic acid-based UPEs generally require two stages. As shown in Figure 1.14, the first stage is the reaction of isophthalic acid with a large excess of propylene glycol to obtain reaction intermediates that mainly consist of propylene glycol-isophthalic acid-propylene glycol adduct and low-molecular-weight propylene glycol-isophthalic acid

oligomers.²⁰ The second stage involves the introduction of maleic anhydride to the reaction intermediates for generating isophthalic acid-based UPEs.

Isophthalic acid-based UPEs generally have much higher molecular weights than the phthalic anhydride-based UPEs. The M_n is typically above 1500 g/mol, the M_w is above 10000 g/mol, and the polydispersity is about 6.7 (M_w/M_n).⁹ Because of the high molecular weights, the isophthalic acid-based UPEs typically require a high amount of styrene, about 40 – 50%, so that the resulting UPE resins have a low viscosity for their easy handling and processing.⁹ With the current emphasis on reduced styrene emissions, some isophthalic acid-based resins with styrene contents between 35 to 40% are also available in the market.

Isophthalic acid-based resins are more expensive than phthalic anhydride-based resins. The higher price is justified by the significantly higher performance of isophthalic acid-based resins than phthalic anhydride-based resins, which generally includes higher strength and toughness, higher chemical and water resistances, and higher thermal stability.^{9, 30}

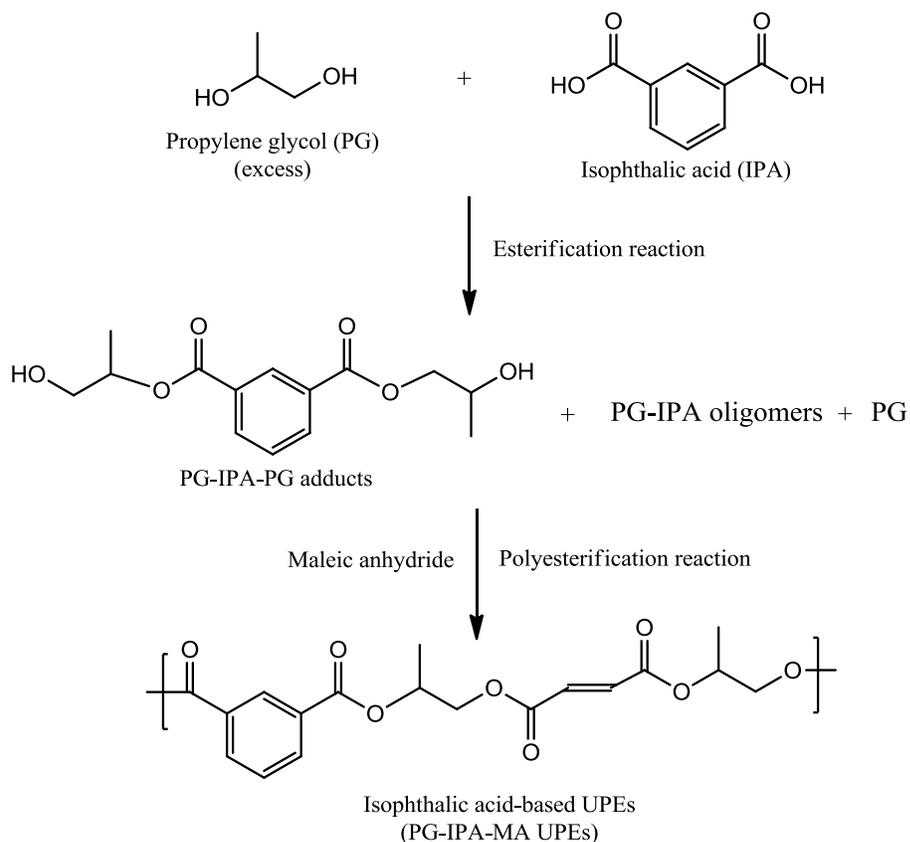


Figure 1.14 Representative synthetic scheme for the preparation of PG-IPA-MA UPEs

1.5.2.2 Propoxylated bisphenol A-fumaric acid-based UPE resins

Commercial propoxylated bisphenol A-fumaric acid-based UPE resins, commonly known as BPA-fumarate resins, are typically mixtures of styrene and propoxylated bisphenol A-fumaric acid-based UPEs that are prepared by the reaction of propoxylated bisphenol A with fumaric acid (Figure 1.15).

Propoxylated bisphenol A-fumaric acid-based UPE resins are particularly useful for applications that require excellent resistances to corrosion and caustic substance.^{29, 54}

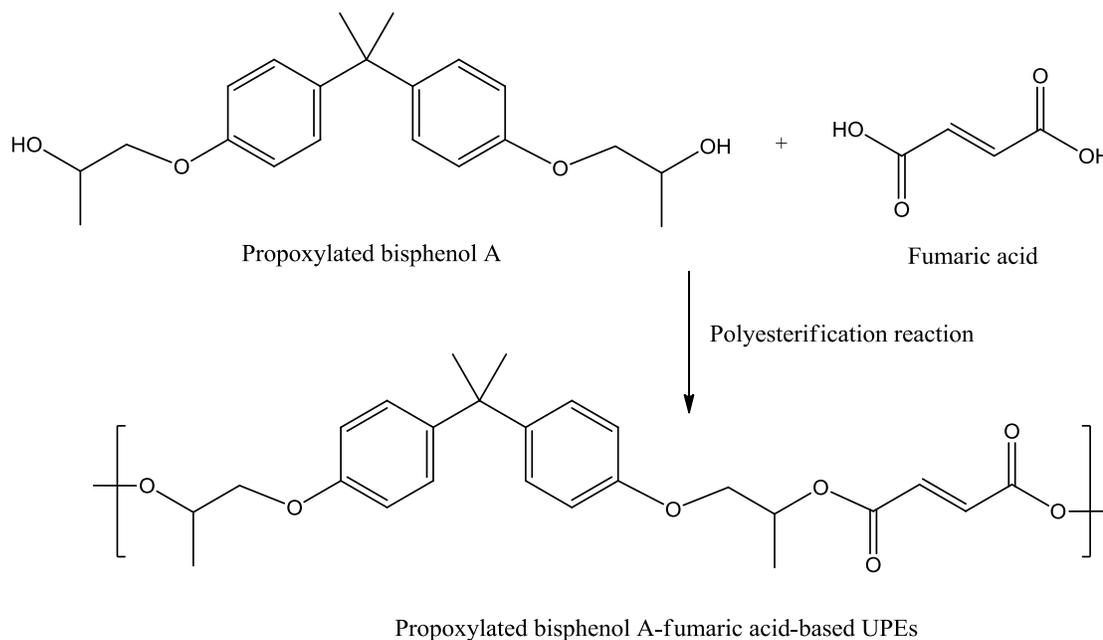


Figure 1.15 Representative synthetic scheme of preparation of PBPA-FA UPEs

1.5.2.3 Chlorendic acid-based UPE resins

Commercial chlorendic acid-based UPE resins, commonly called chlorendic resins, are typically mixtures of styrene and chlorendic acid-based UPEs that are reaction products of diols such as propylene glycol and neopentyl glycol, maleic anhydride, chlorendic acid, and optionally saturated dibasic acids/acid anhydrides such as phthalic anhydride.³⁰ Cured chlorendic acid-based UPE resins typically have excellent flame retardance and chemical resistance (especially to hot, wet chlorine gas and oxidizing acids).^{29, 30} Chlorendic acid-based UPE resins, however, is not useful in caustic environment.⁵²

1.6 Application of UPE resins

Cured UPE resins alone only possess moderate physical properties and thus only have limited applications. The overall properties, especially the mechanical properties can be substantially increased by reinforcing the resins with reinforcing materials that can be fibers (typically glass fibers), fiber mats, or fillers (typically inorganic fillers). The major use of UPE resins is to serve as a matrix for fiber-reinforced UPE composites.³⁰

UPE resins have a very wide range of applications. Table 1.5 summarizes some major industrial sectors and examples of products in each sector.^{1, 9, 20, 30, 55-59}

Table 1.5 Summary of some major industrial sectors and examples of products

Industrial sectors	Examples of products
Building material sector	Bathtubs Shower stall Swimming pools Spas Pultruded window frames Corrugated boards Building panels Flat boards Artificial marbles and onyx Engineered stones Solid surfaces (countertops) Monolithic flooring Porta potti Septic tanks Water tanks Sink Doors Door handles Floor tiles Floor grating Poles and fences

	Wood and furniture finishing Tables and chairs
Automotive sector	Body panels Interior panels Truck containers (general-purpose or freezing) Train containers Bumpers Fenders Cross car beams Grille opening retainers Motor/generator housings Many other fittings
Boat-building sector (typically for pleasure boats, yachts, rescue boats, sail boats, hydrofoils, etc.)	Boat hulls Decks Masts Ventilation ducts Marine cargo containers
Industrial equipment sector	Gasoline tank Water tank Pulp tank Food tanks Livestock feed tanks Pressure vessels Cooling towers Wind turbine blades Pipes and angle members Radomes (radar domes) Equipment housings Scrubber ducts Gratings Utility poles and fences Ladders
Civil engineering sector	Waterproof linings Polymer concretes Composite pipes Manhole blocks Concrete molds Sewer treatment station covers Antiglare barriers
Electric and electronics sector	Encapsulation of electronic assembly Motor shrouds Pump housings Breakers Parabolic antennas

	Insulating panels Switch boxes Insulating troughs Videotape recorders Cabinets Printed circuit boards Chassis
Sporting goods sector	Surfboards Snowboards Jet skis Canoes Golf carts

1.7 Issues related to styrene emission

One of the major issues associated with UPE resins and fiber-reinforced UPE composites is the emission of styrene from the resins and the resulting composites. The emission has caused serious concerns over people's health, air quality, and workplace safety.

1.7.1 Physical and chemical properties

Styrene is a clear, colorless, oily liquid with a distinctive, extremely penetrating, unpleasant odor.⁶⁰ Styrene is a volatile organic compound (VOC) and has a low flash point of 32 °C. The melting point and boiling point of styrene are -31 °C and 145 °C, respectively. The specific gravity of styrene is 0.906 at 20 °C. Styrene is slightly soluble in water, with a water solubility of 0.3 g/L at 25 °C. The vapor density of styrene is 3.6 over 1 for air. The explosion limit of styrene in air is 0.9 – 6.8 vol %. The odor threshold of styrene is 0.1 ppm (1 ppm is equivalent to 0.43 mg/m³). Viscosity is 0.696 cP (1 cP = 0.001 Pa·s) at 25 °C.

Styrene is an aromatic hydrocarbon with a molecular weight of 104.2 g/mol. The C=C bond on the styrene molecule makes it an reactive vinyl monomer that can be polymerized with various techniques, including free radical polymerization, anionic polymerization, and polymerization with complex coordination catalysts.⁴² Styrene can also undergo thermal polymerization even in the absence of a free radical initiator.⁴² It was reported that purified styrene polymerizes at a rate of 0.1% per hour at 60 °C and 2% per hour at 100 °C.⁶¹ The mechanisms for the spontaneous thermal polymerization have been investigated, but are not well understood yet.⁶² Styrene can corrode copper and copper alloys.⁶⁰

1.7.2 Major industrial uses of styrene

Styrene is an important industrial chemical that is extensively used for the productions of rubber latexes, foams, engineering plastics, and resins.² Uses of styrene can be divided into six major categories: polystyrene (50%), styrene-butadiene rubber (15%), glass fiber-reinforced UPE composites (12%), styrene-butadiene latexes (11%), poly(acrylonitrile-butadiene-styrene) (10%), and poly(styrene-acrylonitrile) (1%).²

According to the Styrene Information & Research Center, the fourteen States that have the most styrene-related jobs are California, Florida, Georgia, Illinois, Indiana, Louisiana, Michigan, New Jersey, North Carolina, Ohio, Pennsylvania, Tennessee, Texas, and West Virginia (Figure 1.16).⁶³

States that have the most styrene-related jobs

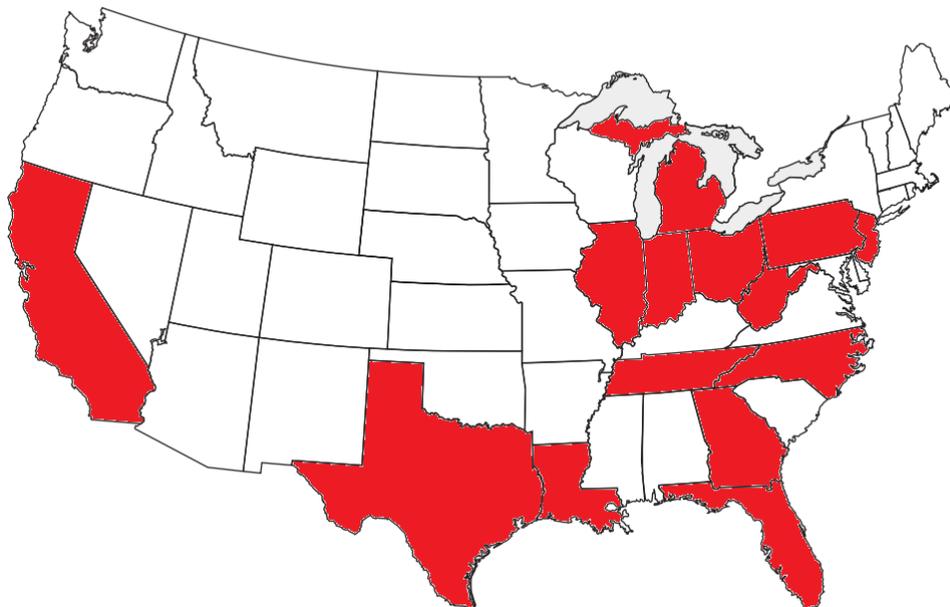


Figure 1.16 States in the U.S. that have the most styrene-related jobs

1.7.3 Hazardous issues of styrene

Styrene is listed as one of the 187 hazardous air pollutants by the U.S. Environmental Protection Agency (EPA).⁶⁴ Under the Clean Air Act, the U.S. EPA is required to regulate the emissions of styrene from manufacturing plants.

Exposure to styrene can be through inhalation, skin absorption, skin contact, eye contact, and ingestion.⁶⁵ The acute toxicity of styrene for eyes, skin, respiratory systems, and central nervous system of humans and experimental animals has been extensively studied.⁶⁶

1.7.3.1 Effects on eyes, nose, throat, and lungs

Styrene vapor can cause irritations to eyes, nose, throat, and lungs for human. Irritations may occur when the concentration of styrene is as low as 10 ppm and can become severe if the concentration exceeds 100 ppm.⁶⁷ Eye irritation symptoms may include stinging, tearing, redness, and swelling of eyes.⁶⁸ Some studies reported that irritations occurred at the concentration of as low as 1 ppm.⁶⁹ Extreme overexposure to styrene may result in pulmonary edema, a potentially fatal condition in which the lungs fill with fluid.⁷⁰ The SDS (safety data sheet) of styrene indicates that styrene is a lachrymator.

1.7.3.2 Effects on skin

Liquid styrene can remove the natural protective oils on skin, which makes the skin more susceptible to affection.⁷⁰ Styrene can cause skin irritation, resulting in redness, burning, and drying and cracking of skin.⁶⁸ Dermatitis (skin rash) can occur after repeated or prolonged skin contact with styrene. Dermatitis-affected skin allows styrene and other chemicals to enter the body more easily than healthy skin.⁷⁰

1.7.3.3 Effects on nervous system

Just like many other organic solvents, styrene is of neurotoxicity. Acute adverse effects on central nervous system include nausea, dizziness, headache, fatigue, vomiting, confusion, loss of balance and coordination, drowsiness, malaise, difficulty in concentrating, a feeling of intoxication, and other central nervous system depression

symptoms.^{67, 70, 71 72} People having these symptoms may also have the increased chances of having accidents such as traffic accidents.

Acute adverse effects can generally occur at an exposure level of around 50 ppm.^{73, 74} More severe symptoms become evident at above 100 ppm.⁷⁰ Some studies have reported that these symptoms can be noticed even at a concentration of as low as 4 ppm.⁶⁹ Styrene also has chronic toxicity for human central nervous system and peripheral nervous system. The chronic toxicity of styrene on human has been extensively reviewed by the California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA).⁷⁵

1.7.3.4 Genetic toxicity

The genetic toxicity of styrene for humans has been mostly investigated in the glass fiber-reinforced UPE composite industry, in which styrene is the main source of VOCs.⁷³ Genotoxic effects of styrene and the binding between styrene and DNA/protein haven been extensively studied and reviewed.⁷⁶⁻⁷⁹

For workers working in composite manufacturing plants with the exposure of styrene at 20 ppm or above, genotoxic effects of styrene were observed in their blood cells.⁷³ After entering the body, styrene will be metabolized to styrene oxide that would react with DNA to form styrene oxide-DNA adducts.² Styrene oxide-DNA adducts were identified in a distinguishable manner even for workers who were exposed to styrene at a concentration of styrene of less than 1 ppm.⁷³

1.7.3.5 Carcinogenicity

The OSHA (Occupational Safety & Health Administration) under the U.S. Department of Labor estimated that about 90,000 workers are potentially exposed to styrene.⁷¹ Through years of scientific study and public input, the National Toxicology Program officially linked styrene to cancer in June 2011 by listing styrene as a “reasonably anticipated human carcinogen” in the 12th Report on Carcinogens.² On the same day of the release of the 12th Report on Carcinogens, a lawsuit was filed against the U.S. Department of Health and Human Services in the District Court for the District of Columbia, challenging the listing.⁸⁰ Judge Reggie B. Walton of the District Court for the District of Columbia rejected the lawsuit in May 2013.⁸¹

At the request of the US Congress, the U.S. Department of Health and Human Services asked the National Academy of Science, a private, nonprofit organization of the country’s leading researchers, to conduct an independent review of the listing and to evaluate the listing criteria in 2012.⁸² The National Research Council under the National Academy of Science started the independent review in February 2013. The National Research Council completed the independent review and endorsed the National Toxicology Program’s listing of styrene in the Report on Carcinogens in July 2014.⁸²

In June 2009, the California Environmental Protection Agency’s Office of Environmental Health Hazard Assessment (OEHHA) issued a notice of intent to list styrene as a known human carcinogen under California Proposition 65, formally

known as the Safe Drinking Water and Toxic Enforcement Act of 1986. The notice of intent was based on a monograph published by the International Agency for Research on Cancer (IARC), a specialized cancer agency of the World Health Organization, located in Lyon, France. The monograph provided some evidences in humans as well as in experimental animals regarding the carcinogenicity of styrene for supporting the classification of styrene as a possibly carcinogenic to humans (Group 2B).⁸³ The notice of intent was challenged; and it was pointed out that IARC's Group 2B identification was only based on "less than sufficient" evidences in humans and animals, which did not meet the Proposition 65 statutory requirements for listing a chemical (i.e. styrene) as "known" to cause cancer.⁸⁴ The Third District Court of Appeal held that the OEHHA may not list such a chemical (i.e., styrene) as causing cancer under Proposition 65 in October 2012. The OEHHA withdrew the intent to list styrene. However, as the OEHHA expressed, its duty was not affected by the court's decision. In January 2013, the OEHHA reissued a notice of intent to list styrene as a known human carcinogen, based on the National Toxicology Program's listing of styrene in 12th Report on Carcinogens and findings of sufficient evidence of carcinogenicity of styrene in experimental animals.⁸⁴ However, the notice was withdrawn in March 2013, pending the result of the lawsuit filed in 2011 against the U.S. Department of Health and Human Services and the result of then ongoing review by the National Research Council. As the National Research Council's independent review confirmed the National Toxicology Program's listing and the lawsuit challenging the listing was rejected, the OEHHA determined that styrene met the

criteria for listing as known to the State to cause cancer under Proposition 65. In February 2015, the OEHHA, for the third time, announced the intent to add styrene into the list.⁸⁵ Thirteen public comments were received as of the deadline of April 29, 2015.⁸⁵ The OEHHA has not yet provided updates on this intent as of March, 2016.

1.7.4 Fire hazards of styrene

Flash point is the minimum temperature at which a liquid gives off vapor with sufficient concentration to form an ignitable mixture.⁸⁶ The flash point is a good indicator on the flammability of a liquid. The lower the flash point the higher the flammability.

A liquid with a flash point lower than 37.8 °C is classified as flammable by the Occupational Safety & Health Administration. Styrene has a low flash point of 32 °C. Due to the presence of styrene, the flash point of styrenated UPE resins is typically below 37.8 °C as well. Consequently, styrenated UPE resins are flammable liquids that can catch fire during storage, transportation, and uses in a workplace.

1.7.5 Sources of the styrene emission

Due to its high volatility, styrene can rapidly emit into the atmosphere even at room temperature when it is exposed to air. Styrene in the air is mainly from the following sources: i) plants where styrene is used for production of glass fiber-reinforced UPE composites, styrene-butadiene rubbers, etc. ii) production plants for styrene, iii)

incineration of polymers that are derived from styrene, iv) automobile exhaust, v) oxyacetylene and oxethylene flames, and vi) cigarette smoke.^{67, 87-89}

Most of the styrene in the air comes from the plants of manufacturing fiber-reinforced thermoset composites. A study in 1990s showed that the composite industry was responsible for 79% of styrene in the air while the usage of styrene in the composite industry only accounted for 9% of the total styrene used at that time.⁹⁰ In the production of fiber-reinforced thermoset composites, open-mold processes emit much more styrene than closed-mold processes. The spray operation for applying thermoset resins to fibers results in the highest level of styrene exposure for workers.⁹¹ Boat building is the sector in which workers have the highest level of styrene exposure.⁹² The U.S. Environmental Protection Agency evaluated the styrene emissions from a plant of making shower stall and bathtub, and found that as many as 4 g of styrene emitted into the air in the workplace for every 100 g of resins sprayed, which accounted for about 10% of the total styrene usage.⁹¹

1.7.6 Exposure limit for styrene

1.7.6.1 Current permissible exposure limits (PELs) for styrene in the U.S.

The occupational exposure limit of a chemical can be given as time-weighted average (TWA), short-term exposure limit (STEL), or ceiling limits (CL).⁹³ The TWA indicates the average exposure level that is allowed over a certain period of time (usually 8 hours). Workers' exposure level may exceed the TWA occasionally in a workday; but not to the extent that the resulting 8-h average exposure level for that

day exceeds the TWA. The STEL specifies the maximum average exposure allowed over a short period of time (normally 15 minutes) during a single work shift (usually no more than 4 shifts in an 8-h workday and at least one hour between two consecutive 15 minutes). The STEL is especially useful for regulating the exposure of styrene during a spray operation in which workers are exposed to a high concentration of styrene for a short period of time. The CL addresses the exposure limit above which workers should never be exposed for any other period of time.

The occupational exposure limits established by governmental agencies are typically called permissible exposure limits (PELs). The PELs established by the OSHA (OSHA PELs) specify legal maximum exposure levels that are allowed in the workplace. Table 1.6 shows the OSHA PELs for styrene.⁹⁴

Table 1.6 The Annotated PELs for styrene (in ppm)

	TWA	STEL	CL
OSHA PELs	100	200	600 ^a
Cal/OSHA PELs	50	100	500
NIOSH RELs	50 ^b	100	
ACGIH [®] TLVs [®]	20	40	

a. for a single time period of up to 5 minutes for any 3 hours⁹⁴

b. for 10 h in a workday, 40 h for a workweek⁹³

The Occupational Safety and Health Act was adopted in 1970, which stated that “employers are responsible for providing safe and healthful workplaces for their

employees”. As required by this Act, the OSHA issued PELs for many workplace hazardous substances at that time. Most of the PELs have not been changed since 1970, including the PELs for styrene. The OSHA recognized that many of these PELs are outdated.⁹⁵ As the OSHA pointed out, over the last few decades, “new scientific data, industrial experience, and developments in technology clearly indicate that in many instances these mandatory limits are not sufficiently protective of workers' health”.⁹⁶ Therefore, the OSHA recommends that employers may consider the use of alternative occupational exposure limits that are more stringent and thus more protective for workers than the OSHA PELs.⁹⁵ Such alternative limits include the California Division of Occupational Safety and Health (Cal/OSHA) PELs (the regulatory limits in the State of California), the National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limits (RELs), American Conference of Governmental Industrial Hygienists (ACGIH[®]) Threshold Limit Values (TLVs[®]).⁹⁵ (The ACGIH[®] TLVs[®] are concentrations of a chemical substance below which it is believed that nearly all workers may be repeatedly exposed to the chemical on a daily basis over a working lifetime without adverse effects.⁹⁵ The ACGIH[®] TLVs[®] are “widely recognized as authoritative and are based solely on health factors with no considerations given to economic or technical feasibility.”⁹⁵)

In October 2013, the OSHA created the Annotated PELs, which contain the OSHA PELs, Cal/OSHA PELs, NIOSH RELs, and ACGIH[®] TLVs[®]. The OSHA recommended that employers can voluntarily adopt newer, more protective exposure

limits for providing better protection to their employees.^{95, 96} Values of these alternative exposure limits for styrene are summarized in Table 1.6.

1.7.6.2 Voluntary occupational exposure limit of styrene

In 1996, the styrene industry, represented by the Styrene Information and Research Center, the International Cast Polymers Association, the National Marine Manufacturers Association, and the Composite Fabricators Association (now the American Composite Manufacturers Association), approached the OSHA and proposed that the industry would encourage composite manufacturers to comply with a voluntary occupational exposure limit of 50 ppm for TWA and 100 ppm for STEL.⁹⁷ This proposal was brought about by the industries for at least two reasons: i) concerns that the 100 ppm (TWA) was not sufficiently protective for workers⁹⁸, and ii) the workplace level of 50 ppm could be achievable by using combinations of engineering controls (such as ventilation) and personal protective equipment such as respirators.⁹⁹ The OSHA agreed with the proposal.

1.7.6.3 Minimal Risk Level for styrene

The Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Level (MRL) is “an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse, non-cancer health effects over a specified duration of exposure”.¹⁰⁰ The ATSDR MRLs for inhalation of styrene is 5 ppm for acute adverse effects to occur and 0.2 ppm for chronic adverse effects to occur.

The regulatory PELs, NOISH RELs, and ACGIH[®] TLVs[®] do not take into account the adverse effects of chronic exposure to styrene for humans. When such adverse effects are considered, a MRL of as low as 0.2 ppm is suggested by the ATSDR. Based on this ATSDR MRL, the worker may be sufficiently protected only when the exposure level is 0.2 ppm and below. This level is apparently too low to be achieved by the composite industry. Yet, the 0.2-ppm MRL does not take into account the cancer-related health effects of styrene.

Based on the previous review, it can be seen that as long as styrene is used, workers in the composite industry are at risk of acute, chronic and potentially cancer-related adverse health effects. Development of styrene-free UPE resins for the composite industry is a viable solution for resolving the issues related to the styrene emission.

1.8 Reference

1. Strong, A.B. In *Fundamentals of Composites Manufacturing: Materials, Methods and Applications*, 2nd ed.; Society of Manufacturing Engineers: Dearborn, MI, 2008. Chapter 3. Pages 47-83
2. U.S. Department of Health and Human Services; National Toxicology Program: Report on Carcinogens, 12th ed.; 2011
3. J. M. Sadler, A.-P. Nguyen, S. M. Greer, G. R. Palmese and J. J. La Scala, *J. Biobased Mater. Bioenergy*, 2012, 6, 86-93
4. E. Senoz, J. F. Stanzione III, K. H. Reno, R. P. Wool and M. E. N. Miller, *J. Appl. Polym. Sci.*, 2013, 128, 983-989
5. W. H. Carothers, *J. Am. Chem. Soc.*, 1929, 51, 2548
6. W. H. Carothers, *J. Am. Chem. Soc.*, 1929, 51, 2560
7. C. Ellis. U.S. Patent 2195362. 1936

8. C. Ellis, U.S. Patent 2255313. 1937
9. Andreas Kandelbauer, Gianluca Tondi, and Sidney H. Goodman. Unsaturated Polyesters and Vinyl esters. In Handbook of Thermoset Plastics, 3rd edition. Hanna Dodiuk, Sydney H Goodman (eds.). William Andrew Publications: San Diego, CA. 2014. Chapter 6. Pages 111-172
10. Wilson A. Reeves, John D. Guthrie. U.S. Patent. 2913436. 1953
11. Milton Kosmin. U.S. Patent. US2828278. 1954
12. Earl E Parker. U.S. Patent. US3419637. 1966
13. Maurice H. Bigelow. U.S. Patent. US2624714. 1950
14. Brian Craig Starr. Inter-relationships between chemistry, network structure and properties of chain growth dimethacrylate thermosets. Ph.D dissertation of the Virginia Polytechnic Institute and State University. 2001
15. Lucintel. Global Unsaturated Polyester Resin Market 2013-2018: Trends, Forecast and Opportunity Analysis, 2013
16. S. S. Feuer, A. Brown, I. Rosenthal and T. E. Bocktähler. *Ind. Eng. Chem.* 1954, *46*, 1643-1645
17. I. Vanso-Szmercsanyi, L. K. Marcos and A. A. Zahran. *J. Appl. Polym. Sci.* 1966, *10*, 513-522
18. F. R. Mayo, F. M. Lewis and C. Walling. *J. A. Chem. Soc.* 1948, *70*, 1529
19. M. Malik, V. Choudhary and I. Varma. *Journal of Macromolecular Science, Part C: Polymer Reviews.* 2000, *40*, 139
20. K. G. Johnson and L. S. Yang. Preparation, Properties and Applications of Unsaturated Polyesters. In Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters. Editor(s): John Scheirs, Timothy E. Long. John Wiley & Sons, Ltd: Chichester, UK. 2004. Chapter 21. Pages 697-713. DOI: 10.1002/0470090685
21. Z. Ordelt and F. Ciganek. *Chemicky Prumsyl*, 1964, *14*, 141
22. Z. Ordelt and V. Soedin. *Macromolecular Chemistry*, 1962, *4*, 110
23. E. E. Parker. *Ind. Eng. Chem.* 1966, *58*, 53-58
24. A. Frandet and E. Marechal, *Macromol. Chem.*, 1982, *188*, 319-329
25. Y. Yang and J. Pascault, *J. Appl. Polym. Sci.*, 1997, *64*, 113

26. I. E. Muskat. U.S. Patent 2426042. 1943
27. W. Gum, W. Riese and H. Ulrich, eds. Reaction Polymers: Polyurethanes, Epoxies, Unsaturated Polyesters, Phenolics, Special Monomers, and Additives: Chemistry, Technology, Applications, Markets. Hanser Publishers: New York, 1992. Chapter C.
28. H. V. Boenig. Unsaturated Polyesters: Structure and Properties. Elsevier Publishing Co.: New York, 1964
29. J. G. Don Kelley and Thom Johnson. Different FRP resins chemistries for different chemical environments. Ashland Inc. Technical report. 2010. <http://www.aiche-cf.org/Clearwater/2010/Paper2/10.2.6.pdf>; accessed in May 2016
30. Debdatta Ratna. Handbook of Thermoset Resins. Smithers Rapra Technology: UK. 2009. Chapter 2. Pages 83-99
31. B. Parkyn. Unsaturated Polyesters. American Elsevier Publishing: New York. 1967. Vol. 2
32. M. S. Mohammadnia, P. Salaryan, Z. K. Azimi and F. T. Seyidov. *International Journal of Chemical and Biochemical Sciences*. 2012, 2, 36-41
33. T. Bradley. *Ind. Eng. Chem.* 1937, 29, 440
34. T. Bradley. *Ind. Eng. Chem.* 1937, 29, 579
35. T. Bradley, E. Kropa and W. Johnston. *Ind. Eng. Chem.* 1937, 29, 1270
36. P. Bharat Dholakiya. Unsaturated Polyester Resin for Specialty Applications. *In Polyester*. Hosam El-Din Saleh (Ed.). InTech. 2012. DOI: 10.5772/48479. Open access. Available at <http://www.intechopen.com/books/polyester/unsaturated-polyester-resin-for-specialty-applications>
37. <http://fiberglassblog.com/2009/02/16/the-different-polyester-resins/>; accessed in May 2016
38. F. Mel Schwartz. Environment and Safety. *In Innovations in Materials Manufacturing, and Environmental Safety*. Mel Schwartz (editor). CRC Press: Boca Raton, FL. 2011. Chapter 22. Pages 743
39. https://www.akzonobel.com/polymer/our_products/organic_peroxides/; accessed in May 2016
40. <http://www.neochemical.ru/File/Akzo%20Data%20110407-Initiators%20for%20High%20Polymers.pdf>; accessed in May 2016

41. http://www.compositesone.com/wp-content/uploads/2010/08/Selecting-the-right-initiator_ts_glo_eng_tb-final-from-Ross.pdf; accessed in May 2016
42. M. P. Stevens. *Polymer Chemistry: An Introduction*. Oxford University Press: New York. 1999. Chapter 6. Pages 167-204
43. R. G. Weatherhead. *FRP Technology: Fibre Reinforced Resin Systems*. Applied Science Publishers LTD: London, UK. 2012. Page 208
44. K. Demmler and J. Schlag. *Kunststoffe*. 1967, 57, 566
45. Gebhart Herbert J Jr, Makin Earle C Jr, Middlebrooks Charles H. U.S. Patent 3557239. 1971
46. Shozo Tsuchiya, Akio Oshima, Hideo Hayshi. U.S. Patent 4360622. 1981.
47. Piotr Penczek, Piotr Czub, and Jan Pielichowski. *Adv. Polym. Sci.* 2005. 184. 1-95
48. Omer E. Curtis, Jr. U.S. Patent 4246367. 1979
49. Herman Alexander Bruson and Thomas W. Riener. *J. Am. Chem. Soc.* 67. 1178-1180
50. Z. Zhao. Chinese Patent 1070657. 1992
51. Herman Alexander Bruson and Thomas W. Riener. *J. Am. Chem. Soc.* 68. 8-10
52. Donald L. Nelson. U.S. Patent 4029848. 1976
53. Herman F. Mark. *Encyclopedia of Polymer Science and Technology, Concise*. Third Edition. 2007. John Wiley & Sons Inc.: Hoboken, NJ. Page 907
54. Derakane™ epoxy vinyl ester resins: The Evolution of Corrosion Resistant FRP. Ashland Inc. Technical Report. Available at http://www.ashland.com/Ashland/Static/Documents/APM/derakane_evolution_of_corrosion_resistant_frp.pdf; accessed in May 2016
55. <http://www.sdk.co.jp/english/products/119/120.html>; accessed in May 2016
56. Ashland Inc. Product Description. <http://www.ashland.com/products/aropol-unsaturated-polyester-resins>; accessed in May 2016
57. Ashland Inc. Product Description. <http://www.ashland.com/products/enguard-gelcoat>; accessed in May 2016
58. Ashland Inc. Product Description. <http://www.ashland.com/products/polaris-unsaturated-polyester-resin>; accessed in May 2016

59. Uday Vaidya. Composites for Automotive, Truck and Mass Transit: Materials, Design, Manufacturing. Volume 2. DEStech Publications, Inc. 2011
60. U.S. Department of Health and Human Services; National Toxicology Program. Chemical Properties of styrene. Available at http://tools.niehs.nih.gov/cebs3/ntpviews/index.cfm?action=testarticle.properties&cas_number=100-42-5; accessed in May 2016.
61. L. C. Rubens and R. F. Boyer. The Polymerization of Styrene. *In Styrene*. R. H. Boundy and R. F. Boyer eds. ACS Monograph 115: Reinhold, New York. 1952. Pages 215-288
62. W. A. Pryor and L. D. Lasswell. *Adv. Free-Radical Chem.* 1975, 5, 27-29
63. Styrene Information & Research Center. About Styrene: U.S. State. Available at <http://styrene.org/us-states/>; accessed in May 2016
64. U.S. Environmental Protection Agency. Initial List of Hazardous Air Pollutants with Modifications. Available at <https://www.epa.gov/haps/initial-list-hazardous-air-pollutants-modifications>; accessed in May 2016
65. The Japan Society for Occupational Health. *J Occup Health.* 2015, 57, 394-417; Available at http://joh.sanei.or.jp/pdf/E57/E57_5_12.pdf; accessed in May 2016
66. California's Office of Environmental Health Hazard Assessment (OEHHA). Acute Toxicity Summary for Styrene. Available at http://oehha.ca.gov/air/acute_rels/pdf/100425A.pdf; accessed in May 2016
67. International Program on Chemical Safety. Environmental Health Criteria 26. Styrene. Available at <http://www.inchem.org/documents/ehc/ehc/ehc26.htm#PartNumber:1>; accessed in May 2016
68. Vanderbilt Aerospace Design Laboratory. Standard Operating Procedure for Polyester Resin: Laboratory Safety Manual and Chemical Hygiene Plan. Available at http://www.vanderbilt.edu/USLI/2016/Reports/SOP/SOP_Polyester_Resin.pdf; accessed in May 2016
69. The National Institute for Occupational Safety and Health (NIOSH). Styrene. Available at <http://www.cdc.gov/niosh/pel88/100-42.html>; accessed in May 2016
70. California Department of Public Health (CDPH). Hazard Evaluation System and Information Service. Styrene. Available at

- <https://www.cdph.ca.gov/programs/hesis/Documents/styrene.pdf>; accessed in May 2016
71. U.S. Department of Labor. Occupational Safety and Health Administration (OSHA). Styrene. Available at <https://www.osha.gov/SLTC/styrene/>; accessed in May 2016
 72. The National Institute for Occupational Safety and Health (NIOSH). Immediately Dangerous To Life or Health (IDLH): Styrene. Available at <http://www.cdc.gov/niosh/idlh/100425.html>; accessed in May 2016
 73. World Health Organization. Styrene. Available at http://www.euro.who.int/__data/assets/pdf_file/0018/123066/AQG2ndEd_5_12Styrene.pdf; accessed in May 2016
 74. Styrene Information & Research Center. Styrene and Human Health. Available at <http://styrene.org/science/human-health/#ototoxicity>; accessed in May 2016
 75. California's Office of Environmental Health Hazard Assessment (OEHHA). Chronic Toxicity Summary for Styrene. 1993. Available at http://oehha.ca.gov/air/chronic_rels/pdf/100425.pdf; accessed in May 2016
 76. International Agency For Research On Cancer (IARC) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 60
 77. D. H. Phillips and P. B. Farmer. *Critical reviews of toxicology*. 1994. 24, S35-S46
 78. R. Barale. *Mutation research*. 1991, 257, 107-126
 79. H. Norppa and M. Sorsa. Genetic toxicity of 1,3-butadiene and styrene. In *Butadiene and styrene: assessment of health hazards*. M. Sorsa et al., eds. Lyon, International Agency for Research on Cancer. 1993. Pages 185-193 (IARC Scientific Publications, No. 127)
 80. Styrene Information & Research Center. About Styrene: U.S. Federal. <http://styrene.org/us-federal/>; accessed in May 2016
 81. Federal Judge Rejects Challenge to NTP Styrene Listing. 2013. Available at <http://prop65news.com/Story-Details/articleid/7484/federal-judge-rejects-challenge-to-ntp-styrene-listing>; accessed in May 2016
 82. NAS Conducts Independent Review of NTP's Styrene Classification. 2013. Available at <http://www.packaginglaw.com/news/nas-conducts-independent-review-ntps-styrene-classification>; accessed in May 2016

83. International Agency For Research On Cancer (IARC) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 82. Available at <http://monographs.iarc.fr/ENG/Monographs/vol82/mono82-9.pdf>; accessed in May 2016
84. California's Office of Environmental Health Hazard Assessment (OEHHA). Regarding Certain IARC (International Agency For Research On Cancer) 2B Chemicals. 2013. Available at http://oehha.ca.gov/prop65/CRNR_notices/010413notice.html; accessed in May 2016
85. California's Office of Environmental Health Hazard Assessment (OEHHA). Notice of Intent to List: Styrene. 2015. Available at http://oehha.ca.gov/prop65/CRNR_notices/admin_listing/intent_to_list/noilstyr ene2015.html; accessed in May 2016
86. U.S. Department of Labor. Occupational Safety and Health Administration (OSHA). Flammable and Combustible Liquids. 29 CFR 1910.106. Available at https://www.osha.gov/dte/library/flammable_liquids/flammable_liquids.html; accessed in May 2016
87. J. W. Pervier, R. C. Barley, D. E. Field, B. M. Friedman and R. B. Morris. Survey reports on atmospheric emissions from the petrochemical industry. 1974. Vol. IV. Page 287
88. R. D. Fleming. Effect of fuel composition on exhaust emissions from a spark-ignition engine. 1970. Washington DC. US Department of the Interior, Bureau of Mines (Report of Investigations 7423)
89. B. D. Crittenden and R. Long. The mechanisms of formation of polynuclear aromatic compounds in combustion systems. *In* Carcinogenesis - A comprehensive survey. Raven Press:New York. 1976. Volume I. Pages 209-223
90. B. Lacovara. Reducing Emissions with Styrene Suppressants. CFA 1999,1-5
91. Larry Felix, Randy Merritt, and Ashley Williamson. Evaluation of styrene emissions from a show stall/bathtub manufacturing facility. 1996. United States Environmental Protection Agency. Center for Environmental Research Information, Cincinnati, OH 45268
92. R. L. Schumacher, P. A. Breysse, W. R. Carlyon, R. P. Hibbard and G. D. Kleinman. *American Industrial Hygiene Association Journal*.1981. 42. 143-149

93. The National Institute for Occupational Safety and Health (NIOSH). NIOSH Pocket Guide to Chemical Hazards. Available at <http://www.cdc.gov/niosh/npg/pgintrod.html>; accessed in May 2016
94. U.S. Department of Labor. Occupational Safety and Health Administration (OSHA). Annotated OSHA Z-2 Table. Available at <https://www.osha.gov/dsg/annotated-pels/tablez-2.html>; accessed in May 2016
95. U.S. Department of Labor. Occupational Safety and Health Administration (OSHA). Permissible Exposure Limits – Annotated Tables. Available at <https://www.osha.gov/dsg/annotated-pels>; accessed in May 2016
96. U.S. Department of Labor. Occupational Safety and Health Administration (OSHA). OSHA releases new resources to better protect workers from hazardous chemicals. Available at https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=NEWS_RELEASES&p_id=24990; accessed in May 2016
97. U.S. Department of Labor. Occupational Safety and Health Administration (OSHA). OSHA Announces That Styrene Industry Has Adopted Voluntary Compliance Program To Improve Worker Protection. Available at https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=NEWS_RELEASES&p_id=377; accessed in May 2016
98. American Composites Manufacturers Association. Styrene OEL in the U.S. – Approximate Chronology. Available at <http://www.acmanet.org/cct/17-member-resources/205-chromology-of-the-styrene-oel>; accessed in May 2016
99. National Marine Manufacturers Association. OSHA Uses New Way to Enforce Styrene Exposure Limits. 2013. Available at <http://www.nmma.org/press/article/18652>; accessed in May 2016
100. Agency for Toxic Substances and Disease Registry (ATSDR). Toxic Substance Portal: Styrene. Available at <http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=74>; accessed in May 2016

Chapter 2 – Literature review on research and development of an replacement for styrene in UPE resins

2.1 Considerations on research and development of a styrene replacement

From previous descriptions about the hazardous issues of styrene, we can see that there is an urgent need for the research and development of an alternative for the replacement of styrene in UPE resins. It is highly desirable that styrene replacements have the following features: no or minimal toxicity, low volatility, low flammability, and low cost. Styrene is a petrochemical and petroleum is not a renewable resource. It is thus preferred that styrene replacements are derived from renewable materials. Last but not least, the desirable styrene replacements should be able to completely replace styrene in UPE resins while the resulting styrene-free resins and the cured products should have satisfactory product properties such as low resin viscosity, high glass transition temperatures, good thermal properties, and high mechanical properties.

2.2 Literature review on styrene replacements

Methyl methacrylate (MMA) and vinyl toluene (VT) are two non-styrene crosslinking agents currently used with UPEs in the industry. The use of MMA for the partial replacement of styrene was found to improve the weathering resistance of the resulting fiber-reinforced composites.¹ Its vapor pressure (1.5 mmHg at 20 °C) is lower than that of styrene (5 mmHg at 20 °C), indicating that VT is less volatile than styrene.^{2,3} The partial replacement of styrene with VT can lower the volatility of the resulting

UPE resins.⁴ There are few reports on the complete replacement of styrene with MMA or VT. U.S. Patent 6646057 (1998) comments that UPE resins with the complete replacement of styrene with either MMA or VT still give off high levels of VOC (volatile organic compound).⁵ MMA is an irritant to skin, eyes, and respiratory systems⁶ and has already been listed as a hazardous air pollutant (HAP) by the EPA (U.S. Environmental Protection Agency)⁷. The SDS (safety data sheet) of MMA reveals that MMA has a higher vapor pressure than styrene, which means that MMA is more volatile than styrene and is thus not a desirable styrene replacement⁶. The SDS of VT shows that VT has acute inhalation toxicities and aspiration hazards, and can cause irritations to skin, eyes, and respiratory systems.² We don't believe VT is a desirable styrene replacement for UPE resins.

Vinyl propionate (VP), vinyl versatate (VV), ethylene glycol dimethacrylate (EGDMA), and their mixtures have been studied as alternatives to styrene in UPE resins.⁹ The complete replacement of styrene with some mixtures of EGDMA and VP, or some mixtures of EGDMA and VV were found to decrease the flexural strength of the non-reinforced cured resins by 20%-50%, but not to compromise the flexural modulus and impact strength.⁹ Viscosity data of the resins are not reported.⁹ The preparation and evaluation of fiber-reinforced UPE composites from these resins are also not reported⁹, which raises the question on whether these styrene-free resins can lead to fiber-reinforced UPE compositions with adequate properties for a targeted application. VP is a flammable liquid, and can cause irritations to eyes and skin.¹⁰ The boiling point of VP (95 °C) is lower than that of styrene (145 °C), indicating that

VP may be more volatile than styrene (the vapor pressure of VP cannot be found in its SDS).¹⁰ EGDMA can cause skin sensitization and irritation to the respiratory system.¹¹ The reported styrene-free resins were thus not highly desirable because of the health and safety hazards.

U.S. Patent 5747597 (1996) describes the complete replacement of styrene with di(ethylene glycol) methyl ether methacrylate (DEGMEMA) in UPE resins.¹² The resulting resins were found to have reduced odors.¹² The curing of the styrene-free resins was less affected by oxygen inhibition than the curing of styrenated resins.¹² The cured resins were evaluated for tensile strength and water resistance.¹² The resins were proposed for use as a coating material.¹² The preparation and evaluation of fiber reinforced composites from these styrene-free resins are not reported.¹² The SDS indicates that DEGMEMA can cause irritations to eyes, skin, and respiratory systems and can also cause skin sensitization.¹³ DEGMEMA is thus not a desirable styrene replacement.

U.S. Patent 6646057 (1998) describes the complete replacement of styrene with a mixture of 2-hydroxyethyl methacrylate (2-HEMA) and a reaction product of polymeric methylene diphenyl diisocyanate and 2-hydroxyethyl methacrylate for lowering the VOC emissions of the UPE resins.⁵ The cured resins were evaluated for the tensile, flexural, and compressive strengths and moduli.⁵ Impact strength and glass transition temperature of the cured resins were also measured.⁵ It is unclear if this replacement can result in superior fiber-reinforced UPE composites because the

preparation and evaluation of the composites are not reported.⁵ The SDS reveals that 2-HEMA is an irritant to eyes and skin; and can cause skin sensitization.¹⁴

U.S. Patent 7396882 (2003)¹⁵ and U.S. Patent 7326752 (2004)¹⁶ each describe the replacement of styrene in UPE resins with mixtures of a hydroxyl-functionalized (meth)acrylate monomer such as 2-HEMA, a multifunctional (meth)acrylate such as 1,6-hexanediol diacrylate (1,6-HDA), and a urethane (meth)acrylate such as the reaction products of methylene diphenyl diisocyanate and hydroxypropyl methacrylate. The disclosed styrene-free resins are reported to have lower emissions of VOCs and HAPs than styrenated resins; and to be cured efficiently at room temperature under an air atmosphere.^{15, 16} The cured resins were evaluated for flexural and tensile strength and modulus, heat distortion temperature, and Barcol hardness. The styrene-free resins were suggested for use as a coating material.¹¹¹ No fiber-reinforced composites from the disclosed styrene-free resins were prepared.^{110,}
¹¹¹ SDSs of 2-HEMA and 1,6-HDA show that both 2-HEMA and 1,6-HDA can cause irritations to eyes and skin; and can cause skin sensitization.¹¹

European Patent 2215136 (2008) describes the complete replacement of styrene with 1,4-butanediol dimethacrylate (1,4-BDDMA) or isobornyl methacrylate (IBMA) in UPE resins.¹⁷ The styrene-free resins have been shown to have lower VOC emissions than styrenated resins.¹⁷ The styrene-free resins were suggested for coating applications.¹⁷ The styrene-free resins were suggested for composite applications; but

no fiber-reinforced composites were prepared and evaluated.¹⁷ 1,4-BDDMA and IBMA are irritants to eyes, skin, and respiratory system.¹¹

Vegetable oils have low viscosity and are not toxic or volatile. They are inexpensive, abundant, and renewable. Methacrylates from reactions of glycidyl methacrylate and various fatty acids were investigated as styrene replacements in vinyl ester resins.^{18, 19} These fatty acid methacrylates are not volatile.^{18, 19} It has been demonstrated that the partial replacement of styrene with the methacrylates in vinyl ester resins did not compromise the resin viscosity and mechanical properties of the cured resins and composites.^{18, 19} However, the complete replacement of styrene with the methacrylates resulted in inferior mechanical properties and high resin viscosity.^{18, 19} It is not known whether the methacrylates can be used for replacement of styrene in UPE resins.

U.S. Patent 20120214940 (2012) reported the complete replacement of styrene with dicyclopentadiene (DCPD) in DCPD-modified UPEs.²⁰ The curing of the DCPD-modified UPEs with DCPD were carried out with a ring-opening metathesis polymerization method.²⁰ The gel time of the resins and the glass transition temperature of the cured resins were measured.²⁰ No fiber-reinforced composites were prepared and evaluated.²⁰ DCPD has a strong, disagreeable, camphor-like odor²¹; and is volatile (vapor pressure: 1.4 mmHg at 20 °C)²¹ and flammable (flash point: 24 °C)²². DCPD is also an irritant to eyes and skin.²² Inhalation of dicyclopentadiene can irritate the nose, throat, and lungs, resulting coughing, wheezing, and/or shortness

of breath.²¹ Long-term, repeated exposure may cause damages on kidney, lung, and the nervous system.²³ DCPD is thus not a desirable styrene replacement.

US20140309378 (2012) describes the complete replacement of styrene in UPE resins with vinyl esters such as vinyl benzoate (VB), divinyl adipate (DVA), VP, vinyl acetate (VA), or their mixtures.²⁴ The glass transition temperature and the storage modulus of the cured resins were determined by dynamic mechanical analysis (DMA). No fiber-reinforced composites were prepared. SDSs of VB, DVA, VP, and VA show that these chemicals are all irritants to skin, eyes, and respiratory systems.^{10, 25-27} In particular, VA is very volatile (vapor pressure: 83 mmHg at 20 °C)²⁸ and has already been classified as a hazardous air pollutant and a possible human carcinogen (Group 2B, IARC)²⁷. These vinyl esters are not desirable styrene replacements.

Vinyl levulinate from bio-based levulinic acid has been investigated as a styrene replacement for UPEs.²⁹ It was found that the impact strength of the cured styrene-free UPE resins was comparable with that of the cured styrenated resins; but the flexural strength and flexural modulus of the former were 35% lower than the latter.²⁹ Vinyl levulinate was found to be less volatile than styrene.²⁹ A study demonstrated that 50 wt% of vinyl levulinate evaporated after 15 h, indicating that vinyl levulinate is very volatile.²⁹ Vinyl levulinate is typically prepared from a palladium-catalyzed vinyl exchange reaction between levulinic acid and VA.^{29,30} The hazardous precursor (VA) and expensive heavy metal (Pd) are used in the preparation. The preparation and evaluation of fiber-reinforced composites are not reported.

2.3 Study objectives

Extensive literature reviews reveal that all styrene replacements reported so far have the following deficiencies: 1) all of them are still volatile and hazardous to various extents except for the fatty acid methacrylates^{18, 19}, 2) some of them have not been demonstrated to be suitable for productions of fiber-reinforced composites, 3) these replacements lead to inferior mechanical properties of the resulting fiber-reinforced composites, 4) most of the styrene replacements reported so far are based on petrochemicals. Therefore, the goals of this study are:

- i) Development of renewable material-based styrene replacements that process no or minimal volatility and toxicity.
- ii) Research and development of styrene-free UPE resins that can be used for production of fiber-reinforced UPE composites whose properties are comparable or superior to those from styrenated UPE resins.

2.4 Reference

1. Robitschek Paul. U.S. Patent 3391222. 1963
2. Safety data sheet of vinyl toluene from Sigma-Aldrich.com; accessed in May 2016
3. Safety data sheet of styrene from Sigma-Aldrich.com; accessed in May 2016
4. Andreas Kandelbauer, Gianluca Tondi, and Sidney H. Goodman. Unsaturated Polyesters and Vinyl esters. In Handbook of Thermoset Plastics, 3rd edition. Hanna Dodiuk, Sydney H Goodman (eds.). William Andrew Publications, San Diego, CA. 2014. Chapter 6. Pages 111-172

5. Richard M. Anders, Kenneth R. Anders, Dale K. Becker. U.S. Patent 6646057. 1998
6. Safety data sheet of methyl methacrylate from Sigma-Aldrich.com; accessed in May 2016
7. U.S. Environmental Protection Agency. Initial List of Hazardous Air Pollutants with Modifications. Available at <https://www.epa.gov/haps/initial-list-hazardous-air-pollutants-modifications>; accessed in May 2016
8. Guiseppe Raffaello Palmese, John Joseph LaScala, James Matthew Sands. U.S. Patent 8372926. 2008
9. P. E. Froehling. *J. Appl. Polym. Sci.* 1982, 27, 3577–3584
10. Safety data sheet of vinyl propionate from Sigma-Aldrich.com; accessed in May 2016
11. Safety data sheet of ethylene glycol dimethacrylate from Sigma-Aldrich.com; accessed in May 2016
12. Yukiko Fujita, Shinya Ueno, Yoko Kawasaki, Kumiko Fukakusa, Hidefumi Matsuya, Tomomasa Mitani, Akira Komori, Mika Matsumura. U.S. Patent 5747597. 1996
13. Safety data sheet of di(ethylene glycol) methyl ether methacrylate from Sigma-Aldrich.com; accessed in May 2016
14. Safety data sheet of 2-hydroxyethyl methacrylate from Sigma-Aldrich.com; accessed in May 2016
15. John C. Hewitt, John E. McAlvin, Paul Taylor Hutson, Amber E. Craig, Marjorie Krantz, Derek K. Rivers. U.S. Patent 7396882. 2003
16. John E. McAlvin, Daniel A. Oakley, Paul Taylor Hutson, David J. Zwissler, Thomas J. Folda. U.S. Patent 7326752. 2004
17. Perez Jordi Albalat, José Antonio Garcia. European Patent. EP2215136. 2008
18. E. Can, J. J. La Scala, J. M. Sands, and G. R. Palmese. *J. Appl. Polym. Sci.* 2007, 106, 3833–3842
19. La Scala, J. J.; Sands, J. M.; Orlicki, J. A.; Robinette, E. J.; and Palmese, G. R. *Polymer* 2004, 45, 7729–7737

20. Chih-Pin Hsu, Ming Yang Zhao, Steven L. Voeks. U.S. Patent 20120214940. 2012
21. New Jersey Department of Health and Senior Services. Hazardous Substance Fact Sheet: Dicyclopentadiene. Available at <http://nj.gov/health/eoh/rtkweb/documents/fs/0681.pdf>; accessed in May 2016
22. Safety data sheet of dicyclopentadiene from Sigma-Aldrich.com; accessed in May 2016
23. Virginia Department of Health. Frequently Asked Questions about Dicyclopentadiene (DCPD). Available at <http://www.vdh.virginia.gov/epidemiology/dee/PublicHealthToxicology/documents/pdf/FAQ-dicyclopentadiene.pdf>; accessed in May 2016
24. Johan Franz Gradus Antonius Jansen, Iris Hilker, Guido Joseph Elisabeth Hensen, Di Silvana Rensina Antonietta Silvestre. U.S. Patent 20140309378. 2012
25. Safety data sheet of vinyl benzoate from Sigma-Aldrich.com; accessed in May 2016
26. Safety data sheet of divinyl adipate from polysciences.com. Available at <http://cdsm.polysciences.com/skin/frontend/default/polysciences/pdf/25338.pdf>; accessed in May 2016
27. Safety data sheet of vinyl acetate from Sigma-Aldrich.com; accessed in May 2016
28. Agency for Toxic Substances and Disease Registry (ATSDR). Chemical and Physical Information: Vinyl Acetate. Available at <https://www.atsdr.cdc.gov/toxprofiles/tp59-c3.pdf>; accessed in May 2016
29. S. Cousinet, A. Ghadban, I. Allaoua, F. Lortie, D. Portinha, E. Drockenmuller and J.-P. Pascault. *J. Polym. Sci., Part A: Polym. Chem.* 2014, 52, 3356–3364
30. I. Allaoua, B. Eleuterio Goi, M. M. Obadia, A. Debuigne, C. Detrembleur, E. Drockenmuller, *Polym. Chem.* 2014, 5, 2973–2979

**Chapter 3 - Replacement of styrene with acrylated epoxidized
soybean oil in an unsaturated polyester resin from propylene glycol,
isophthalic acid and maleic anhydride**

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3.1 Abstract

Commercial unsaturated polyester (UPE) resins typically contain a high amount of volatile toxic styrene. A non-volatile acrylated epoxidized soybean oil (AESO) was found to be an excellent replacement of styrene in a commercially available UPE resin (designated as Styrene-(PG-IPA-MA)) that is derived from propylene glycol (PG), isophthalic acid (IPA), and maleic anhydride (MA) in terms of the mechanical properties of the resulting kenaf fiber-reinforced composites. The AESO-(PG-IPA-MA) resins had low viscosity and long pot life below 70 °C for a typical fiber-reinforced composite application. AESO and PG-IPA-MA were not able to form a strong polymer matrix individually for fiber-reinforced composites. However, a combination of AESO and PG-IPA-MA saw strong synergistic effects between them. The flexural, tensile, and water absorption properties of kenaf fiber-reinforced composites made from AESO-(PG-IPA-MA) resins were comparable with or even superior to those from the Styrene-(PG-IPA-MA) resin. The AESO/(PG-IPA-MA) weight ratio was investigated for maximizing the mechanical properties of the kenaf fiber reinforced composites. The curing mechanism of the AESO-(PG-IPA-MA) resins is discussed in detail.

Keywords: styrene-free/styrene replacement; unsaturated polyester (UPE); natural fiber; composite; vegetable oil/soybean oil

3.2 Introduction

Glass fiber-reinforced thermoset composites are widely used for productions of automobile parts, boat hulls, oil tanks and pipes, bathtubs, and many other products.¹ The production of glass fibers is energy-consuming and the human exposure to fine glass fiber or its dust can cause irritation to eyes, skin, and the respiratory system.² Replacements of glass fibers with renewable natural fibers in fiber-reinforced composites have drawn much attention in recent years because natural fibers are generally inexpensive, abundant, renewable, safe to handle, and nonabrasive to processing equipment. Kenaf fibers have been a popular choice for replacing the glass fibers because kenaf can grow fast and the specific modulus of kenaf fibers is even higher than that of E-glass.³

Unsaturated polyester (UPE) resins are currently the most commonly used thermoset resins for fiber-reinforced thermoset composites.¹ They are less expensive than vinyl ester resins and epoxy resins.¹ One of the commercially available UPE resins from Ashland Inc. (Dublin, Ohio) is a mixture of styrene and PG-IPA-MA plastic that is derived from propylene glycol (PG), isophthalic acid (IPA) and maleic anhydride (MA) (designated as Styrene-(PG-IPA-MA)).

The PG-IPA-MA plastic is solid at room temperature and cannot flow for wetting reinforcing fibers. Styrene is typically used to dissolve the PG-IPA-MA plastic so that the resulting solution has a low viscosity at room temperature. Styrene acts as a solvent (more commonly called a diluent) and a crosslinking agent so that styrene is

incorporated into the thermoset polymer matrix after being cured. Styrene is currently the most commonly used reactive diluent because it is inexpensive and can significantly improve stiffness, strengths, water resistance, and thermal stability of the final fiber-reinforced composites.¹ However, styrene is volatile, toxic, and of strong unpleasant odor. It is classified as a hazardous air pollutant (HAP) and a reasonably anticipated human carcinogen by the National Toxicology Program (NTP) in 2011.⁴ It has been reported that unreacted styrene could continue to emit during the lifetime of a fiber-reinforced composite product.^{5,6} The emissive styrene causes air pollutions and poses health hazard for people who manufacture and use styrene, styrene-containing thermoset resins, and fiber-reinforced composites. The emission limits for styrene are regulated by government agencies and have gradually come down in recent years. The regulated emission limits are becoming more and more difficult to comply.¹ Therefore, there is a pressing need for development of a safer reactive diluent for the replacement of styrene.

Acrylate monomers such as methyl methacrylate and butyl (meth)acrylate and styrene analogs such as α -methylstyrene, vinyl toluene, and 4-*tert*-butylstyrene are also used as reactive diluents for UPE resins in industry.^{1,7} However, they are not an ideal styrene replacement because they are still harmful volatile organic compounds.

Vinyl propionate (VP), vinyl versatate (VV), ethylene glycol dimethacrylate (GDMA), or their mixtures have been investigated as replacements of styrene in UPE resins.⁸ It was found that the GDMA-VP or GDMA-VV mixture was comparable with styrene in

terms of the flexural modulus and impact strength of the cured resins.⁸ However, the flexural strength of the styrene-free resins was significantly lower than that of the styrenated counterparts (i.e., 20%-50% lower).⁸ Resin viscosity and volatility of VP, VV, and GDMA were not reported.

Vinyl levulinate from bio-based levulinic acid has been investigated as a styrene replacement in UPE resins.⁹ The impact strength of the styrene-free UPE resins was comparable with that of the styrenated counterparts; but the flexural strength and flexural modulus of the styrene-free resins were 35% lower than those of the styrenated resins.⁹ Viscosity and volatility of the styrene-free resins were also not reported.

Vegetable oils have low viscosity at room temperature and are not toxic or volatile. They are inexpensive, abundant, and renewable. Methacrylates from reactions of glycidyl methacrylate and various fatty acids were found to be not volatile.^{10,11} It has been demonstrated that the partial replacement of styrene in vinyl ester resins with the methacrylates did not compromise the resin viscosity and mechanical properties of the cured resins and composites.^{10,11} However, the complete replacement of styrene resulted in inferior mechanical properties and resin viscosity.^{10,11} It is not known whether the methacrylates can be used for the replacement of styrene in UPE resins.

Acrylated epoxidized soybean oil (AESO) is a reaction product of epoxidized soybean oil and acrylic acid. It is not volatile or hazardous. AESO has been extensively investigated for the preparation of bio-based coatings¹², adhesives¹³, coupling agents¹⁴,

resins^{15,16}, and foams¹⁷. In this study we found that AESO was able to replace styrene in the commercially available PG-IPA-MA-based UPE resins for production of superior kenaf fiber-reinforced composites.

3.3 Experimental

3.3.1 Materials

Acrylated epoxidized soybean oil (AESO) (containing 4,000 ppm monomethyl ether hydroquinone) was purchased from Sigma-Aldrich (St. Louis, MO). *tert*-Butyl peroxybenzoate (TBPB) was obtained from Akzo Nobel (Chicago, IL). Kenaf fibers were purchased from Kenaf Industries Ltd (Raymondville, TX). The PG-IPA-MA plastic and the Styrene-(PG-IPA-MA) resin (a mixture of the PG-IPA-MA plastic and styrene) were obtained from Ashland Inc. (Dublin, OH). The PG-IPA-MA plastic was slowly ground into powder before use.

3.3.2 Preparation of kenaf fiber mats

Kenaf fiber mats were prepared in accordance with a previously described method.¹⁸⁻²⁰ Specifically, kenaf fiber bundles (130 g, 1 inch in length) were fed into a LOUET drum carder for separating the large fiber bundles into small bundles or individual fibers. Through the carding, layering, and needle-punching process, a large piece of fine, unidirectionally oriented fiber mat was formed. The large mat was cut into five small square mats (200 mm × 200 mm) by a paper cutter. The fiber mats were dried in

an air circulating oven at 103 °C for at least 20 h before use. The total weight of five oven-dried fiber mats was 78 g.

3.3.3 Preparation of AESO-(PG-IPA-MA) resins

AESO (71.6 g) was heated to 90 °C in a 250-mL beaker equipped with a mechanical stirrer and an oil bath. The PG-IPA-MA plastic (47.7 g) was slowly added into AESO over 5 min. The mixture was stirred for 10 min to generate a homogenous and pourable resin. The resin was purged with nitrogen for 3 min and cooled to 70 °C. Subsequently, TBPB initiator (1.83 g, 1.5 wt% based on the total weight of AESO and the PG-IPA-MA plastic) was added into the resin and then stirred for 3 min. The resulting AESO-(PG-IPA-MA) resin had an AESO/(PG-IPA-MA) weight ratio of 60/40 and was designated as AESO60. AESO50 and AESO70 had the AESO/(PG-IPA-MA) weight ratio of 50/50 and 70/30, respectively, and were prepared with the same procedure as described for AESO60. Styrene-(PG-IPA-MA) was mixed with TBPB (1.5 wt% based on Styrene-(PG-IPA-MA) and used as a control. A mixture of AESO and TBPB (1.5 wt% based on AESO) was also used as a control.

3.3.4 Preparation of kenaf fiber-reinforced AESO-(PG-IPA-MA) composites

AESO60 (7.8 g) was slowly poured onto the upper surface of a kenaf fiber mat that was placed in the chamber of a stainless steel mold with a dimension of 200 mm × 200 mm × 3 mm. The mat was flipped and subsequently coated with the same amount of resin on the opposite surface. Afterwards, a second fiber mat was stacked above the

first mat with the fiber direction parallel to each other, and subsequently coated with AESO60 on both surfaces with the same procedures as described previously. The same procedure was repeated until five fiber mats were saturated with the resin. The beaker containing the AESO60 resin was stored in a hot water bath at 70 °C during the application of the resin onto the fiber mats for maintaining the low viscosity of the resin. A stack of the five resin-saturated fiber mats in the mold was covered by a stainless steel plate on top and was pressed at 3.5 MPa with an automatic Benchtop Carver press (Carver Inc., Wabash, IN) for 10 min at room temperature, and subsequently pressed at 4.5 MPa for 40 min with the temperature being raised to 160 °C at about 10 °C/min. The mold was then placed between two plywood panels, pressed under a pressure of 4.5 MPa, and allowed to slowly cool down for 100 min. The resulting kenaf fiber-reinforced AESO-UPE panel was removed from the mold, designated as kenaf-AESO60, and stored at room temperature overnight before being evaluated for its mechanical properties and water resistance. Two panels were made for each resin formulation. Kenaf-AESO50 and Kenaf-AESO70 composite panels were prepared with the same procedure as described previously. Kenaf-Styrene-(PG-IPA-MA) composite panels were prepared with the same procedure as described previously, except that the Styrene-(PG-IPA-MA) resin was kept at 40 °C during the resin application. Kenaf-AESO composite panels were prepared with the same procedure as described previously, except that the AESO resin was kept at 55 °C during the resin application.

3.3.5 Determination of flexural properties of the composites

The test specimens with the dimension of 65 mm × 12.7 mm × 3 mm and with the fibers aligning along the lengthwise direction of the specimen were evaluated for the flexural strength and flexural modulus through a three-point bending test that was performed according to ASTM D790, with a span of 50 mm and a rate of crosshead motion of 1.28 mm/min. At least six specimens were tested and averaged values were reported.

3.3.6 Determination of tensile properties of the composites

The tensile strength and tensile modulus were obtained from a tensile test in accordance with ASTM D3039. For the preparation of dumbbell shape specimens for the tensile test, the composite panels were first cut into rectangular specimens with the dimension of 58 mm × 14.5 mm × 3 mm and the fibers aligning along the lengthwise direction of the specimen. The rectangular specimens were further cut into dumbbell shape specimens that had a gripping length of 11 mm on each end, a width of the narrow section of 8.5 mm, and a length of the narrow section of 30 mm. The distance between grips was 36 mm, the rate of crosshead motion was 0.5 mm/min, and the time to failure was about 2 min. At least six specimens were tested and averaged values were reported.

3.3.7 Statistical analysis

Data from the flexural and the tensile tests were statistically analyzed by one-way ANOVA with SAS software (SAS Institute, Cary, North Carolina). All comparisons were based on a 95% confidence interval.

3.3.8 Measurements of water absorption of the composites

The water absorption tests were performed according to ASTM D570. Test specimens had the dimension of 76.2 mm × 25.4 mm × 3 mm. Prior to the tests, the specimens were dried in an oven for 24 h at 50 °C, cooled in a desiccator, and weighed. Subsequently, the specimens were immersed in distilled water. At predetermined intervals, the specimens were removed from water, wiped with dry tissue papers, weighed, and replaced in the water. The water absorption was determined by the ratio of the weight gain to the dry weight of the specimen. Three specimens were tested and averaged values were reported.

3.3.9 Differential scanning calorimetry (DSC) analysis

DSC experiments were performed on a TA Q2000 analyzer (TA Instruments, Inc., New Castle, DE). The DSC was calibrated in three steps: the first with nothing in the chamber to get a baseline correction, the second with sapphire to calibrate the heat capacity, and the third with indium for temperature calibration. The specimen chamber was purged with nitrogen during the experiments with a flow rate of 75 mL/min. For temperature sweep, test specimen in standard aluminum pan with lid

was heated from room temperature to 210 °C at a rate of 10 °C/min. An empty aluminum pan with a lid was used as a reference.

3.3.10 Measurements of resin viscosity

The resin viscosity was measured with an AR 2000ex rheometer (TA Instruments, Inc., New Castle, DE) with parallel plate geometry (25 mm in diameter). The gap between two plates was 400 µm. Test specimens (0.20 g) were steady-sheared at a shear rate of 5 Hz and a ramp rate of 5 °C/min. Sampling delay time was 10 s.

3.3.11 Measurements of a resin pot life

For the measurement of a resin pot life at use temperatures, an oscillatory time sweep was performed with the same AR 2000ex rheometer as described previously. Sampling delay time was set at 10 s. At t_0 , test specimens were started to be oscillatory-sheared at 5 Hz with a strain amplitude of 50% at a set temperature of 65, 70, 75, and 80 °C, respectively. As the curing began, the storage modulus (G') increased rapidly. At t_1 , G' was equal to the loss modulus (G''). The time between t_0 and t_1 was defined as the pot life for the resin in this study. Three specimens were tested and averaged values were reported.

3.4 Results and discussion

3.4.1 Determination of curing conditions

As shown in Figure 3.1, the curing of AESO started at around 102 °C and ended at 190 °C, with an exothermal peak at 130.5 °C (i.e., the temperature with the highest curing rate). The curing of AESO60 started at around 110 °C and ended at 190 °C with an exothermal peak at 133.7 °C. The shifts in the onset curing temperature from 102 to 110 °C and in the exothermal peak from 130.5 to 133.7 °C indicated that copolymerization between AESO and the PG-IPA-MA plastic occurred during the curing of AESO60.

The hot-press condition of 160 °C for 40 min was expected to be sufficient for the complete cure of the resin in the preparation of kenaf-AESO60 composites. DSC analysis indeed showed that there were no residual exothermal peaks for the kenaf-AESO60 composites (DSC graph not shown). The resulting kenaf-AESO60 composites had hard and smooth surfaces and had no visually detectable defects such as warpage, voids, blisters, cracks, and delamination, which also indicates the good curing of the resins.

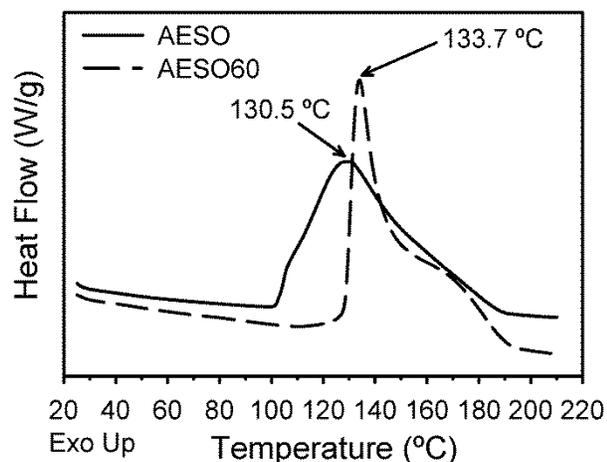


Figure 3.1 DSC curves for the course of curing of AESO and AESO60 (ramp rate: 10 °C/min)

3.4.2 Effects of the AESO content on the mechanical properties and water resistance of the composites

As shown in Figure 3.2, increasing the AESO content in the AESO-(PG-IPA-MA) resin from 50 to 60 wt% did not significantly change the flexural strength, but significantly increased the flexural modulus of the composites. Further increasing the AESO content from 60 to 70 wt% decreased the flexural strength significantly, but did not significantly decrease the flexural modulus. Composites prepared from AESO60 had better flexural properties than those from AESO50 and AESO70. Kenaf-AESO60 composites had a significantly higher flexural strength than and a comparable flexural modulus to kenaf-Styrene-(PG-IPA-MA) composites.

As shown in Figure 3.3, increasing the AESO content from 50 to 60 wt% didn't significantly change the tensile strength, but significantly increased the tensile

modulus of the composites. Further increasing the AESO content did not significantly change the tensile strength, but significantly decreased the tensile modulus. Kenaf-AESO60 had better tensile properties than kenaf-AESO50 and kenaf-AESO70. Compared to the kenaf-Styrene-(PG-IPA-MA) composites, the kenaf-AESO60 composites had a comparable tensile strength and a significantly higher tensile modulus. These results demonstrated that the optimum AESO content was about 60% and the AESO60 resin was superior to the Styrene-(PG-IPA-MA) resin in terms of the flexural and the tensile properties of the kenaf-reinforced composites.

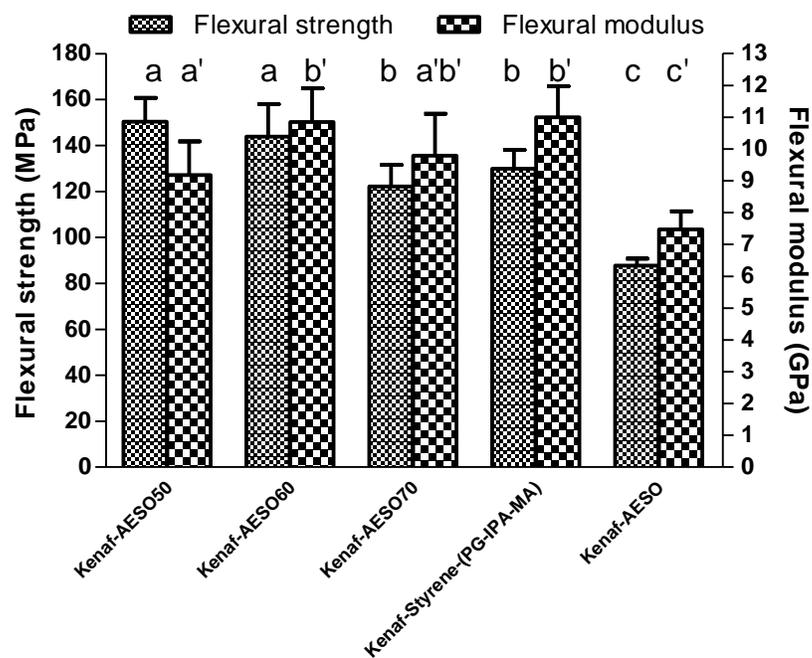


Figure 3.2 Effects of the AESO content on the flexural properties of the composites.

(The means between two groups significantly differ if the letters on top of error bars are different)

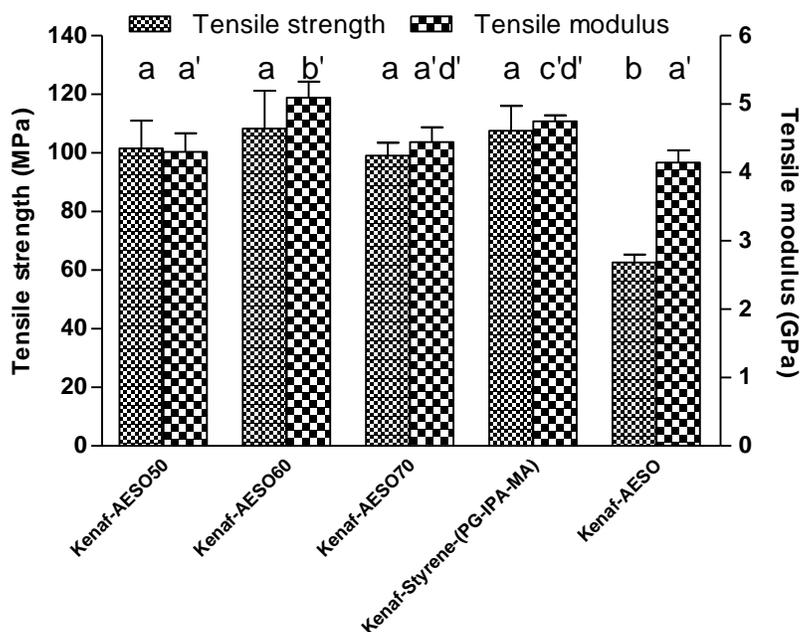


Figure 3.3 Effects of the AESO content on the tensile properties of the composites. (The means between two groups significantly differ if the letters on top of error bars are different)

As shown in Figure 3.4, the water absorption for the kenaf-AESO composites was much higher than any other composites at any given measurement time. For all other composites, the water absorption increased with increasing immersion time and then leveled out. Kenaf-AESO50 had approximately the same water absorption behavior as kenaf-Styrene-(PG-IPA-MA). As the AESO content increased from 50 to 70 wt%, the water absorption of the resulting composites increased. These results showed that AESO50 was comparable with Styrene-(PG-IPA-MA) and better than AESO60 and AESO70 in terms of the water absorption of the kenaf-reinforced composites.

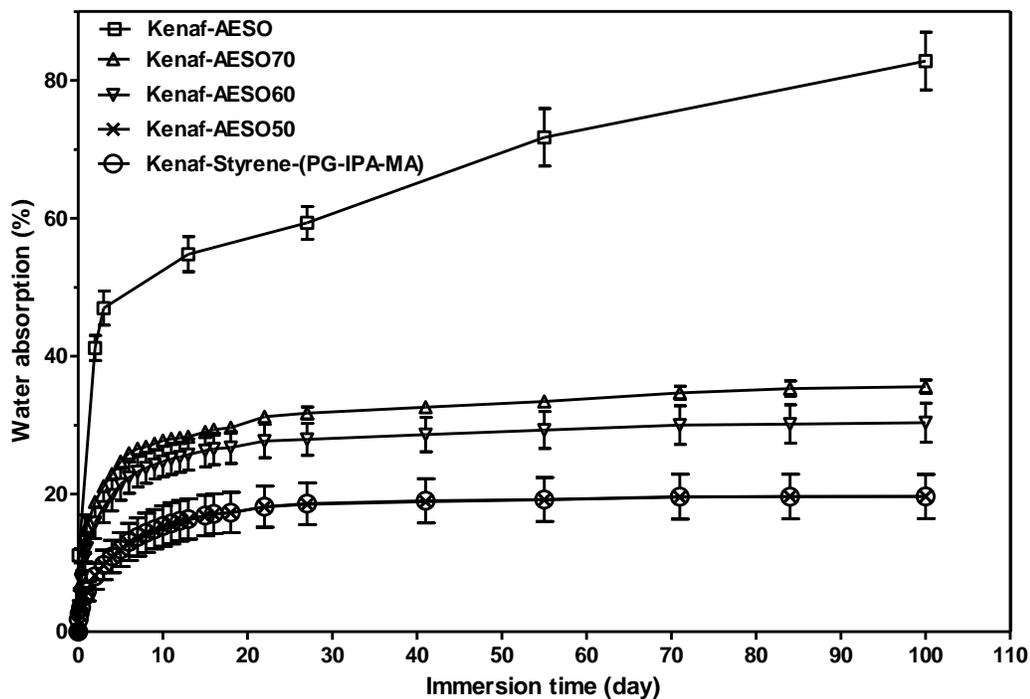


Figure 3.4 Effects of the AESO content on the water absorption of the composites

The representative structures of the AESO and the PG-IPA-MA plastic are shown in Figure 3.5 and 3.6, respectively. AESO (~1260 g/mol) has a higher molecular weight than styrene (104 g/mol). The C=C bonds in AESO have greater steric hindrance than those of styrene and cannot move as freely as styrene for polymerization reactions. We speculated that the C=C bonds in AESO cannot efficiently polymerize to form strong polymeric matrixes, which is consistent with the fact that kenaf-AESO composites have significantly lower strength (Figure 3.2 and 3.3) and higher water absorption (Figure 3.4) than the kenaf-Styrene-(PG-IPA-MA) composites. The C=C bonds in the PG-IPA-MA plastic are distributed along the polymer chains and cannot freely move around without carrying the polymer chains. There is considerable steric

hindrance surrounding the C=C bonds when two C=C bonds try to collide with each other for reactions because both ends of the C=C bonds are linked to the polymer chains. The inability of the C=C bonds to freely move around and the steric hindrance make the reactions among the C=C bonds in the UPE plastics very inefficient. As a result, the crosslinking/polymerization of the PG-IPA-MA plastic alone typically leads to weak and brittle polymeric matrixes containing substantial amounts of unreacted C=C bonds. It was unexpected that the mixture of AESO and the PG-IPA-MA plastic had strong synergistic effects between them and led to the generation of kenaf fiber-reinforced composites that had higher flexural and tensile properties than the kenaf-Styrene-(PG-IPA-MA) composites (Figure 3.2 – 3.4).

The proposed curing/crosslinking reactions between AESO and the PG-IPA-MA plastic are shown in Figure 3.7. AESO has multiple C=C bonds that can homopolymerize by themselves or copolymerize with the C=C bonds in the PG-IPA-MA plastic. The C=C bonds on the PG-IPA-MA polymer chains may also react with each other. These reactions together generated rigid, crosslinked networks.

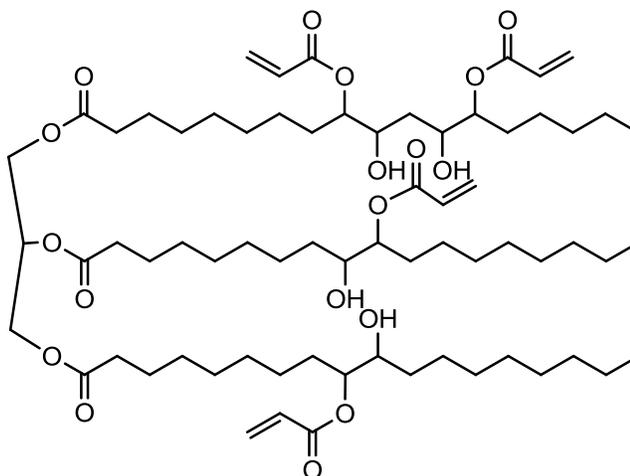


Figure 3.5 Representative structure of AESO

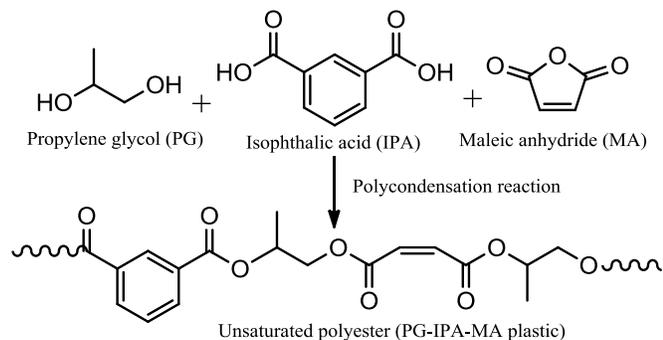


Figure 3.6 Representative structure of the PG-IPA-MA UPE plastic

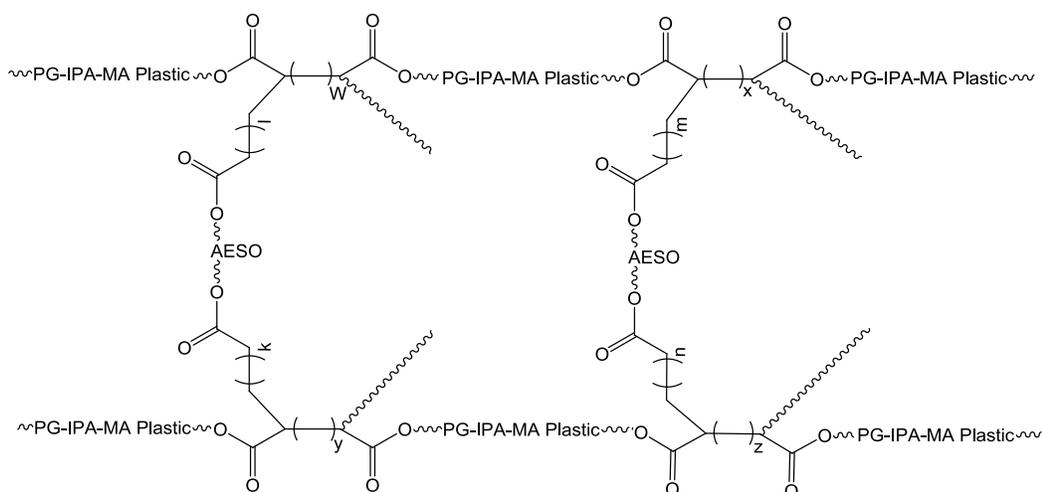


Figure 3.7 Proposed crosslinking reaction between AESO and the PG-IPA-MA UPE plastic

3.4.3 Resin viscosity

A viscosity of 10 Pa·s for a UPE resin was considered good for a hand lay-up resin application. The PG-IPA-MA plastic had to be heated to 160 °C for reaching the

viscosity of 10 Pa·s, whereas AESO60 only needed to be heated to 56 °C for reaching the same viscosity (Figure 3.8). The viscosity of AESO60 rapidly decreased from 10 to 3 Pa·s when the temperature was raised from 56 to 70 °C. The viscosity continued to decrease as the temperature increased and was about 1 Pa·s at 80 °C. The viscosity began to increase rapidly when the temperature was raised to 105 °C, which was in good agreement with the DSC results that the resin began to cure at 110 °C (Figure 3.1).

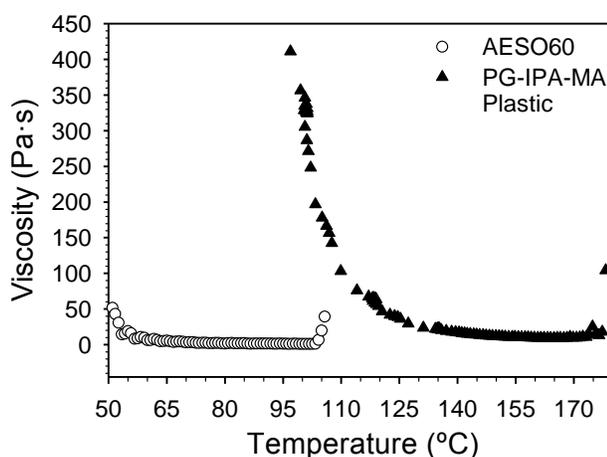


Figure 3.8 Effects of temperature on the resin viscosity (AESO60 contained 1.5 wt% of TBPB. The PG-IPA-MA UPE plastic didn't contain TBPB)

3.4.4 Resin pot life

Compared with the commercial styrene-(PG-IPA-MA) that has a low viscosity at room temperature, it is a drawback that AESO60 has to be heated and maintained at 56-80 °C so that it has a low viscosity for its easy application. As shown in Figure 3.9,

the pot life decreased along with the increase in temperature, which is consistent with the fact that TBPB decomposes faster at a higher temperature. At 70 °C, AESO60 had a long pot life of 134 min and a low viscosity of 3 Pa·s, which are very convenient conditions for a hand lay-up resin application process. For some composite fabrication processes that require an even lower viscosity, the temperature can be raised to about 80 °C at which the viscosity of the AESO60 resin is about 1 Pa·s. However, at this temperature, the resin has to be applied to fibers within 20 min.

Increase in the concentration of the inhibitor, monomethyl ether hydroquinone (MEHQ), is an effective way to increase the pot life of the resin. As shown in Figure 3.9, the pot life of AESO60 at 80 °C increased from 20 min to 50 min when the concentration of MEHQ was raised from 4000 ppm to 8500 ppm based on AESO.

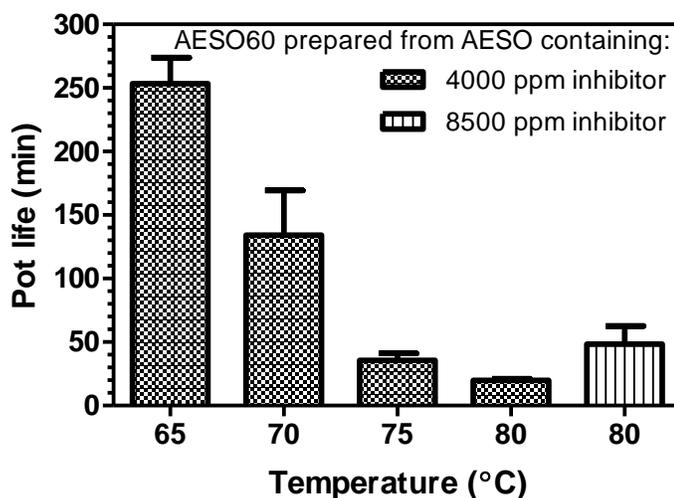


Figure 3.9 Effects of temperature on the pot life of AESO60

3.5. Conclusions

Styrene-free UPE resins with AESO as a styrene replacement and their kenaf fiber reinforced composites were successfully prepared and evaluated. DSC analysis showed that the composites were completely cured when the composites were pressed at 160 °C for 40 min. Kenaf-AESO60 had higher flexural and tensile strengths and moduli than kenaf-AESO50 or kenaf-AESO70. Kenaf-AESO60 had a higher flexural strength and a higher tensile modulus than kenaf-Styrene-(PG-IPA-MA). Kenaf-AESO60 had comparable flexural modulus and comparable tensile strength to kenaf-Styrene-(PG-IPA-MA). The water absorption of kenaf-AESO50 was lower than that of kenaf-AESO60 or kenaf-AESO70, and was comparable with that of kenaf-Styrene-(PG-IPA-MA). Kenaf-AESO50 had a higher flexural strength than kenaf-Styrene-(PG-IPA-MA) and had a comparable tensile strength to kenaf-Styrene-(PG-IPA-MA). AESO60 had low viscosity of 3 Pa·s and a sufficiently long pot life of 134 min at 70 °C for a hand lay-up process. Increase in temperature reduced the resin viscosity, but shorten the pot life of the resin. Increase in the concentration of the inhibitor, MEHQ, effectively increased the pot life of the resin.

3.6 Acknowledgement

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Li's group. We thank Ashland Inc. (Dublin, OH) for providing the commercial Styrene-(PG-IPA-MA) resin and the PG-IPA-MA plastic.

3.7 Reference

1. Strong, A.B. In *Fundamentals of Composites Manufacturing: Materials, Methods and Applications*, 2nd ed.; Society of Manufacturing Engineers: Dearborn, MI, **2008**; Chapter 3, pp 47-83.
2. U.S. Department of Labor, Chemical Sampling Information: Fibrous Glass Dust. https://www.osha.gov/dts/chemicalsampling/data/CH_242120.html (accessed July 1, 2015)
3. Akil, H. M., Omar, M. F., Mazuki, A. A. M., Safiee, S., Ishak, Z. A. M. and Bakar, A. A. *Mater. Des.* **2011**, *32*, 4107–4121.
4. U.S. Department of Health and Human Services; National Toxicology Program: Report on Carcinogens, 12th ed.; **2011**.
5. Senoz, E., Stanzione III, J. F., Reno, K. H., Wool, R. P. and Miller, M. E. N. *J. Appl. Polym. Sci.* **2013**, *128*, 983–989.
6. Sadler, J. M., Nguyen, A.-P., Greer, S. M., Palmese, G. R. and La Scala, J. J. *J. Biobased Mater. Bioenergy* **2012**, *6*, 86–93.
7. Hewitt, J. C., McAlvin, J. E., Hutson, P. T., Craig, A. E., Krantz, M. and Rivers, D. K. (Aoc, Llc). U.S. Patent 7,396,882, July 8, 2008.
8. Froehling, P. E. *J. Appl. Polym. Sci.* **1982**, *27*, 3577–3584.
9. Cousinet, S., Ghadban, A., Allaoua, I., Lortie, F., Portinha, D., Drockenmuller, E. and Pascault, J.-P. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 3356–3364.
10. La Scala, J. J., Sands, J. M., Orlicki, J. A., Robinette, E. J. and Palmese, G. R. *Polymer* **2004**, *45*, 7729–7737.
11. Can, E., La Scala, J. J., Sands, J. M. and Palmese, G. R. *J. Appl. Polym. Sci.* **2007**, *106*, 3833–3842.
12. Habib, F. and Bajpai, M. *Chem. Chem. Technol.* **2011**, *5*, 317–326.

13. David, S., Sathiyalekshmi, K. and Gnana Raj, G. *J. Mater. Sci.: Mater. Med.* **2009**, *20*, S61–S70.
14. Ren, X. and Li, K. *J. Appl. Polym. Sci.* **2013**, *128*, 1101–1109.
15. Khot, S. N., LaScala, J. J., Can, E., Morye, S. S., Williams, G. I., Palmese, G. R., Kusefoglou, S. H. and Wool, R. P. *J. Appl. Polym. Sci.* **2001**, *82*, 703–723.
16. Åkesson, D., Skrifvars, M. and Walkenström, P. *J. Appl. Polym. Sci.* **2009**, *114*, 2502–2508.
17. Bonnaillie, L. M. and Wool, R. P. *J. Appl. Polym. Sci.* **2007**, *105*, 1042–1052.
18. Ren, X., Li, C. and Li, K. *Polym. Eng. Sci.* **2013**, *53*, 1605–1613.
19. Ren, X., Qiu, R., Fifield, L. S., Simmons, K. L., and Li, K. *J. Adhes. Sci. Technol.* **2012**, *26*, 2277–2289.
20. Ren, X., Qiu, R. and Li, K. *J. Appl. Polym. Sci.* **2012**, *125*, 2846–2853.

Chapter 4 - Replacement of styrene with acrylated epoxidized soybean oil in an unsaturated polyester resin from propylene glycol and maleic anhydride

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4.1 Abstract

Styrene is a volatile, toxic component of most commercial unsaturated polyester (UPE) resins. A non-volatile, vegetable-oil based chemical, acrylated epoxidized soybean oil (AESO) was demonstrated to be a good replacement of styrene in one of commercial UPE resins (styrene-(PG-MA)) that is a mixture of styrene and a UPE plastic from propylene glycol and maleic anhydride (PG-MA). Neither AESO nor PG-MA was capable of forming a strong matrix, respectively, for glass fiber-reinforced composites. However, when a mixture of AESO and PG-MA was used as a thermoset resin (AESO-(PG-MA)) for glass fiber-reinforced composites, the resulting composites were comparable or even superior to those from styrene-(PG-MA) in terms of the flexural and tensile properties. While the non-reinforced cured styrene-(PG-MA) resin had cracking issues, the cured AESO-(PG-MA) resins were crack-free. Viscoelastic properties of the cured resins and the corresponding glass fiber-reinforced composites

were measured and discussed in detail. Effects of AESO contents on the mechanical and viscoelastic properties of the AESO-(PG-MA) resins and glass fiber-reinforced composites were investigated. Resin viscosity and resin pot life as a function of temperature were studied. The curing mechanism of the AESO-(PG-MA) resins is discussed in detail.

Keywords: styrene-free/styrene replacement; unsaturated polyester (UPE)/vinyl ester (VE); glass fiber; composite; vegetable oil/soybean oil

4.2. Introduction

Our previous study demonstrated that AESO was a great replacement of styrene in a commercially available UPE resin that is a mixture of styrene and PG-IPA-MA (designated as styrene-(PG-IPA-MA)) in terms of the flexural and tensile properties of the resulting kenaf fiber-reinforced composites.¹ PG-IPA-MA is derived from propylene glycol (PG), isophthalic acid (IPA), and maleic anhydride (MA).

The styrene-(PG-MA) resin that is a mixture of styrene and PG-MA is another widely used UPE resin in the industry. PG-MA is derived from PG and MA. When compared with PG-IPA-MA, PG-MA does not contain the aromatic IPA, has a higher degree of unsaturation, and is less expensive. The curing of the styrene-(PG-MA) resin is typically very fast and the degree of crosslinking is very high. As a result, the cured resin is very brittle and usually has lots of cracks. Because of the cracking issue, the styrene-(PG-MA) resin is seldom used alone in the industry. It is often blended

into other UPE resins for adjusting the speed of curing and the degree of crosslinking. In this study, we found that the complete replacement of styrene in the styrene-(PG-MA) resin with AESO enabled the resins to be used alone for the production of crack-free cured resins and glass fiber-reinforced composites with high strengths and moduli.

4.3 Experimental

4.3.1 Materials

Acrylated epoxidized soybean oil (AESO) (containing 4,000 ppm monomethyl ether hydroquinone) was purchased from Sigma-Aldrich (St. Louis, MO). *tert*-Butyl peroxybenzoate (TBPB) was obtained from Composite One (Vancouver, WA). PG-MA, the styrene-(PG-MA) resin (a mixture of PG-MA and styrene), and glass fiber mats with randomly oriented glass fibers were obtained from Ashland Inc. (Dublin, OH). The glass fiber mats were cut into the dimension of 200 mm × 200 mm by a paper cutter before use. Each glass fiber mat had a weight of about 17 g.

4.3.2 Preparation of AESO-(PG-MA) resins

AESO (107.6 g) was heated to 90 °C in a 600-mL beaker equipped with a mechanical stirrer and an oil bath. PG-MA (72.0 g) was added into AESO. The mixture was stirred for 10 min to generate a homogenous and pourable resin. The resin was purged with nitrogen for 10 min and cooled to 70 °C. Subsequently, TBPB (5.4 g, 3.0 wt% based on the total weight of AESO and PG-MA) was added into the resin and then stirred for 3 min. The resulting AESO-(PG-MA) resin had an AESO/(PG-MA) weight

ratio of 60/40 and was designated as AESO60(PG-MA). AESO50(PG-MA) and AESO40(PG-MA) had the AESO/(PG-MA) weight ratios of 50/50 and 40/60, respectively, and were prepared with the same procedure as described for AESO60(PG-MA). The styrene-(PG-MA) resin was mixed with TBPB (3.0 wt% based on styrene-(PG-MA)) and used as a control. A mixture of AESO and TBPB (3.0 wt% based on AESO) was also used as a control.

4.3.3 Preparation of glass fiber-reinforced AESO-(PG-MA) composites

AESO60(PG-MA) resin (18 g) was evenly poured onto the upper surface of a glass fiber mat that was placed in the chamber of a stainless steel mold with a dimension of 200 mm × 200 mm × 3 mm. Subsequently, the mat was flipped over and applied with 36 g of the resin on the surface. A second glass fiber mat was stacked above the first mat and was applied with 36 g of resin on the surface. A third glass fiber mat was stacked above the second mat and was applied with 36 g of resin on the surface. A fourth glass fiber mat was stacked above the third mat and was applied with 18 g of resin on the surface. During the resin application, the beaker containing the resin was kept in a 50 °C water bath when the resin was not poured onto the glass fiber mats. After the resin application, the mats were placed onto a hot plate (around 70 °C) and rolled by a rubber roller by hand for about 5 min for removing air inside the resin-saturated glass fiber mats. Afterwards, the mats in the stainless steel mold was first pressed at 3 MPa by an automatic Benchtop Carver press (Carver Inc., Wabash, IN) for 10 min, and subsequently pressed at the same pressure for 60 min with the

temperature rising to 160 °C at about 10 °C/min. The mold was then taken out of the press and cooled down at room temperature overnight. The resulting composite board was designated as glass-fiber-AESO60(PG-MA). Glass-fiber-AESO50(PG-MA) and glass-fiber-AESO40(PG-MA) were prepared with the same procedures as described previously for the preparation of glass-fiber-AESO60(PG-MA), except that the resin was kept at 60 and 75 °C during resin application, respectively. Glass-fiber-styrene-(PG-MA) was prepared with the same procedure as described previously for glass-fiber-AESO60(PG-MA), except that the resin was kept at room temperature during the resin application and the rolling for air removal. Glass-fiber-AESO was prepared with the same procedure as described previously for glass-fiber-AESO60(PG-MA). All resulting composite boards had a weight of about 154 g (excessive resins flowed out of the mold during the pressing process) and a dimension of 200 mm × 200 mm × 2.5 mm. The fiber content was calculated to be about 44% by weight for all composite boards. At least two boards were made and tested for each composition.

4.3.4 Determination of flexural properties of the composites

The test specimens with the dimension of 65 mm × 12.7 mm × 2.5 mm were prepared and evaluated for the flexural strength and flexural modulus through a three-point bending test in accordance with ASTM D790, with a span of 40 mm and a rate of crosshead motion of 1.28 mm/min. At least eighteen specimens were tested and averaged values were reported.

4.3.5 Determination of tensile properties of the composites

The tensile strength and tensile modulus were obtained from a tensile test in accordance with ASTM D638-10. For the preparation of type I dumbbell-shaped specimens, the composite boards were first cut into rectangular specimens with the dimension of 180 mm × 19 mm × 2.5 mm. The rectangular specimens were further cut to dumbbell-shaped specimens that had the width of the narrow section of 13 mm and the length of the narrow section of 57 mm. The distance between grips was 115 mm and the rate of crosshead motion was 5 mm/min. Five to eight specimens were tested and averaged values were reported.

4.3.6 Statistical analysis

Data from the flexural and the tensile tests were statistically analyzed by permutation test with RStudio statistical software (RStudio, Inc., Boston, MA). All comparisons were based on a 95% confidence interval.

4.3.7 Dynamic Mechanical Analysis (DMA)

Both non-reinforced cured resins and glass fiber-reinforced composites were characterized with DMA. For the preparation of the non-reinforced cured resins, uncured resins were heated to 80~90 °C and poured into the chamber that was created by putting a 3-mm thick rubber cord in between two glass plates with the dimension of 200 mm × 200 mm × 3 mm. The resins were subsequently cured in an air-circulating oven at 135 °C for 1 h, followed by a post cure at 160 °C for one more hour. Glass

fiber-reinforced composite specimens were cut from the same boards as those used for the flexural and tensile tests.

The DMA experiments were conducted by Ashland Inc. (Dublin, OH) with a TA Q800 analyzer (TA Instruments, Inc., New Castle, DE) using the 35-mm single cantilever clamp. Test specimens were surface ground to achieve the thickness of 1.75 mm. Test specimens with the dimension of 17.8 mm × 12.5 mm × 1.75 mm were tested at a constant frequency of 1 Hz. The specimens were first cooled to -100 °C, tested from -100 to 200 °C (first scan), cooled to -100 °C again, and retested from -100 to 200°C (second scan), with a ramp rate of 2 °C/min. Data from the second scan were used. The temperature at Tan δ maximum (i.e., peak value) was considered the glass transition temperature (T_g).

4.3.8 Differential scanning calorimetry (DSC) analysis

DSC experiments were performed on a TA Q2000 analyzer (TA Instruments, Inc., New Castle, DE). The analyzer was calibrated in three steps: the first with nothing in the chamber to get a baseline correction, the second with sapphire to calibrate the heat capacity, and the third with indium for temperature calibration. The specimen chamber was purged with nitrogen during the experiments with a flow rate of 50 mL/min. For temperature sweep, test specimen (10 mg) in hermetic aluminum pan with a lid was heated from room temperature to 250 °C at a rate of 10 °C/min. An empty hermetic aluminum pan with a lid was used as a reference.

4.3.9 Measurements of resin viscosity

The resin viscosity was measured with an AR 2000ex Rheometer (TA Instruments, Inc., New Castle, DE) with a cone-and-plate geometry (cone angle: 1 degree 59 min 17 sec; cone diameter: 40 mm; truncation gap 52 micro m). For the temperature sweep, test specimens were steady-sheared at a shear rate 1 Hz, from 90 to 25 °C at a rate of 5 °C/min.

4.3.10 Measurements of a resin pot life

For the measurement of a resin pot life at use temperatures, an oscillatory time sweep was performed with the same AR 2000ex rheometer as described previously with a parallel-plate geometry (25 mm in diameter). The gap between two plates was 400 µm. Sampling delay time was set at 10 s. At t_0 , test specimens were started to be oscillatorily sheared at 5 Hz with a strain amplitude of 50% at a set temperature of 70, 80 and 90 °C, respectively. As the curing began, the shear storage modulus (G') increased rapidly. At t_1 , G' was equal to the shear loss modulus (G''). The time between t_0 and t_1 was defined as the pot life for the resin in this study. Two to five specimens were tested.

4.4 RESULTS AND DISCUSSION

4.4.1 Determination of curing conditions

As shown in Figure 4.1, the curing of AESO60(PG-MA) started at 110 °C and ended at 195 °C with exothermal peaks at 127 °C and 165 °C. The curing of styrene-(PG-MA) started at 110 °C and ended at 200 °C with a sharp exothermal peak at 130 °C and a lower exothermal peak at 169 °C. Hot pressing at 160 °C for 60 min was expected to be able to completely cure the AESO-(PG-MA) resins and the styrene-(PG-MA) resin in the production of glass fiber-reinforced composites. Characterization of the resulting composites from all these resins with DSC from room temperature to 250 °C indeed revealed no exothermal peaks (DSC graph not shown). All the resulting glass fiber-reinforced composites prepared in this study had hard and smooth surfaces. No visually detectable defects such as cracks, warpage and delamination were identified.

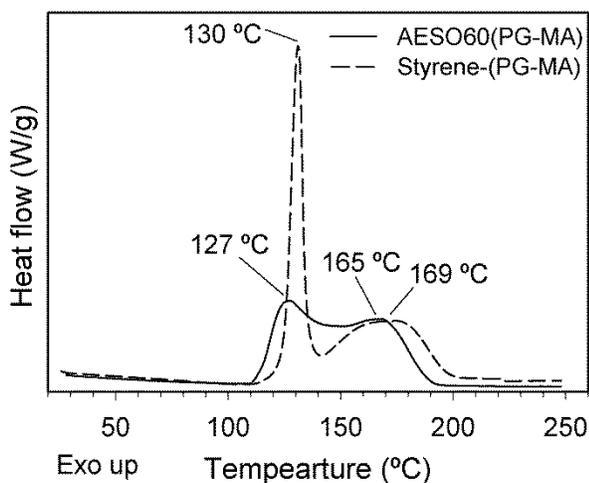


Figure 4.1 DSC curves for the course of curing of AESO60(PG-MA) and Styrene-(PG-MA) (ramp rate: 10 °C/min)

4.4.2 Effects of the AESO content on the mechanical properties of the composites

PG-MA cannot work as a good matrix for composites. The C=C bonds in PG-MA are distributed along the polymer chains and cannot freely move around without carrying the polymer chains. Because both ends of the C=C bonds are linked to the polymer chains, there are considerable steric hindrance surrounding the C=C bonds when two C=C bonds try to collide with each other. The inability of the C=C bonds to freely move around and the steric hindrance make the reactions among the C=C bonds in PG-MA very inefficient. As a result, the crosslinking/homopolymerization of PG-MA in the presence of a free radical initiator typically results in a weak and brittle polymeric matrix containing substantial amounts of unreacted C=C bonds.

AESO alone cannot work well as a matrix for composites as well. As shown in Figure 4.2 and 4.3, glass-fiber-AESO had the lowest flexural and tensile properties among all composites, indicating that cured AESO by itself was not a strong matrix.

However, mixtures of AESO and PG-MA appeared to have strong synergistic effects between them. As shown in Figure 4.2, glass-fiber-AESO60(PG-MA), glass-fiber-AESO50(PG-MA), and glass-fiber-AESO40(PG-MA) all had significantly higher flexural strength and flexural modulus than glass-fiber-styrene-(PG-MA). The reduction of the AESO content in the AESO-(PG-MA) resins from 60 to 50, and to 40

wt% did not significantly change the flexural strength. The flexural modulus of glass-fiber-AESO60(PG-MA) was higher than that of glass-fiber-AESO50(PG-MA); but was not significantly different from that of glass-fiber-AESO40(PG-MA). The flexural modulus of glass-fiber-AESO50(PG-MA) was not significantly different from that of glass-fiber-AESO40(PG-MA).

As shown in Figure 4.3, the tensile strength and tensile modulus of glass-fiber-AESO60(PG-MA) were not significantly different from those of glass-fiber-styrene-(PG-MA), respectively. The reduction of the AESO content from 60 to 50 wt% did not significantly change the tensile properties of the composites. The reduction of the AESO content from 60 to 40 wt% resulted in significantly lower tensile strength, but did not significantly change the tensile modulus.

Previous results demonstrated that the optimum AESO content in the AESO-(PG-MA) resins was 60 wt%, and that AESO60(PG-MA) was superior to styrene-(PG-MA) in terms of the mechanical properties of the glass fiber-reinforced composites.

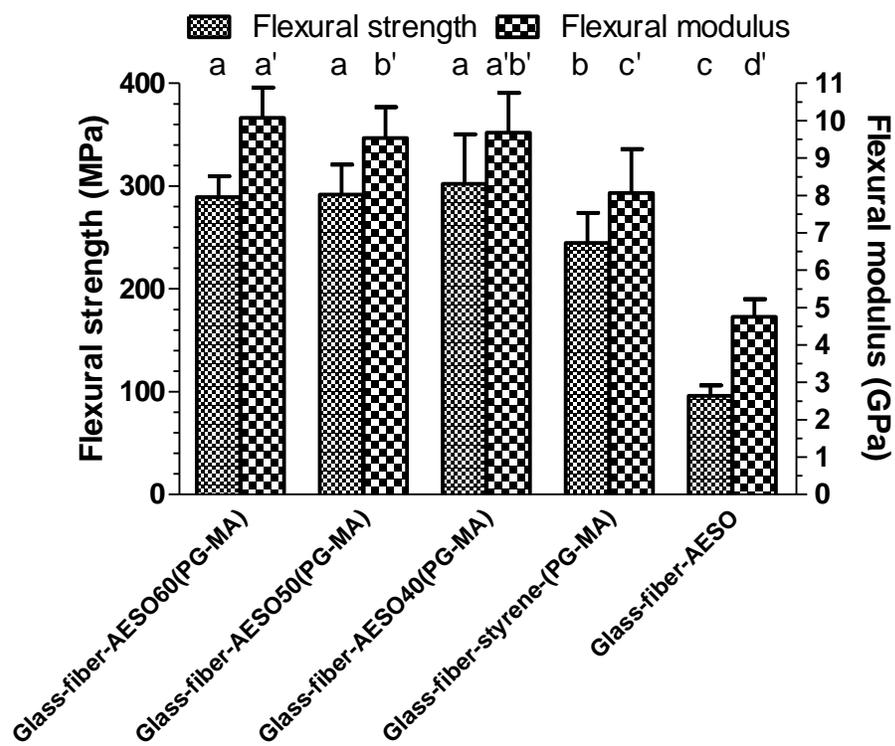


Figure 4.2 Effects of the AESO content on the flexural properties of the composites.

(The means between two groups significantly differ if the letters on top of error bars are different)

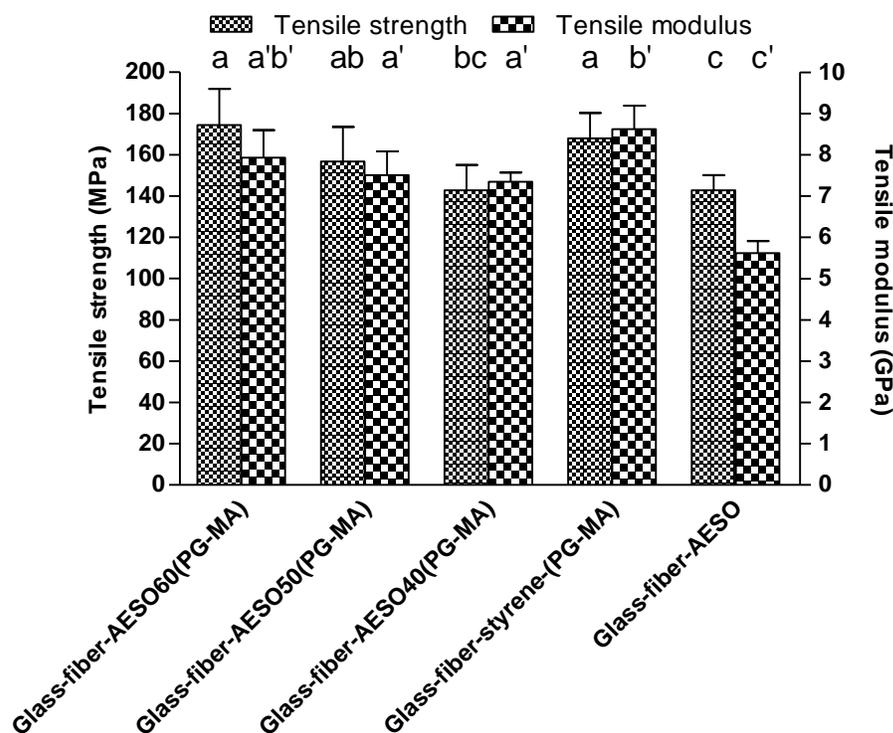


Figure 4.3 Effects of the AESO content on the tensile properties of the composites. (The means between two groups significantly differ if the letters on top of error bars are different)

The representative structures of the AESO and PG-MA are shown in Figure 3.5 and 4.4, respectively. The proposed crosslinking reactions between AESO and PG-MA are shown in Figure 4.5. The following three types of reactions are proposed to occur during the crosslinking reactions: 1) homopolymerization of the acryloyl C=C bonds of AESO (linkage I), 2) homopolymerization of the C=C bonds of PG-MA(linkage II), and 3) copolymerization of the acryloyl C=C bonds of AESO and the C=C bonds of PG-MA (linkage III). Because PG-MA cannot homopolymerize well, the amount of

the linkage II should be low. All these are proposed to result in rigid, crosslinked network structures for superior mechanical properties.

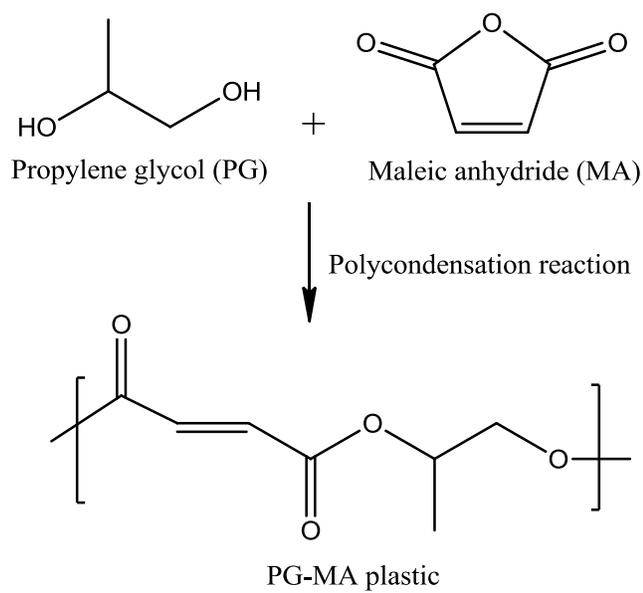


Figure 4.4 Representative structure of PG-MA

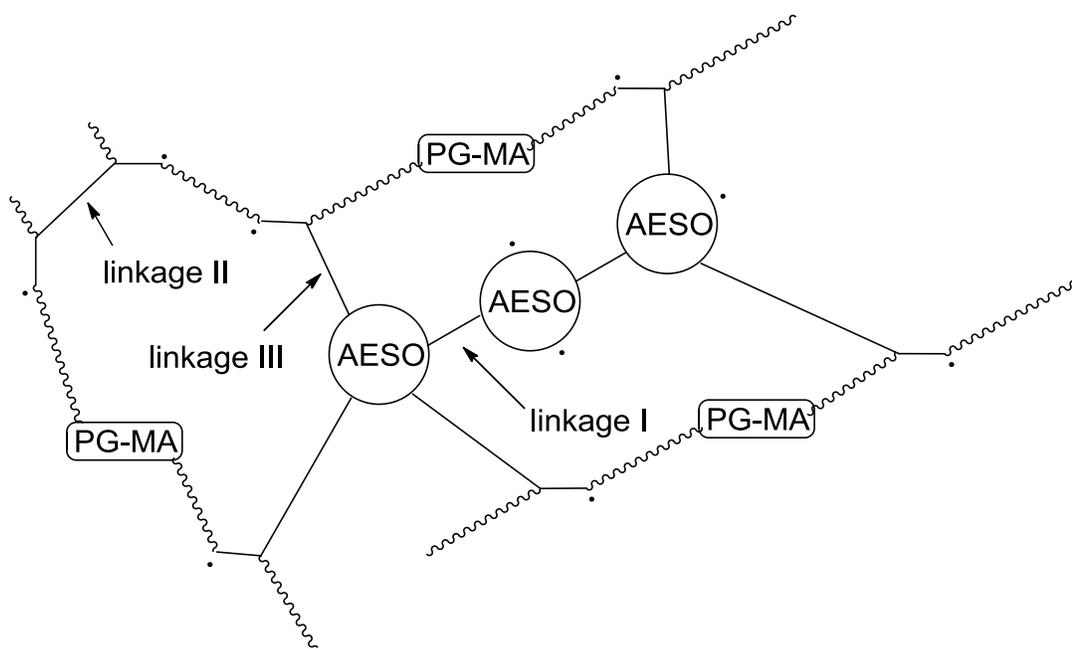


Figure 4.5 Proposed crosslinking reaction between AESO and PG-MA

4.4.3 Dynamic Mechanical Analysis (DMA)

The storage modulus (E') at 25 °C, Tan δ maximum, and T_g , determined from DMA provided insights into the viscoelastic properties of the cured resins and glass fiber-reinforced composites (Table 4.1).

Table 4.1 Summary of DMA data for non-reinforced cured resins and glass fiber-reinforced composites

Cured products	E' at 25 °C (GPa)	Tan δ maximum	T_g (°C)
<i>Non-reinforced cured resins</i>			
AESO	0.45	0.27	45.8
AESO60(PG-MA)	1.3	0.19	66.4
AESO50(PG-MA)	1.6	0.15	65.9
AESO40(PG-MA)	2.0	0.11	74.4
Styrene-(PG-MA)*	/	/	/
<i>Glass fiber-reinforced composites</i>			
Glass-fiber-AESO60(PG-MA)	7.0	0.060	104.0
Glass-fiber-AESO50(PG-MA)	6.3	0.054	104.8
Glass-fiber-AESO40(PG-MA)	6.5	0.051	112.7
Glass-fiber-styrene-(PG-MA)	7.2	0.038	178.2

* Cured styrene-(PG-MA) resin had a significant amount of cracks in it (Figure 4.6b), making it not usable for DMA measurements.

4.4.3.1 Storage modulus (E')

E' is a measure of the elastic character or solid-like nature of a viscoelastic material.

It is proportional to the material's ability to store recoverable energy during a loading

cycle. In a physical sense, E' is related to the stiffness of the material.^{2,3} As shown in Table 4.1, the cured AESO had the lowest E' . Cured AESO-(PG-MA) resins had significantly higher E' 's than the cured AESO resin, indicating that copolymers from AESO and PG-MA processed a more rigid polymer network than the polymers from AESO. As the AESO content increased from 40 to 60%, the E' of the cured resins decreased, indicating that the cured resins became less rigid with a higher usage of flexible AESO. Reinforcement of the cured resins with glass fibers changed this trend. Glass-fiber-AESO60(PG-MA) had the highest E' , which is in good agreement with its highest mechanical properties (Figure 4.2 and 4.3). It is believed that the wet-out of glass fibers with AESO60(PG-MA) was better than that with AESO50(PG-MA) or AESO40(PG-MA), as evidenced by the lower viscosity of AESO60(PG-MA) than AESO50(PG-MA) or AESO40(PG-MA) (Figure 4.7). The improved fiber wet-out is supposed to improve the interfaces between the cured resins (i.e., matrixes) and fibers in the resulting composites. The contribution of improved interfaces is believed to surpass the inherent lower E' of the cured AESO60(PG-MA) than the cured AESO50(PG-MA) or the cured AESO40(PG-MA), which thus leads to higher mechanical properties of the glass-fiber-AESO60(PG-MA) composites than the glass-fiber-AESO50(PG-MA) composites or the glass-fiber-AESO50(PG-MA) composites.

4.4.3.2 *Tan δ maximum*

Tan δ , also known as the damping factor or loss tangent, is the ratio of loss modulus (E'') to E' . E'' is a measure of the viscous character or liquid-like nature of a viscoelastic material, and is proportional to the material's ability to dissipate energy

during a loading cycle. A higher $\text{Tan } \delta$ indicates higher energy loss and more viscous behavior, whereas a lower $\text{Tan } \delta$ indicates lower energy loss and higher elastic behavior. A high $\text{Tan } \delta$ maximum generally indicates good toughness and good damping properties, which are useful against vibrational fatigue failure and noise in various applications.⁴

The cured AESO resin had the highest $\text{Tan } \delta$ maximum of 0.27. The cured AESO-(PG-MA) resins all had the $\text{Tan } \delta$ maximum of less than 0.2. A $\text{Tan } \delta$ maximum of smaller than 0.2 is a good sign of the presence of a highly crosslinked polymer network.⁵ As the AESO content increased from 40 to 60 wt%, the $\text{Tan } \delta$ maximum increased from 0.11 to 0.19, indicating the resulting polymer networks became tougher. Reinforcement with glass fibers did not change this trend.

4.4.3.3 Glass transition temperature (T_g)

The T_g represents a temperature over which glass transition occurs for an amorphous material. Glass transition is a reversible transition from a hard, glassy state (below the T_g) to a pliable, rubbery state (above the T_g). For structural applications, fiber-reinforced composites typically should have the T_g to be higher than the use temperature, typically room temperature, so that the material is in hard, glassy state and has the desired mechanical properties. The T_g can be defined either by the onset of E' , the E'' peak, or the $\text{Tan } \delta$ peak. DMA experiments for all the cured products in Table 4.1 showed that all the E' curves did not have a characteristic plateau in the glassy region¹⁵, making the onset transition not distinguishable. All the E'' curves

were found to be unusually broad, with a rather flat “peak” stretching over a width of 30~60 °C. Therefore, the determination of the T_g from either of these two curves was difficult and also arbitrary. The Tan δ curves, however, gave a distinguishable peak. Therefore, this study used the Tan δ peak temperature as the T_g .

The cured AESO resin had the low T_g of 45.8 °C. The cured AESO-(PG-MA) resins had higher T_g than the cured AESO resin. As the AESO content decreased from 60 to 50 wt%, T_g did not change significantly. A further decrease in AESO content to 40 wt% saw an increase in the T_g . Reinforcement of the cured AESO-(PG-MA) resin with glass fibers significantly increased the T_g by approximately 40 °C. Although the T_g s of glass-fiber-AESO-(PG-MA) (104~112.7 °C) were lower than that of glass-fiber-styrene-(PG-MA) (178.2 °C), they were well above room temperature. As a result, these composites are useful materials.

While the cured AESO resin and the cured AESO-(PG-MA) resins were a clear, rigid and strong plastic board at room temperature (Figure 4.6a), the cured styrene-(PG-MA) resin was very brittle and had lots of cracks and voids (Figure 4.6b). These defects made the preparation of test specimens unsuccessful and therefore no DMA experiments could be done for measuring the E' , Tan δ maximum, and T_g of the cured styrene-(PG-MA) resin (Table 4.1). Attempts for measuring the T_g using the DSC technique were made. However, it was found that DSC was not sensitive enough to show any transitions for this highly crosslinked thermoset (DSC curve not shown).

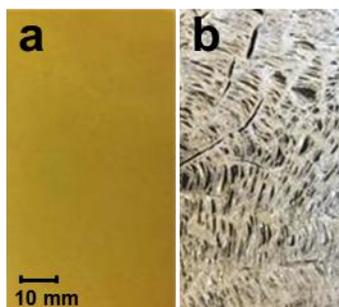


Figure 4.6 Appearance of the non-reinforced cured resins of (a) AESO60(PG-MA) and (b) Styrene-(PG-MA) (Picture was taken from a representative section of a 200 mm × 200 mm × 3 mm board)

4.4.4 Effects molecular nature of AESO

The molecular nature of AESO is proposed to be responsible for the lower T_g s of the glass-fiber-AESO-(PG-MA) composites than that of styrene-(PG-MA) and the crack-free appearance of the cured AESO-(PG-MA) resins, which can be explained in two aspects as follows. The first one is the “bulky and flexibility effect”. The AESO molecule has a triglyceride structure with three long and flexible fatty acid chains (Figure 3.5). This bulky, flexible triglyceride structure is supposed to introduce large free volume into the polymer network of AESO-(PG-MA). The large free volume can result in easy chain movements, which reduces the T_g s of the cured products.

The second one is the “low mobility effect”. The molecular weight of AESO (~1260 g/mol) is much higher than styrene (104 g/mol). In addition, AESO molecules contain a substantial amount of hydroxyl groups along the fatty acid chains, which is expected to introduce hydrogen bonding to the molecules. AESO molecule is supposed to have

a much lower mobility than styrene. While one styrene molecule only contains one single C=C bond for crosslinking reactions, one AESO molecule contains approximately 4.2 acryloyl C=C bonds for crosslinking reactions. This means that AESO molecule can quickly become essentially immobile after only one C=C bond of AESO participates in the crosslinking reactions. Because the C=C bonds of AESO cannot move around for crosslinking reactions with PG-MA as freely as the C=C bonds of styrene, the polymer network of the cured AESO-(PG-MA) resins is expected to have lower crosslinking density and thus be less compact than that of the cured styrene-(PG-MA). The less compact network is supposed to result in lower T_g s in the cured products. The lower crosslinking density is believed to effectively reduce brittleness and cracks in the cured products.

4.4.4 Resin viscosity and pot life

Depending on intended applications, commercial styrenated liquid resins typically have a viscosity in the range of 0.05 Pa·s to 6 Pa·s or even higher.⁷ The viscosity of the commercial styrene-(PG-MA) used in this study was 1.0 Pa·s. As shown in Figure 4.7, the viscosity of AESO40-(PG-MA), AESO50(PG-MA), and AESO60(PG-MA) was 821, 165, and 80 Pa·s, respectively, at room temperature, indicating that the viscosity decreased as the AESO content increased. The viscosities of the AESO-(PG-MA) resins also decreased rapidly as the temperature increased. A viscosity of 10 Pa·s was considered to be sufficiently low for a hand lay-up resin application.¹ The viscosity of AESO60(PG-MA) was reduced to 10 Pa·s at 45 °C, 6 Pa·s at 52 °C, and

1.0 Pa·s at 79 °C. For AESO50(PG-MA), the viscosity dropped to 10 Pa·s as the temperature increased to 58 °C that was slightly higher than the 45 °C for AESO60(PG-MA) at 10 Pa·s. However, for AESO40(PG-MA), its viscosity only dropped to 16 Pa·s even at the temperature of 90 °C.

As shown in Figure 4.8, the pot life of AESO60(PG-MA) decreased as temperature increased, which is expected because the initiator decomposes faster at a higher temperature. At 70 °C, AESO60(PG-MA) had the pot life of longer than 10 h (the tests were intentionally stopped at 10 h because such a pot life was considered long enough for many processes) and the viscosity of 1.7 Pa·s (Figure 4.7). As the temperature increased to 80 °C, the pot life dropped to 3 h that was still quite long and the viscosity was reduced to 0.97 Pa·s (Figure 4.7). Further increase in the temperature to 90 °C lowered the pot life to 38 min, but a very low viscosity of 0.5 Pa·s was achieved (Figure 4.7).

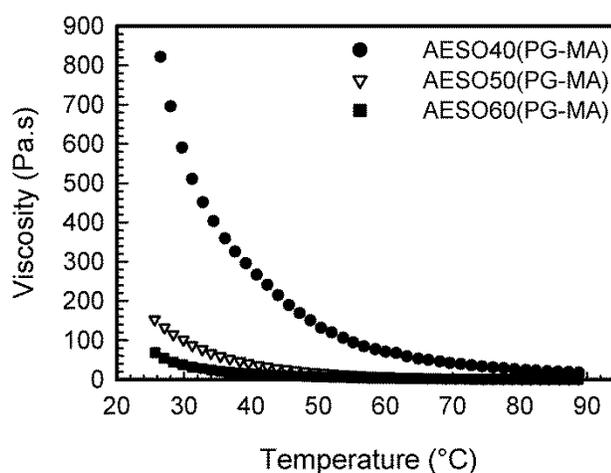


Figure 4.7 Effects of temperature on viscosity of AESO-(PG-MA) resins

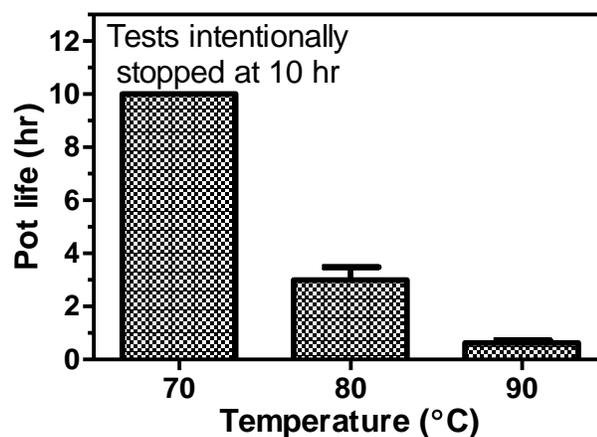


Figure 4.8 Effects of temperature on the pot life of AESO60(PG-MA)

AESO60(PG-MA) has to be used in an appropriate temperature range so that it has a desired viscosity and a sufficiently long pot life. In our experiments, AESO60(PG-MA) was maintained around 50 °C during the hand lay-up process. Maintaining the resin at such a temperature should be easily achieved both in the lab and in an industrial process by putting the container containing the resins in a 50 °C water bath.

Styrene is hazardous, volatile and flammable. Styrene-(PG-MA) can only be used in an enclosed area such as a fume hood with good ventilation so that workers' exposure to hazardous styrene can be minimized. Because AESO is not volatile, the handling of AESO60(PG-MA) is much safer than that of styrene-(PG-MA), and can be done in an open bench without a ventilation.

The fiber-reinforced UPE composites industry has an increased interest in the use of more renewable and more sustainable raw materials over petrochemicals.⁸ The

AESO60(PG-MA) resin contains about 43 wt% of renewable vegetable oil. Vegetable oil is supposed to be more sustainable than petroleum-based styrene. Because of its superior mechanical and viscoelastic properties, the glass-fiber-AESO60(PG-MA) composite may find applications in structural or non-structural building materials, automotive industry, marine industry, wind turbine industry, and more. AESO is a promising replacement for styrene in styrene-(PG-MA) resins.

4.5. Conclusions

The glass fiber-reinforced AESO-(PG-MA) composites were completely cured when pressed at 160 °C for 60 min. All glass fiber-reinforced AESO-(PG-MA) composites had significantly higher flexural strength and flexural modulus than glass-fiber-styrene-(PG-MA). The tensile strength and tensile modulus of glass-fiber-AESO60(PG-MA) were comparable to those of glass-fiber-styrene-(PG-MA). Glass-fiber-AESO60(PG-MA) had high E' at 25 °C as well as high $\text{Tan } \delta$ maximum, indicating good stiffness, good toughness, and good damping properties of this composite. The T_g (104 °C) of glass-fiber-AESO60(PG-MA) was sufficiently higher than normal indoor and outdoor use temperatures for fiber-reinforced UPE composites. While the non-reinforced cured styrene-(PG-MA) resin had cracking issues, the cured AESO-(PG-MA) resins were free of cracks. The viscosity of AESO60(PG-MA) was higher than styrene-(PG-MA) at room temperature; but decreased rapidly when the temperature increased. AESO60(PG-MA) at 45 °C had the viscosity of 10 Pa·s and was easily used in our hand lay-up applications.

AESO60(PG-MA) at 79 °C had the same viscosity (1 Pa·s) as styrene-(PG-MA), and had a pot life of 3 h

4.6. Acknowledgement

The authors are grateful to Dr. Willie E. Rochefort for his assistance on DSC analysis, viscosity measurements, and pot life measurements. This study was supported by return royalty fee income of patented wood adhesive technologies invented by K. Li's group. We thank Ashland Inc. (Dublin, OH) for providing the commercial Styrene-(PG-MA) resin and PG-MA, and for assistance on DMA measurements.

4.7 Reference

1. Chapter 3 - Replacement of styrene with acrylated epoxidized soybean oil in an unsaturated polyester resin from propylene glycol, isophthalic acid and maleic anhydride
2. Chartoff, R. P., Menczel, J. D. and Dillman, S. H. (2009) Dynamic Mechanical Analysis (DMA), in *Thermal Analysis of Polymers: Fundamentals and Applications* (eds J. D. Menczel and R. B. Prime), John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9780470423837.ch5 Dynamic mechanical analysis
3. Joseph F. Stanzione III, Philip A. Giangiulio, Joshua M. Sadler, John J. La Scala, and Richard P. Wool. Lignin-Based Bio-Oil Mimic as Biobased Resin for Composite Applications. *ACS Sustainable Chem. Eng.*, 2013, 1 (4), pp 419–426
4. Senoz, E., Stanzione, J. F., Reno, K. H., Wool, R. P. and Miller, M. E. N. (2013), Pyrolyzed chicken feather fibers for biobased composite reinforcement. *J. Appl. Polym. Sci.*, 128: 983–989. doi: 10.1002/app.38163
5. Joseph F. Stanzione III, Joshua M. Sadler, John J. La Scala, Kaleigh H. Reno and Richard P. Wool (2012) Vanillin-based resin for use in composite applications. *Green Chemistry*. 14: 2346-2352

6. Shrikant N. Khot, John J. Lascalea, Erde Can, Shantaram S. Morye, George I. Williams, Giuseppe R. Palmese, Selim H. Kusefoglu, Richard P. Wool, Development and Application of Triglyceride-Based Polymers and Composites, JAPS, Volume 82, Issue 3, 17 October 2001, Pages 703–723
7. Andreas Kandelbauer, Gianluca Tondi, and Sidney H. Goodman. Unsaturated Polyesters and Vinyl esters. In Handbook of Thermoset Plastics, 3rd edition. Hanna Dodiuk, Sydney H Goodman (eds.). William Andrew Publications, San Diego, CA. 2014. Chapter 6. Pages 111-172
8. Richard P. Wool and Xiuzhi Susan Sun. Bio-Based Polymers and Composites. Elsevier Academic Press, Burlington, MA. 2005

Chapter 5 - Replacement of styrene with acrylated epoxidized soybean oil in a dicyclopentadiene-modified unsaturated polyester resin

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5.1 Abstract

Styrene is commonly used in commercial unsaturated polyester (UPE) resins and is volatile and hazardous. Acrylated epoxidized soybean oil (AESO), a non-volatile, vegetable-oil based chemical, was investigated as a styrene replacement in a commercial UPE resin (a mixture of styrene and a dicyclopentadiene(DCPD)-modified UPE (DCPD-UPE)). DCPD-UPE is prepared from ethylene glycol, diethylene glycol, maleic anhydride, and DCPD. Mixtures of AESO and DCPD-UPE (AESO-(DCPD-UPE) resins) were found to result in superior glass fiber-reinforced composites and kenaf fiber-reinforced composites. The composites from the AESO-(DCPD-UPE) resins were comparable or even superior to those from the mixture of styrene and DCPD-UPE in terms of the flexural and tensile strength. Viscoelastic properties of the cured AESO-(DCPD-UPE) resins and the corresponding glass fiber-

reinforced composites were characterized. Viscosities and pot lives of the AESO-(DCPD-UPE) resins as a function of temperature were studied. The curing mechanism of the AESO-(DCPD-UPE) resins are discussed.

5.2 Introduction

AESO has been previously investigated as styrene replacements for two commercial UPE resins in our lab: i) styrene-(PG-IPA-MA) that was a mixture of styrene and PG-IPA-MA that was derived from propylene glycol (PG), isophthalic acid (IPA), and maleic anhydride (MA)¹, and ii) styrene-(PG-MA) that was a mixture of styrene and PG-MA that was derived from PG and MA². Another widely used commercial UPE resin is styrene-(DCPD-UPE) that is a mixture of styrene and a dicyclopentadiene-modified UPE (DCPD-UPE) derived from ethylene glycol, diethylene glycol (DEG), MA, and dicyclopentadiene (DCPD).

DCPD-UPE was of interest because it was very different from the UPEs previously used in our studies including PG-IPA-MA and PG-MA. The polar end groups including the carboxylic acid group and the hydroxyl group on the polyester chains were capped by DCPD (see Figure 5.6), which made DCPD-UPE less polar than PG-IPA-MA and PG-MA. The incorporation of DCPD inside the UPE chains also increases the content of hydrocarbon chains in the DCPD-UPE. Each AESO molecule consists of three non-polar hydrocarbon chains. Based on the principle of “like dissolves like”, it is believed that the capping of the UPE chains and the incorporation of DCPD inside the UPE chains make the DCPD-UPE more soluble in AESO than

PG-IPA-MA or PG-MA, which would result in lower viscosities of the resulting mixtures of AESO and DCPD-UPE (AESO-(DCPD-UPE) resins).

In this study, we found that AESO-(DCPD-UPE) resins were clear, homogenous, and pourable solutions and could serve as good matrixes for glass fiber-reinforced composites and kenaf fiber-reinforced composites, respectively. The resulting composites from AESO-(DCPD-UPE) were comparable or even superior to those from styrene-(DCPD-UPE) in terms of the flexural and tensile strength.

5.3 Experimental

5.3.1 Materials

Acrylated epoxidized soybean oil (AESO) (containing 4,000 ppm monomethyl ether hydroquinone) was purchased from Sigma-Aldrich (St. Louis, MO). *tert*-Butyl peroxybenzoate (TBPB) was obtained from Composite One (Vancouver, WA). DCPD-UPE, styrene-(DCPD-UPE), and glass fiber mats with randomly oriented glass fibers were obtained from Ashland Inc. (Dublin, OH). The glass fiber mats were cut into the dimension of 200 mm × 200 mm with a paper cutter before use. Each glass fiber mat had a weight of about 17 g. Kenaf fibers were purchased from Kenaf Industries Ltd (Raymondville, TX).

5.3.2 Preparation of AESO-(DCPD-UPE) resins

AESO (100.9 g) and DCPD-UPE (100.9 g) were added to a 600-mL beaker equipped with a mechanical stirrer and an oil bath. The mixture was heated to 90 °C and stirred for 10 min to generate a clear, homogenous solution. The solution was purged with nitrogen for 10 min and cooled to 60 °C. Subsequently, the TBPB initiator (6.0 g, 3.0 wt% based on the total weight of the solution) was added into the solution and the solution was stirred for 3 min. The resulting solution was poured into a container. The container was placed in a centrifuge (Labofuge 400, Heraeus Instrument, Germany) and was centrifuged at 3000 rpm for 3 min for the removal of air bubbles in the solution. The resulting AESO-(DCPD) resin had an AESO/(DCPD-UPE) weight ratio of 50/50 and was designated as AESO50(DCPD-UPE). AESO60(DCPD-UPE) and AESO40(DCPD-UPE) had the AESO/(DCPD-UPE) weight ratio of 60/40 and 40/60, respectively, and were prepared with the same procedure as described for AESO50(DCPD-UPE). The styrene-(DCPD-UPE) resin was mixed with TBPB (3.0 wt% based on styrene-(DCPD-UPE)) and used as a control.

5.3.3 Preparation of glass fiber-reinforced AESO-(DCPD-UPE) composites

The AESO50(DCPD-UPE) resin (18 g) was evenly poured onto the upper surface of a glass fiber mat that was placed in the chamber of a stainless steel mold with the dimension of 200 mm × 200 mm × 3 mm. Subsequently, the mat was flipped over and applied with 32 g of the resin on the surface. A second glass fiber mat was stacked above the first mat and was applied with 32 g of the resin on the surface. A third glass

fiber mat was stacked above the second mat and was applied with 32 g of the resin on the surface. A fourth glass fiber mat was stacked above the third mat and was applied with 18 g of resin on the surface. After the resin application, for the removal of air inside the resin-coated glass fiber mats, the mats were placed onto a hot plate (~50 °C) and rolled by a rubber roller by hand for about 5 min. Afterwards, the mats were placed in the stainless steel mold and were covered by a stainless steel plate on top. The mold was first pressed at 3 MPa by an automatic Benchtop Carver press (Carver Inc., Wabash, IN) at room temperature for 10 min, and subsequently pressed at the same pressure for 60 min with the temperature being raised to 160 °C at about 10 °C/min. Afterwards, the mold was taken out from the press and cooled down at room temperature. The resulting composite board was designated as glass-fiber-AESO50(DCPD-UPE). Glass-fiber-AESO60(DCPD-UPE) and glass-fiber-AESO40(DCPD-UPE) were prepared with the same procedure as described previously for glass-fiber-AESO50(DCPD-UPE). Glass-fiber-styrene-(DCPD-UPE) was prepared with the same procedure as described previously glass-fiber-AESO50(DCPD-UPE), except that the rolling for the removal of air inside the mats was conducted at room temperature. The resulting composite boards had a weight of about 151 g (excessive resins flowed out of the mold during the pressing process) and the dimension of 200 mm × 200 mm × 2.5 mm. The fiber content was calculated to be about 45% by weight for all composite boards. Two boards were made and tested for each composition.

5.3.4 Preparation of kenaf fiber-reinforced AESO-(DCPD-UPE) composites

Kenaf fiber mats were prepared according to the procedure reported in our previous study.¹⁶ AESO50(DCPD-UPE) (9.0 g) was slowly poured onto the upper surface of a kenaf fiber mat that was placed in the chamber of the stainless steel mold with the dimension of 200 mm × 200 mm × 3 mm. The mat was flipped and subsequently coated with the same amount of resin on the opposite surface. A second fiber mat was stacked above the first mat with the fiber direction parallel to each other, and subsequently coated with AESO50(DCPD-UPE) on both surfaces with the same procedure as described previously. The same procedure was repeated until five fiber mats were coated with the resin. A stack of the five resin-coated fiber mats in the mold was covered by a stainless steel plate on top and was pressed at 3.8 MPa with the Benchtop Carver press for 10 min at room temperature, and subsequently for 60 min under the same pressure with the temperature being raised to 160 °C at about 10 °C/min. Afterwards, the mold was taken out from the press and cooled down at room temperature. The resulting kenaf fiber-reinforced composite board was designated as kenaf-fiber-AESO50(DCPD-UPE). Kenaf-fiber-AESO60(DCPD-UPE), kenaf-fiber-AESO40(DCPD-UPE), and kenaf-fiber-styrene-(DCPD-UPE) were prepared with the same procedure as previously described for kenaf-fiber-AESO50(DCPD-UPE). The resulting composite boards had a weight of about 121 g (excessive resins flowed out of the mold during the pressing process) and a dimension of 200 mm × 200 mm × 2.8 mm. The fiber content was calculated to be about 65% by weight for all composite boards. Two boards were made and tested for each composition.

5.3.5 Determination of flexural properties of the composites

For glass fiber-reinforced composites, test specimens with the dimension of 65 mm × 12.7 mm × 2.5 mm were prepared and evaluated for the flexural strength and flexural modulus through a three-point bending test in accordance with ASTM D790, with a span of 40 mm and a rate of crosshead motion of 1.28 mm/min. Eighteen specimens were tested and averaged values were reported.

For kenaf fiber-reinforced composites, test specimens with the dimension of 65 mm × 12.7 mm × 2.8 mm and with the fibers aligning along the lengthwise direction of the specimens were prepared and evaluated for the flexural strength and flexural modulus through a three-point bending test in accordance with ASTM D790, with a span of 42 mm and a rate of crosshead motion of 1.11 mm/min. Eighteen specimens were tested and averaged values were reported.

5.3.6 Determination of tensile properties of the composites

For glass fiber-reinforced composites, the tensile strength and tensile modulus were obtained from a tensile test in accordance with ASTM D638. For the preparation of type I dumbbell-shaped specimens, the composite boards were first cut into rectangular specimens with the dimension of 180 mm × 19 mm × 2.5 mm. The rectangular specimens were further cut to dumbbell-shaped specimens that had a width of narrow section of 13 mm and a length of narrow section of 57 mm. The distance between grips was 115 mm, and the rate of crosshead motion was 5 mm/min. At least five specimens were tested and averaged values were reported.

For kenaf fiber-reinforced composites, the same procedure previously described were used, except that test specimens with the thickness of 2.8 mm and with the fibers aligning along the lengthwise direction of the specimens were used, and the rate of crosshead motion was 2 mm/min. At least five specimens were tested and averaged values were reported.

5.3.7 Statistical analysis

Data from the flexural and the tensile tests were statistically analyzed by permutation test using RStudio (RStudio, Inc., Boston, MA). All comparisons were based on a 95% confidence interval.

5.3.8 Dynamic Mechanical Analysis (DMA)

Both non-reinforced cured resins and glass fiber-reinforced composites were characterized with DMA. For the preparation of the non-reinforced cured resins, uncured resins were poured into the chamber that was created by putting a 3-mm thick rubber cord in between two glass plates with the dimension of 200 mm × 200 mm × 3 mm. The resins were subsequently cured in an air-circulating oven at 135 °C for 1 h, followed by a post cure at 160 °C for one more hour. Glass fiber-reinforced composite specimens were cut from the same boards as those used for the flexural and tensile tests.

The DMA experiments were conducted by Ashland Inc. (Dublin, OH) with a TA Q800 analyzer (TA Instruments, Inc., New Castle, DE) using the 35-mm single

cantilever clamp. Test specimens were surface ground to achieve the thickness of 1.75 mm. Test specimens with the dimension of 17.8 mm × 12.5 mm × 1.75 mm were tested at a constant frequency of 1 Hz. The specimens were first cooled to -100 °C, tested from -100 to 200 °C (first scan), cooled to -100 °C again, and retested from -100 to 200°C (second scan), with a ramp rate of 2 °C/min. Data from the second scan were used. The temperature at $\tan \delta$ maximum (i.e., peak value) was considered the glass transition temperature (T_g).

5.3.9 Differential scanning calorimetry (DSC) analysis

DSC experiments were performed on a TA Q2000 analyzer (TA Instruments, Inc., New Castle, DE). The analyzer was calibrated in three steps: the first with nothing in the chamber to get a baseline correction, the second with sapphire to calibrate the heat capacity, and the third with indium for temperature calibration. The specimen chamber was purged with nitrogen during the experiments with a flow rate of 50 mL/min. For temperature sweep, test specimen (10 mg) in hermetic aluminum pan with a lid was heated from room temperature to 250 °C at a rate of 10 °C/min. An empty hermetic aluminum pan with a lid was used as a reference.

5.3.10 Measurements of resin viscosity

The resin viscosity was measured with an AR 2000ex Rheometer (TA Instruments, Inc., New Castle, DE) with a cone-and-plate geometry (cone angle: 1 degree 59 min 17 sec; cone diameter: 40 mm; truncation gap 52 micro m). For the temperature

sweep, test specimens were steady-sheared at the shear rate 1 Hz, from 25 to 90 °C at the rate of 1 °C/min.

5.3.11 The measurement of a resin pot life

For the measurement of a resin pot life at use temperatures, an oscillatory time sweep was performed with the same AR 2000ex rheometer as described previously with a parallel-plate geometry (25 mm in diameter). The gap between two plates was 400 μm . Sampling delay time was set at 10 s. At t_0 , test specimens were started to be oscillatorily sheared at 5 Hz with a strain amplitude of 50% at a set temperature of 50 and 62 °C, respectively. As the curing began, the shear storage modulus (G') increased rapidly. At t_1 , G' was equal to the shear loss modulus (G''). The time between t_0 and t_1 was defined as the pot life for the resin in this study. Two specimens were tested and averaged values were reported.

5.4 Results and discussion

5.4.1 Determination of curing conditions

As shown in Figure 5.1, the curing of the AESO-(DCPD-UPE) resins and the styrene-(DCPD-UPE) resin all started at around 110 °C and ended at around 195 °C. The exothermal peak for AESO40(DCPD-UPE), AESO50(DCPD-UPE), and AESO60(DCPD-UPE) were 159.8, 151.7, and 141.6 °C, respectively, indicating that the exothermal peak (i.e., peak reaction rate) occurred at a lower temperature as the AESO content increased. This can be explained as follows. The acryloyl C=C bonds

on AESO have a higher reactivity (i.e., require a lower temperature/energy input to activate) for polymerization reactions than the 1,2-disubstituted C=C bonds on DCPD-UPE. As the AESO content increases (or the DCPD-UPE content decreases) in the AESO-(DCPD-UPE) resin, the total amount of more reactive acryloyl C=C bonds in the resin increases while the total amount of less reactive 1,2-disubstituted C=C bonds in the resin is reduced, which is supposed to make the peak reaction rate occur at a lower temperature. The curing of styrene-(DCPD-UPE) showed two exothermal peaks, a higher peak at 134.7 °C and a lower peak at 165.8 °C.

Hot pressing at 160 °C for 60 min was expected to be able to completely cure the AESO-(DCPD-UPE) resins and the styrene-(DCPD-UPE) resin in the preparation of glass fiber-reinforced composites and kenaf fiber-reinforced composites, respectively. DSC analysis on the cured composites did not show any exothermal peaks in the temperature range of 25 to 250 °C, which confirmed the complete curing of the resins in the composites (DSC graph not shown). All glass fiber-reinforced composites and kenaf fiber-reinforced composites prepared in this study had hard and smooth surfaces. No visually detectable defects such as cracks, warpage, and delamination were identified.

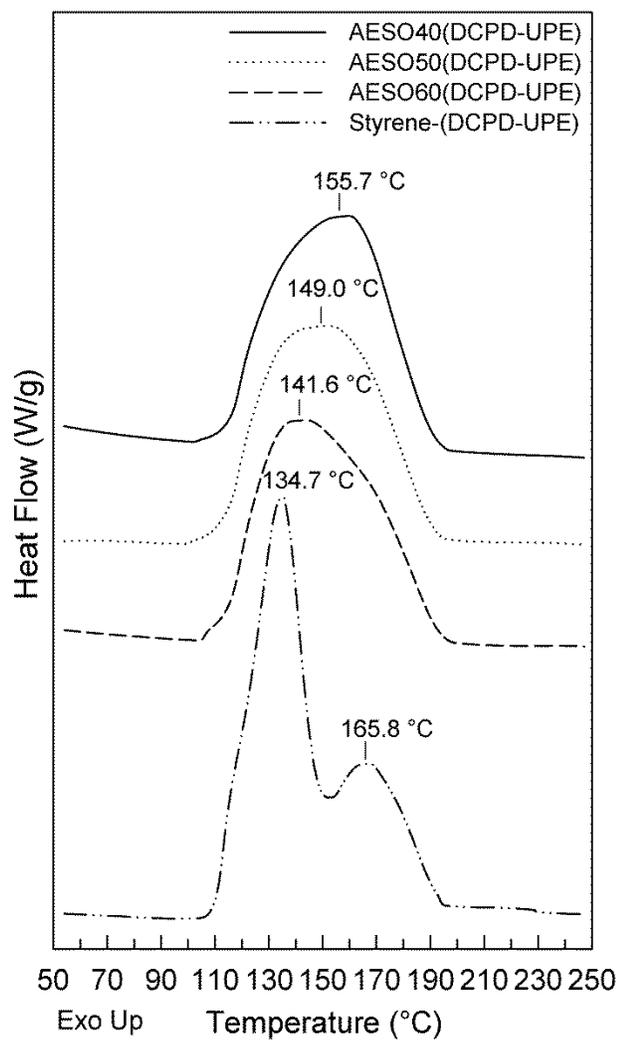


Figure 5.1 DSC curves for the course of curing of AESO-(DCPD-UPE) and styrene-(DCPD-UPE) (ramp rate: 10 °C/min)

5.4.2 Effects of the AESO content on the flexural and tensile properties of the glass fiber-reinforced composites and kenaf fiber-reinforced composites

As shown in Figure 5.2, the flexural strength of the glass fiber-reinforced composites increased when the AESO content decreased from 60 to 40%. The flexural strength of glass-fiber-styrene-(DCPD-UPE) was not significantly different from that of glass-fiber-AESO50(DCPD-UPE) or glass-fiber-AESO40(DCPD-UPE), but was higher than that of glass-fiber-AESO60(DCPD-UPE). The flexural moduli of glass-fiber-AESO50(DCPD-UPE) and glass-fiber-AESO40(DCPD-UPE) were not significantly different from each other, were both higher than that of glass-fiber-AESO60(DCPD-UPE), but were both lower than those of glass-fiber-styrene-(DCPD-UPE).

As shown in Figure 5.3, the tensile strengths of all glass fiber-reinforced composites were not significantly different from each other. The tensile moduli of glass-fiber-AESO60(DCPD-UPE), glass-fiber-AESO50(DCPD-UPE), and glass-fiber-AESO40(DCPD-UPE) were not significantly different from each other; but were lower than those of glass-fiber-styrene-(DCPD-UPE).

Previous results demonstrated that both AESO50(DCPD-UPE) and AESO40(DCPD-UPE) were comparable to styrene-(DCPD-UPE) in terms of the flexural and tensile strength of the resulting glass fiber-reinforced composites; but were inferior to styrene-(DCPD-UPE) in terms of the flexural and tensile moduli of the resulting glass fiber-reinforced composites.

As shown in Figure 5.4, the flexural strength and flexural modulus of the kenaf fiber-reinforced composites increased when the AESO content decreased from 60 to 50%. The reduction in the AESO content from 50% to 40% did not significantly change the flexural strength and flexural modulus of the composites. The flexural strength of kenaf-fiber-styrene-(DCPD-UPE) were not significantly different from that of kenaf-fiber-AESO50(DCPD-UPE) or kenaf-fiber-AESO40(DCPD-UPE). The flexural modulus of kenaf-fiber-styrene-(DCPD-UPE) was not significantly different from that of kenaf-fiber-AESO40(DCPD-UPE), but was higher than that of kenaf-fiber-AESO50(DCPD-UPE).

As shown in Figure 5.5, the tensile strength of the kenaf fiber-reinforced composites increased when the AESO content decreased from 60 to 50%. The reduction in the AESO content from 50% to 40% did not significantly change the tensile strength. The tensile strength of kenaf-fiber-styrene-(DCPD-UPE) was not significantly different from that of kenaf fiber-AESO60(DCPD-UPE); but was lower than that of kenaf-fiber-AESO50(DCPD-UPE) or kenaf-fiber-AESO40(DCPD-UPE). As the AESO content decreased from 60 to 40%, the tensile modulus of each kenaf fiber-reinforced composite was not significantly different from each other, but was lower than that of kenaf-fiber-styrene-(DCPD-UPE).

Previous results demonstrated that both AESO50(DCPD-UPE) and AESO40(DCPD-UPE) were comparable to styrene-(DCPD-UPE) in terms of the flexural strength of the resulting kenaf fiber-reinforced composites, superior to styrene-(DCPD-UPE) in

terms of the tensile strength of the resulting kenaf fiber-reinforced composites, but inferior to styrene-(DCPD-UPE) in terms of the tensile modulus of the resulting kenaf fiber-reinforced composites. AESO40(DCPD-UPE) was comparable to styrene-(DCPD-UPE) in terms of the flexural modulus of the resulting kenaf fiber-reinforced composites.

AESO is supposed to work as a crosslinking agent for DCPD-UPE. An insufficient amount of AESO would result in the low degree of crosslinking, thus lowering the mechanical properties; whereas an excessive amount of AESO would not participate the crosslinking reactions and result in weak phase in the cured AESO-(DCPD-UPE) matrixes, thus lowering the mechanical properties as well. That most mechanical properties of the resulting composites did not changed significantly when the AESO content increased from 40 to 50% (Figures 5.2–5.5) suggests that the 40% AESO was sufficient for crosslinking reactions, and 50% AESO was not excessive. The 60% AESO appeared to be excessive because the mechanical properties decreased when the AESO content was raised from 50% to 60%.

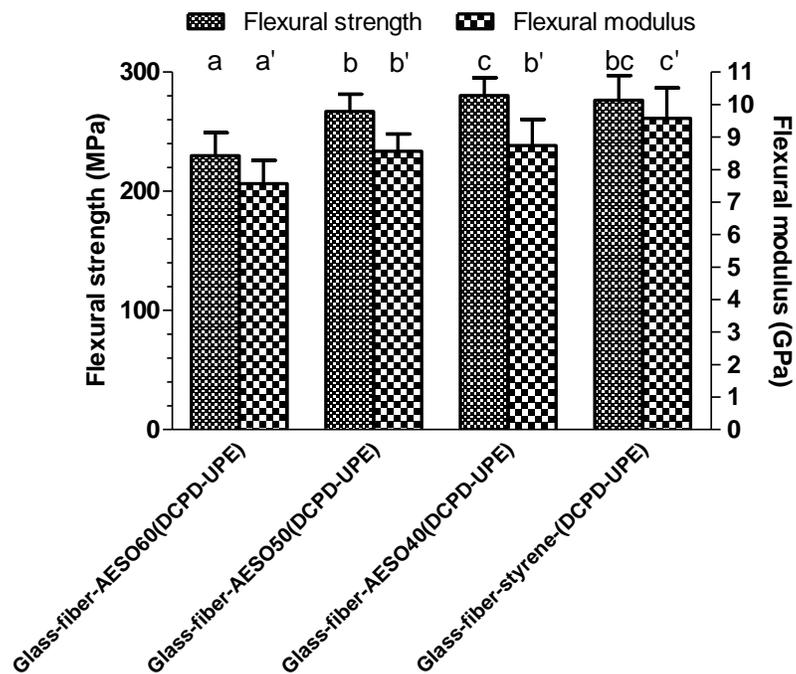


Figure 5.2 Effects of the AESO content on the flexural properties of the glass fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

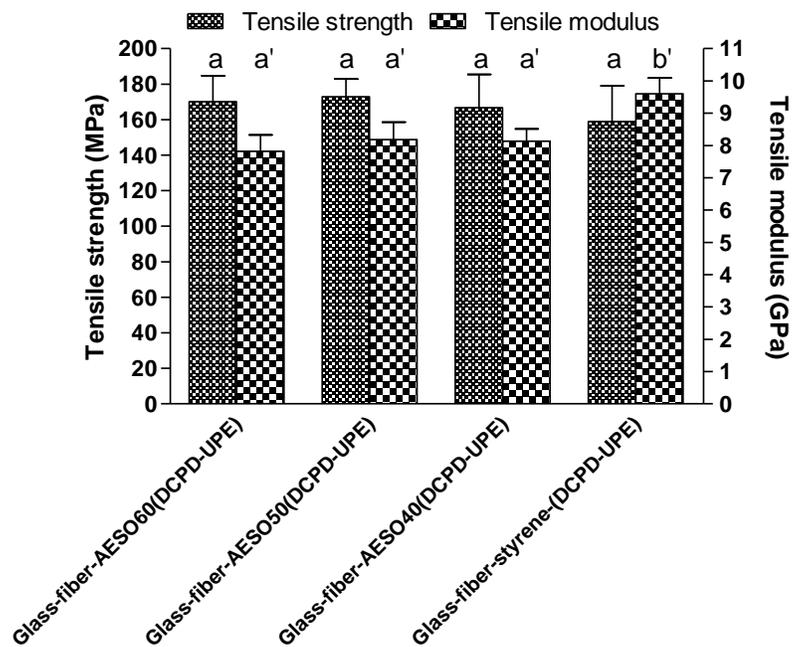


Figure 5.3 Effects of the AESO content on the tensile properties of the glass fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

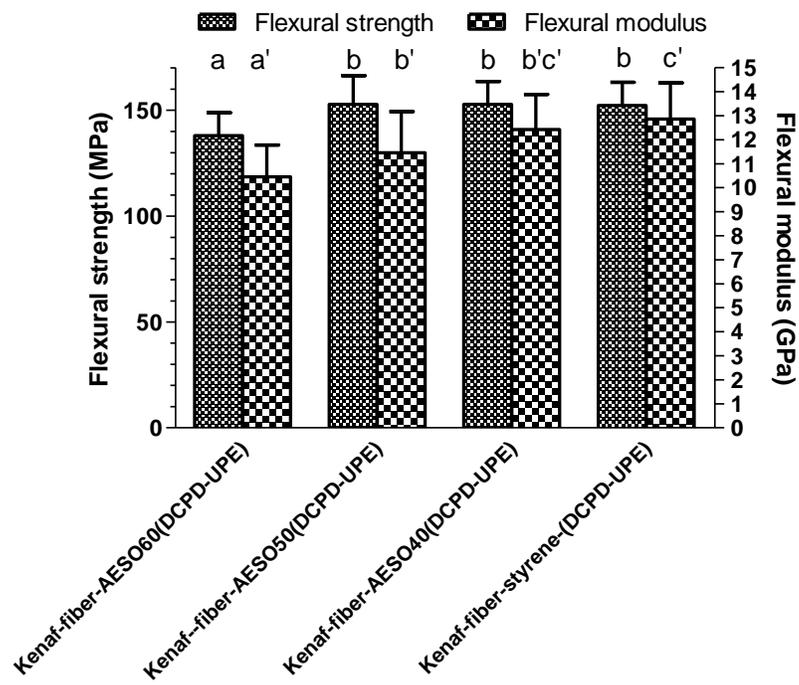


Figure 5.4 Effects of the AESO content on the flexural properties of the kenaf fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

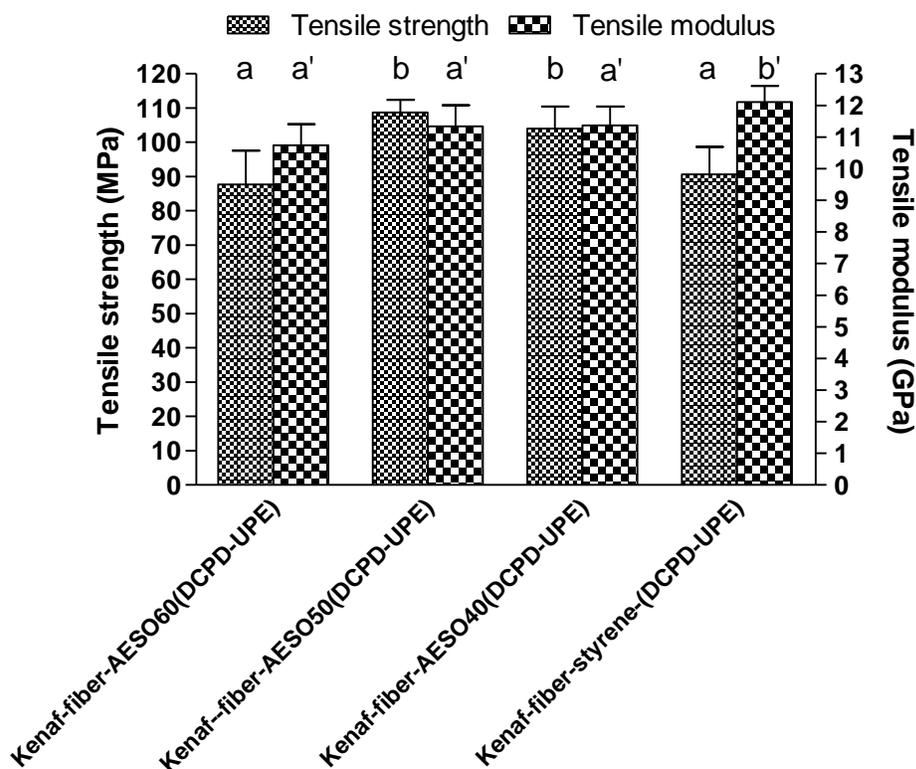


Figure 5.5 Effects of the AESO content on the tensile properties of the kenaf fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

5.4.3 Proposed network structures of the cured AESO-(DCPD-UPE) matrix

DCPD can be easily obtained from cyclopentadiene (CPD), an inexpensive and readily available petrochemical.^{3,4} CPD can dimerize to form DCPD at room temperature (Figure 5.6). However, DCPD can go back to CPD via the retro-Diels-Alder reaction at above 150 °C (Figure 5.6).^{3,4} The representative structures of the AESO and DCPD-UPE are shown in Figure 3.5. and 5.7, respectively. The structure of DCPD-UPE

shown in the Figure 5.7 only illustrates that DCPD can be incorporated onto the ends of UPE chains or in the UPE chains. The specific structures of DCPD-UPE are not well understood. The following reactions may be involved in the incorporation of DCPD in the UPE: i) the reactions of a C=C bond of DCPD with carboxylic acid groups of dibasic acid monomers in the preparation of the UPE or with those at the chain ends of the resulting UPE⁵, ii) the reaction of a C=C bond of DCPD with hydroxyl groups of diols in the preparation of the UPE or with those at the chain ends of the resulting UPE⁶, and iii) the Diels-Alder reaction between the C=C bond MA and the C=C bonds of CPD from degradation of DCPD.⁴ The reactions i and ii occur typically at 120-140 °C, while the reaction iii occurs at above 150 °C.⁴

A proposed network structure of a cured AESO-(DCPD-UPE) resin is shown in Figure 5.8. Three types of linkages are proposed to exist in the cured AESO-(DCPD-UPE) resin and they are proposed to result from the following crosslinking reactions: 1) the linkage I is from the homopolymerization of the acryloyl C=C bonds of AESO, 2) the linkage II is from the copolymerization of the acryloyl C=C bonds of AESO and the C=C bonds on the polymer chains of the DCPD-UPE, and 3) the linkage III is from the homopolymerization of the C=C bonds on the polymer chains of DCPD-UPE. The 1,2-disubstituted C=C bonds in DCPD-UPE are difficult to polymerize and therefore the amount of the linkage III is believed to be low. All these linkages are proposed to result in rigid, crosslinked network structures for high mechanical properties.

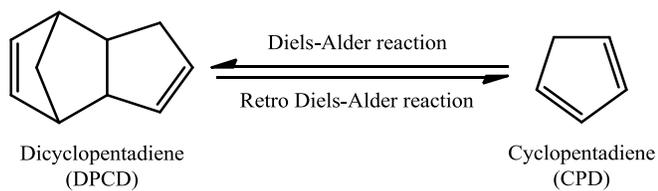


Figure 5.6 Conversions between DCPD and CPD

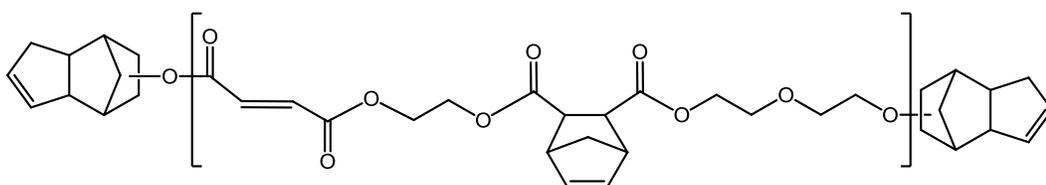


Figure 5.7 Representative structure of the DCPD-modified UPE plastic (DCPD-UPE)

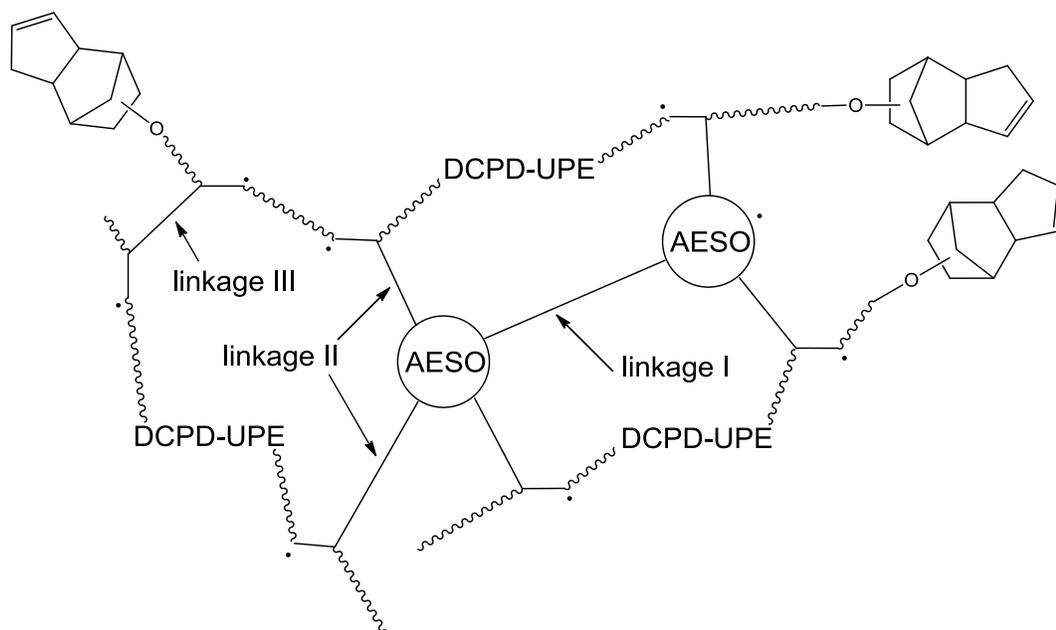


Figure 5.8 Proposed structural network of a cured AESO-(DCPD-UPE) resin

5.4.4 Glass transition temperatures (T_g)

The T_g of a fiber-reinforced composite is typically required to be higher than the use temperature, typically room temperature, so that the composite is rigid and has the desired mechanical properties. As shown in Table 5.1, the T_g s of the non-reinforced cured resins and the glass-fiber reinforced composites decreased when the AESO content increased from 40 to 60 wt%. Homopolymers of AESO had flexible networks, as evidenced by its low T_g of 45.8 °C². The increase in the AESO content is believed to increase the amount of homopolymers of AESO and the amount of the linkage I (Figure 5.8) in the cured products, which therefore decrease the T_g s of the cured products.

The cured styrene-(DCPD-UPE) resin and the corresponding glass fiber-reinforced composites had higher T_g s than the cured AESO-(DCPD-UPE) resins and the corresponding glass fiber-reinforced composites, respectively. That the replacement of styrene with AESO lowered the T_g s for the cured resins and the resulting glass fiber-reinforced composites has been observed in our previous study on the AESO-(PG-MA) resins.² The decrease in the T_g s is speculated to be due to the soft and flexible nature of AESO structures.²

Although the T_g s for the glass fiber-reinforced composites prepared from AESO-(DCPD-UPE) resins were lower than that from the styrene-(DCPD-UPE) resin, they are still sufficiently higher than normal indoor and outdoor use temperatures, which makes the composites useful materials.

Table 5.1 T_g for non-reinforced cured resins and glass fiber-reinforced composites

Cured products	T_g (°C)
<i>Non-reinforced cured resins</i>	
AESO60(DCPD-UPE)	85.1
AESO50(DCPD-UPE)	99.1
AESO40(DCPD-UPE)	113.5
Styrene-(DCPD-UPE)	168.3
<i>Glass fiber-reinforced composites</i>	
Glass-fiber-AESO60(DCPD-UPE)	83.6
Glass-fiber-AESO50(DCPD-UPE)	95.0
Glass-fiber-AESO40(DCPD-UPE)	107.2
Glass-fiber-styrene-(DCPD-UPE)	164.7

5.4.5 Viscosities and pot lives of the resins

Commercial styrenated UPE resins have different viscosities for different applications. The viscosity of the styrene-(DCPD-UPE) used in this study was 1.7 Pa·s at room temperature. As shown in Figure 5.9, the viscosities of the AESO-(DCPD-UPE) resins decreased when the AESO content increased from 40 to 60%, which is consistent with the facts that AESO has lower molecular weights and much lower viscosity than the UPE and acts as a diluent for the UPE. The viscosities of the AESO-(DCPD-UPE) resins dropped rapidly when the temperature increased (Figure 5.9). For the AESO40(DCPD-UPE) resin, the viscosities of 6 Pa·s and 1.7 Pa·s were achieved at 52 °C and 67 °C, respectively. For the AESO50(DCPD-UPE) resin, the viscosities of 6 Pa·s and 1.7 Pa·s were obtained at 48 °C and 62 °C, respectively. At 50 °C, the pot life

of the AESO50(DCPD-UPE) resin was longer than 6 h (the tests were intentionally stopped at 6 h because such a pot life was considered long enough for many processes). At 62 °C, the AESO50(DCPD-UPE) resin still had the long pot life of 5.2 h.

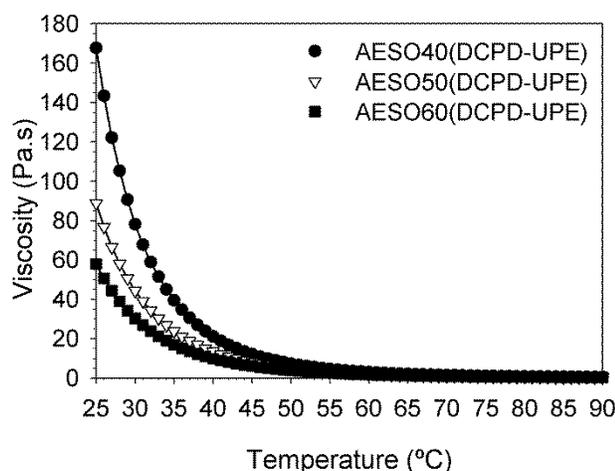


Figure 5.9 Effects of temperature on the viscosity of AESO-(DCPD-UPE) resins

5.4.6 Improved compatibility

As shown in Figure 5.10, the AESO-(DCPD-UPE) resin was a homogeneous, clear, pourable solution at room temperature, whereas the AESO-(PG-IPA-MA) resin or the AESO-(PG-MA) resin was a cloudy mixture that was not pourable at room temperature. This difference in the resin appearance supports that the hydrophobic AESO is more compatible with the more hydrophobic DCPD-UPE than PG-IPA-MA or PG-MA. The viscosity data also support the improved compatibility between AESO and DCPD-UPE. At the same AESO content of 60%, AESO60(DCPD-UPE)

had the viscosity of 54 Pa·s at room temperature (Figure 5.9) that was lower than that (396 Pa·s) of AESO60(PG-IPA-MA)¹ or that (80 Pa·s) of AESO60(PG-MA)² at room temperature.

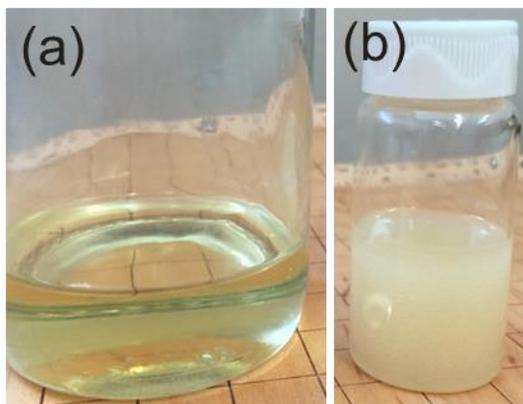


Figure 5.10 Appearance of (a) the AESO-(DCPD-UPE) resin and (b) the AESO-(PG-MA) resin (the AESO-(PG-IPA-MA) resin had the same appearance as the AESO-(PG-MA) resin)

5.5 Conclusions

Glass fiber- and kenaf-fiber reinforced AESO-(DCPD-UPE) composites were fully cured after being pressed at 160 °C for 60 min. The flexural strength, flexural modulus, and tensile strength of glass-fiber-AESO40(DCPD-UPE) were comparable to glass-fiber-styrene-(DCPD-UPE). The flexural strength and modulus of kenaf-fiber-AESO40(DCPD-UPE) were comparable to kenaf-fiber-styrene-(DCPD-UPE). The tensile strength of kenaf-fiber-AESO40(DCPD-UPE) was superior to kenaf-fiber-styrene-(DCPD-UPE). Increase in the AESO content from 40 to 50% did not reduce

the flexural and tensile properties of the resulting composites, except for the flexural strength of the glass fiber-reinforced composites. The T_g s of the cured AESO-(DCPD-UPE) resins and the corresponding glass fiber-reinforced composites were all well above room temperature. The AESO-(DCPD-UPE) resins could be easily used for preparation of fiber-reinforced composites because they were clear, homogenous, and pourable liquid solutions at room temperature. Viscosities of the resins decreased rapidly along with the increase in the temperature of the resins. AESO50(DCPD-UPE) had the same viscosity (1.7 Pa·s) as styrene-(DCPD-UPE) at 62 °C, and had a long pot life of 5.2 h.

5.6 Acknowledgement

The authors are grateful to Dr. Willie E. Rochefort for his assistance on DSC analysis, viscosity measurements, and pot life measurements. This study was supported by return royalty fee income of patented wood adhesive technologies invented by K. Li's group. We thank Ashland Inc. (Dublin, OH) for providing the commercial styrene-(DCPD-UPE) resin and DCPD-UPE, and for assistance on T_g measurements.

5.7 Reference

1. Chapter 3 - Replacement of styrene with acrylated epoxidized soybean oil in an unsaturated polyester resin from propylene glycol, isophthalic acid and maleic anhydride
2. Chapter 4 - Replacement of styrene with acrylated epoxidized soybean oil in an unsaturated polyester resin from propylene glycol and maleic anhydride

3. Gebhart H. J. Jr. Makin E. C. Jr. and Middlebrooks C. H. U.S. Patent 3557239. **1971**
4. Penczek, P. Czub, P. and Pielichowski J. *Adv. Polym. Sci.* **2005**, *184*, 1–95
5. Bruson H. A. and Riener T. W. *J. Am. Chem. Soc.* **1945**, *67*, 1178–1180
6. Bruson H. A. and Riener T. W. *J. Am. Chem. Soc.* **1946**, *68*, 8–10

Chapter 6 - Replacement of styrene with methyl cinnamate or ethyl cinnamate in an unsaturated polyester resin from propylene glycol and maleic anhydride

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6.1 Abstract

Non-hazardous methyl cinnamate (MC) and ethyl cinnamate (EC) were investigated as replacements of styrene in a commercial unsaturated polyester (UPE) resin, a mixture of styrene and a UPE plastic (PG-MA) that is derived from propylene glycol (PG) and maleic anhydride (MA). Neither MC nor PG-MA could be cured for formation of a usable matrix for fiber-reinforced thermoset composites. However, mixtures of MC (or EC) and PG-MA were cured well and resulted in glass fiber- and kenaf fiber-reinforced composites with high strengths and moduli. Both MC and PG-MA are solid at room temperature, which is not a desirable feature for the production of fiber-reinforced composites. However, mixtures of MC and PG-MA were found to be clear, homogenous, and easily pourable liquids at room temperature. The cured EC-(PG-MA) was crack-free, whereas the cured styrene-(PG-MA) had lots of cracks. Glass transition temperatures (T_g s) of the cured resins and the corresponding glass fiber-reinforced composites were measured and discussed in detail. Resin viscosity

and resin pot life were investigated. Effects of the MC content on the mechanical properties, T_g , and viscosities were studied. The curing mechanism of the MC-(PG-MA) resins is discussed.

6.2 Introduction

Most commercial unsaturated polyester (UPE) resins contain volatile and hazardous styrene. It is desirable to develop non-hazardous alternatives for the replacement of styrene in UPE resins. Methyl cinnamate (MC) and ethyl cinnamate (EC) are present in the essential oil of various plants. The essential oil of *Eucalyptus olida*¹ (commonly known as strawberry gum) or basil² such as cinnamon basil has a high amount of MC. EC is mostly found in the essential oil of cinnamon³ or *Kaempferia galanga*⁴ (commonly known as sand ginger). MC and EC are non-hazardous chemicals⁵, are permitted by the FDA (U.S. Food and Drug Administration) for direct addition to food for human consumption⁶, and are widely used as flavoring additives in beverages, ice cream, candy, baked goods, chewing gum, gelatin desserts, and condiments⁷. MC or EC can be obtained by the steam distillation of plant materials that contain MC (or EC) or by esterification of cinnamic acid with methanol (or ethanol).

The styrene-(PG-MA) resin is a mixture of styrene and a UPE plastic (PG-MA) that is derived from propylene glycol (PG) and maleic anhydride (MA). PG-MA has a higher degree of unsaturation than those UPEs that include structures from saturated dibasic acids or acid anhydrides. The curing of styrene-(PG-MA) resin is usually very fast and the degree of crosslinking in the cured resin is very high, which typically

results in a brittle cured resin with a considerable amount of cracks. Because of the cracking issue, the styrene-(PG-MA) resin is rarely used alone, and is typically used with other UPE resins for adjusting the curing rate and the degree of crosslinking.

In this study, we found that the complete replacement of styrene with MC (or EC) in styrene-(PG-MA) enabled the resins to be used alone for the production of crack-free cured resins and superior glass fiber- and kenaf fiber-reinforced composites with high strengths, high moduli, and high glass transition temperatures.

6.3 Experimental

6.3.1 Materials

MC and EC were purchased from Sigma-Aldrich (St. Louis, MO). *tert*-Butyl peroxybenzoate (TBPB) was obtained from Composite One (Vancouver, WA). PG-MA, styrene-(PG-MA), and glass fiber mats with random orientation of the fibers were obtained from Ashland Inc. (Dublin, OH). The glass fiber mats were cut into the dimension of 200 mm × 200 mm by a paper cutter before use. Each glass fiber mat had a weight of about 17 g. Kenaf fibers were purchased from Kenaf Industries Ltd (Raymondville, TX).

6.3.2 Preparation of MC-(PG-MA) resins and EC-(PG-MA) resins

The mixture of MC (149.7 g) and PG-MA (349.9 g) in a 600-mL beaker was stirred at 90 °C for 10 min to generate a colorless, clear, homogenous, and pourable solution.

The solution was purged with nitrogen for 10 min and cooled to 60 °C. Subsequently, TBPB (15 g, 3 wt% based on the total weight of the solution) was added into the solution and then stirred for 3 min. The resulting solution was poured into a container. The container was placed in a centrifuge (Labofuge 400, Heraeus Instrument, Germany) and was centrifuged at 3000 rpm for 3 min for the removal of air bubbles in the solution. The resulting MC-(PG-MA) resin had the MC/(PG-MA) weight ratio of 30/70 and was designated as MC30(PG-MA). MC40(PG-MA) with the MC/(PG-MA) weight ratio of 40/60, and EC30(PG-MA) with the EC/(PG-MA) weight ratio of 30/70 were prepared with the same procedure as described previously for MC30(PG-MA). The styrene-(PG-MA) resin was mixed with TBPB (3 wt% based on styrene-(PG-MA)) and used as a control.

6.3.3 Preparation of glass fiber-reinforced composites

The MC30(PG-MA) resin (18 g) was evenly poured onto the upper surface of a glass fiber mat that was placed in the chamber of a stainless steel mold with the dimension of 200 mm × 200 mm × 3 mm. Subsequently, the mat was flipped over and applied with 30 g of the resin on the surface. A second glass fiber mat was stacked above the first mat and was applied with 30 g of resin on the surface. A third glass fiber mat was stacked above the second mat and was applied with 30 g of resin on the surface. A fourth glass fiber mat was stacked above the third mat and was applied with 18 g of resin on the surface. After the resin application, the mats were placed onto a hot plate (50 °C) and rolled by a rubber roller by hand for about 5 min for removing air inside

the resin-saturated glass fiber mats. Afterwards, the mats in the stainless steel mold was covered by a stainless steel plate on top and was first pressed at 3 MPa by an automatic Benchtop Carver press (Carver Inc., Wabash, IN) for 10 min, and subsequently pressed at the same pressure for 60 min with the temperature rising to 160 °C at about 10 °C/min. The mold was then taken out of the press and cooled down at room temperature. The resulting composite board was designated as glass-fiber-MC30(PG-MA). Glass-fiber-MC40(PG-MA) and glass-fiber-EC30(PG-MA) were prepared with the same procedure as described previously for the preparation of glass-fiber-MC30(PG-MA). Glass-fiber-styrene-(PG-MA) was prepared with the same procedure as described previously for glass-fiber-MC30(PG-MA), except that the resin was kept at room temperature during the rolling for air removal. All resulting composite boards had a weight of about 154 g (excessive resins flowed out of the mold during the pressing process) and a dimension of 200 mm × 200 mm × 2.5 mm. The fiber content was calculated to be about 44% by weight. At least two boards were made and tested for each composition.

6.3.4 Preparation of kenaf fiber-reinforced composites

Kenaf fiber mats were prepared according to the procedure reported in our previous study.⁸ MC30(PG-MA) (9.0 g) was slowly poured onto the upper surface of a kenaf fiber mat that was placed in the chamber of the stainless steel mold with the dimension of 200 mm × 200 mm × 3 mm. The mat was flipped and subsequently applied with the same amount of resin on the opposite surface. A second fiber mat was stacked

above the first mat with the fiber direction parallel to each other, and subsequently applied with MC30(PG-MA) on both surfaces with the same procedure as described previously. The same procedure was repeated until five fiber mats were coated with the resin. A stack of the five resin-coated fiber mats in the mold was covered by the stainless steel plate on top and was pressed at 3.8 MPa with the Benchtop Carver press for 10 min at room temperature, and subsequently for 60 min under the same pressure with the temperature being raised to 160 °C at about 10 °C/min. Afterwards, the mold was taken out from the press and cooled down at room temperature. The resulting kenaf fiber-reinforced composite board was designated as kenaf-fiber-MC30(PG-MA). Kenaf-fiber-MC40(PG-MA) and kenaf-fiber-styrene-(PG-MA) were prepared with the same procedure as previously described for kenaf-fiber-MC30(PG-MA). The resulting composite boards had a weight of about 124 g (excessive resins flowed out of the mold during the pressing process) and a dimension of 200 mm × 200 mm × 2.8 mm. The fiber content was calculated to be about 63% by weight for all composite boards. At least two boards were made and tested for each composition.

6.3.5 Determination of flexural properties of the composites

For glass fiber-reinforced composites, test specimens with the dimension of 65 mm × 12.7 mm × 2.5 mm were prepared and evaluated for the flexural strength and flexural modulus through a three-point bending test in accordance with ASTM D790, with a span of 40 mm and a rate of crosshead motion of 1.28 mm/min. At least eighteen specimens were tested and averaged values were reported.

For kenaf fiber-reinforced composites, test specimens with the dimension of 65 mm × 12.7 mm × 2.8 mm and with the fibers aligning along the lengthwise direction of the specimens were prepared and evaluated for the flexural strength and flexural modulus through a three-point bending test in accordance with ASTM D790, with a span of 42 mm and a rate of crosshead motion of 1.11 mm/min. At least eighteen specimens were tested and averaged values were reported.

6.3.6 Determination of tensile properties of the composites

For glass fiber-reinforced composites, the tensile strength and tensile modulus were obtained from a tensile test in accordance with ASTM D638. For the preparation of type I dumbbell-shaped specimens, the composite boards were first cut into rectangular specimens with the dimension of 180 mm × 19 mm × 2.5 mm. The rectangular specimens were further cut to dumbbell-shaped specimens that had a width of narrow section of 13 mm and a length of narrow section of 57 mm. The distance between grips was 115 mm, and the rate of crosshead motion was 5 mm/min. At least five specimens were tested and averaged values were reported.

For kenaf fiber-reinforced composites, the same procedure previously described were used, except that test specimens had the thickness of 2.8 mm with the fibers aligning along the lengthwise direction of the specimens, and the rate of crosshead motion was 2 mm/min. At least five specimens were tested and averaged values were reported.

6.3.7 Statistical analysis

Data from the flexural and the tensile tests were statistically analyzed by permutation test with RStudio statistical software (RStudio, Inc., Boston, MA). All comparisons were based on a 95% confidence interval.

6.3.8 Dynamic Mechanical Analysis (DMA)

Both non-reinforced cured resins and glass fiber-reinforced composites were characterized with DMA. For the preparation of the non-reinforced cured resins, uncured resins were poured into the chamber that was created by putting a 3-mm thick rubber cord in between two glass plates with the dimension of 200 mm × 200 mm × 3 mm. The resins were subsequently cured in an air-circulating oven at 135 °C for 1 h, followed by a post cure at 160 °C for one more hour. Glass fiber-reinforced composite specimens were cut from the same boards as those used for the flexural and tensile tests.

The DMA experiments were conducted by Ashland Inc. (Dublin, OH) with a TA Q800 analyzer (TA Instruments, Inc., New Castle, DE) using the 35-mm single cantilever clamp. Test specimens were surface ground to achieve the thickness of 1.75 mm. Test specimens with the dimension of 17.8 mm × 12.5 mm × 1.75 mm were tested at a constant frequency of 1 Hz. The specimens were first cooled to -100 °C, tested from -100 to 200 °C (first scan), cooled to -100 °C again, and retested from -100 to 200°C (second scan), with the ramp rate of 2 °C/min. Data from the second

scan were used. The temperature at $\text{Tan } \delta$ maximum (i.e., peak value) was considered the glass transition temperature (T_g).

6.3.9 Differential scanning calorimetry (DSC) analysis

DSC experiments were performed on a TA Q2000 analyzer (TA Instruments, Inc., New Castle, DE). The analyzer was calibrated in three steps: the first with nothing in the chamber to get a baseline correction, the second with sapphire to calibrate the heat capacity, and the third with indium for temperature calibration. The specimen chamber was purged with nitrogen during the experiments with a flow rate of 50 mL/min. For temperature sweep, test specimen (10 mg) in hermetic aluminum pan with a lid was heated from room temperature to 250 °C at the rate of 10 °C/min. An empty hermetic aluminum pan with a lid was used as a reference.

6.3.10 Measurements of resin viscosity

The resin viscosity was measured with an AR 2000ex Rheometer (TA Instruments, Inc., New Castle, DE) with a cone-and-plate geometry (cone angle: 1 degree 59 min 17 sec; cone diameter: 40 mm; truncation gap 52 micro m). For the temperature sweep, test specimens were steady-sheared at a shear rate 1 Hz, from 25 to 80 °C at the rate of 5 °C/min.

6.3.11 Measurements of a resin pot life

For the measurement of a resin pot life at use temperatures, an oscillatory time sweep was performed with the same AR 2000ex rheometer as described previously with a

parallel-plate geometry (25 mm in diameter). The gap between two plates was 400 μm . Sampling delay time was set at 10 s. At t_0 , test specimens were started to be oscillatorily sheared at 5 Hz with a strain amplitude of 50% at the temperature of 70 $^{\circ}\text{C}$. As the curing began, the shear storage modulus (G') increased rapidly. At t_1 , G' was equal to the shear loss modulus (G''). The time between t_0 and t_1 was defined as the pot life for the resin in this study.

6.4 Results and discussion

6.4.1 Determination of curing conditions

As shown in Figure 6.1, the curing of styrene-(PG-MA) occurred in the temperature range of 110 - 200 $^{\circ}\text{C}$ with exothermal peaks at 130 $^{\circ}\text{C}$ (sharp) and 169 $^{\circ}\text{C}$ (broad), respectively. The curing of MC30(PG-MA), MC40(PG-MA), and EC30(PG-MA) started around 115 $^{\circ}\text{C}$ and ended at 200 $^{\circ}\text{C}$ with exothermal peaks around 160 $^{\circ}\text{C}$. Hot pressing at 160 $^{\circ}\text{C}$ for 60 min was expected to be able to completely cure the resins in the production of glass fiber-reinforced composites and kenaf fiber-reinforced composites. DSC analysis of the resulting composites from these resins did not show any exothermal peaks (DSC graph not shown), which indicated that the resins were fully cured. The resulting glass fiber-reinforced composites and kenaf fiber-reinforced composites were rigid and had dry and smooth surfaces. No defects such as cracks, warpage and delamination were found with visual inspection.

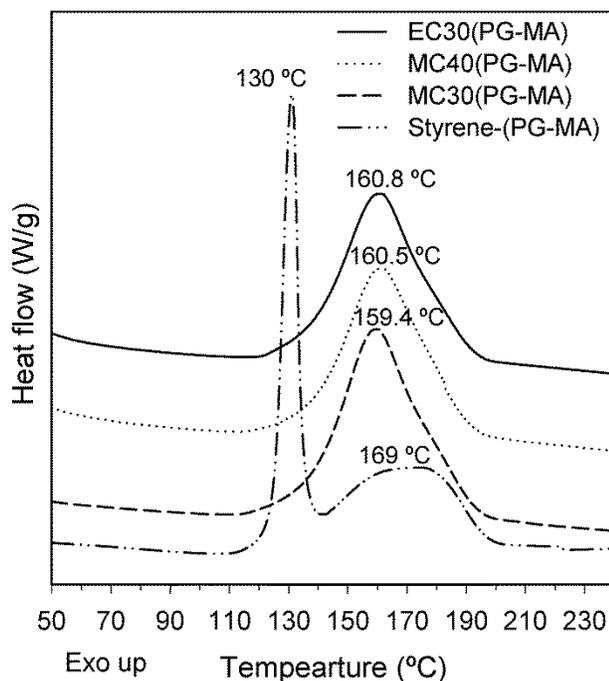


Figure 6.1 DSC curves for the course of curing (ramp rate: 10 °C/min)

6.4.2 Mechanical properties of the composites

6.4.2.1 Effects of the MC content

Glass fiber-reinforced composites. As shown in Figure 6.2, the flexural strength and modulus of the glass fiber-reinforced composites increased significantly when the MC content decreased from 40 to 30%. Glass-fiber-MC40(PG-MA) had lower flexural strength than glass-fiber-styrene-(PG-MA); but the flexural moduli between the two were not significantly different. Glass-fiber-MC30(PG-MA) had higher flexural modulus than glass-fiber-styrene-(PG-MA), but the flexural strengths between the two were not significantly different. As shown in Figure 6.3, the reduction of the MC content from 40 to 30% did not significantly change the tensile strength and modulus

of the glass fiber-reinforced composites. The tensile strength of glass-fiber-MC30(PG-MA) was not significantly different from that of glass-fiber-styrene-(PG-MA); but the tensile modulus of the former was lower than that of the latter. Previous results demonstrated that the MC content of 30% was optimal and MC30(PG-MA) was superior to styrene-(PG-MA), in terms of the flexural modulus of the resulting glass fiber-reinforced composites.

Kenaf fiber-reinforced composites. As shown in Figure 6.4, the reduction of the MC content from 40 to 30% did not significantly change the flexural strength and modulus. The flexural strength and modulus of kenaf-fiber-MC40(PG-MA) or kenaf-fiber-MC30(PG-MA) were not significantly different from those of kenaf-fiber-styrene-(PG-MA). As shown in Figure 6.5, the reduction of the MC content from 40 to 30% significantly increased the tensile strength, but did not significantly change the tensile modulus. The tensile strength and modulus of kenaf-fiber-MC30(PG-MA) were not significantly different from those of kenaf-fiber-styrene-(PG-MA). Previous results showed that the MC content of 30% was optimal and MC30(PG-MA) was comparable to styrene-(PG-MA) in terms of the flexural and tensile properties of the resulting kenaf fiber-reinforced composites.

As described previously, effects of the MC content on the mechanical properties were also dependent upon the reinforcing fibers. For example, the flexural strength and modulus significantly increased for the glass fiber-reinforced composites, but did not significantly change for the kenaf fiber-reinforced composites when the MC content

was reduced from 40 to 30%. The mechanism by which different fibers affect the effects of the MC content on the mechanical properties warrants further investigation.

6.4.2.2 Comparison between MC and EC

As shown in Figure 6.2, glass-fiber-MC30(PG-MA) had significantly higher flexural strength and modulus than glass-fiber-EC30(PG-MA). However, the flexural strength and modulus of glass-fiber-EC30(PG-MA) were not significantly different from those of glass-fiber-styrene-(PG-MA). As shown in Figure 6.3, the tensile strength and modulus of glass-fiber-MC30(PG-MA) were not significantly different from those of glass-fiber-EC30(PG-MA). Previous results demonstrated that MC was superior to EC in terms of the flexural properties of the resulting glass fiber-reinforced composites. This may be explained by the fact that the methyl group in the MC is smaller than the ethyl group in the EC, and the MC has thus a lower steric hindrance, and is more reactive for crosslinking reactions with PG-MA than the EC (Figure 6.7 and 6.8).

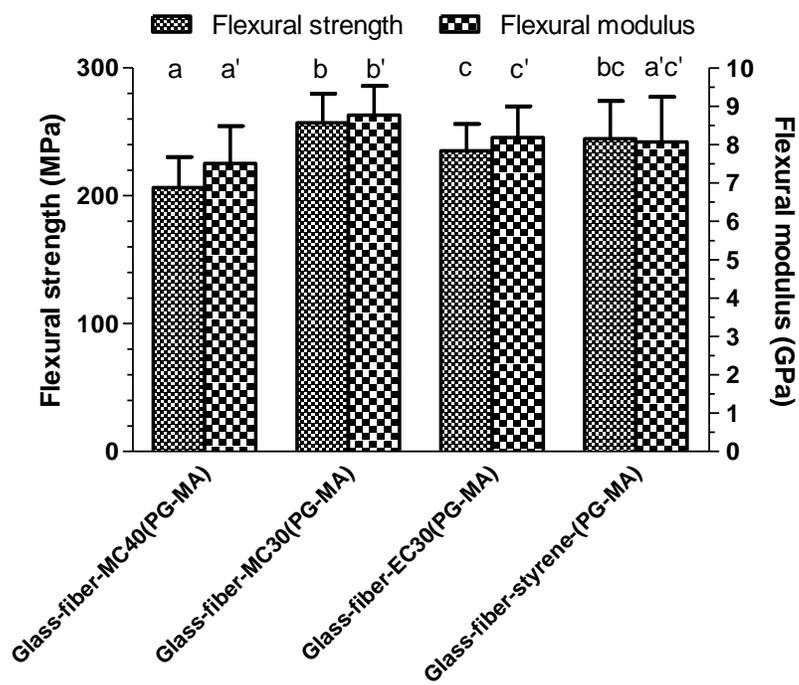


Figure 6.2 The flexural properties of the glass fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

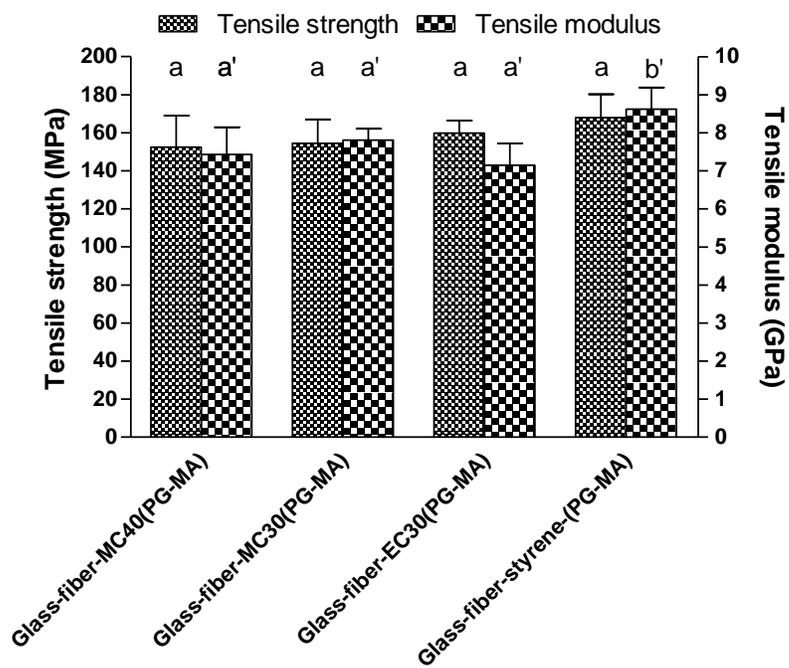


Figure 6.3 The tensile properties of the glass fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

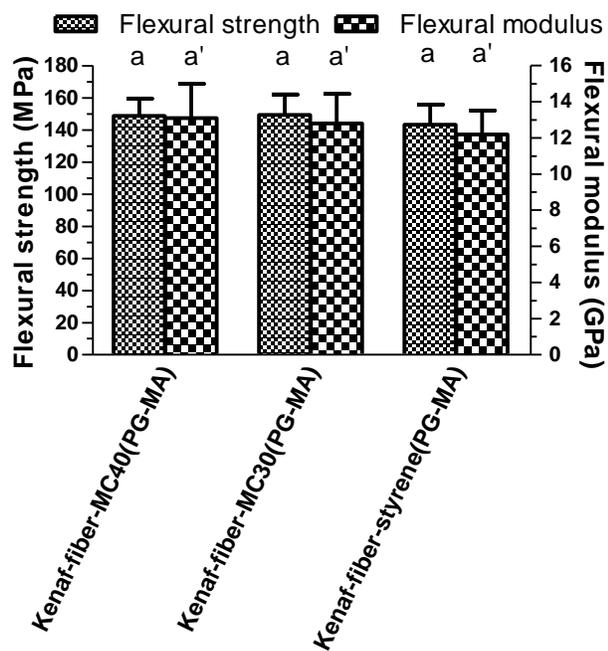


Figure 6.4 The flexural properties of the kenaf fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

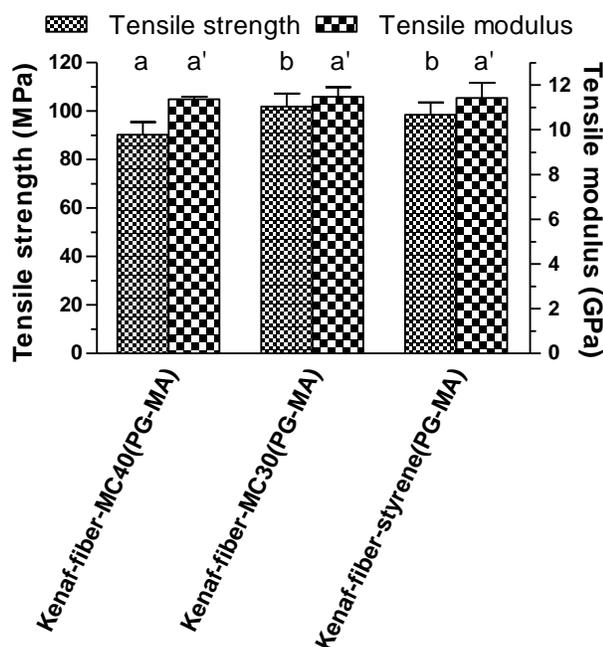


Figure 6.5 The tensile properties of the kenaf fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

6.4.3 A proposed network structure of the cured MC-(PG-MA)

A representative structure of PG-MA is shown in Figure 4.4. The C=C bonds in PG-MA are known to be difficult to polymerize among themselves because they are 1, 2-disubstituted and have high steric hindrance around them (Figure 6.6).⁹ The C=C bonds in PG-MA have low mobility because both ends are connected to polyester chains, which make it even more difficult for them to polymerize with each other. Consequently, the curing of PG-MA alone typically does not have a high C=C bond

conversion, and leads to polymer networks with the strengths being too low to be usable as matrixes for fiber-reinforced composites.

Both MC and EC are 1,2-disubstituted on their C=C bonds (Figure 6.7) and do not homopolymerize well.¹⁰ It has been reported that poly(MC) and poly(EC) were obtained only with the molecular weight of 2300 g/mol and 7600 g/mol¹⁰, which corresponds to the degree of polymerization (DP) of 14 and 43, respectively. Such a molecular weight is apparently too low to make poly(MC) or poly(EC) a usable matrix for fiber-reinforced polymer composites, as evidenced by the very low flexural strength (8.0 MPa) and tensile strength (7.6 MPa) of the kenaf fiber-reinforced poly(MC) composites.¹¹ Molecules with the DP of 14 (or 43) are sufficiently long for serving as crosslinks between two UPE chains although they cannot serve as strong matrixes by themselves for fiber-reinforced composites, which explain the superior mechanical properties of fiber-reinforced MC-(PG-MA) composites (Figures 6.2, 6.3, 6.4, and 6.5).

To our best knowledge, no 1,2-disubstituted unsaturated monomers have been investigated as crosslinking agents for UPEs so far. It is unexpected that mixtures of two 1,2-disubstituted monomers (MC and PG-MA, or EC and PG-MA) that are difficult to homopolymerize by itself had strong synergistic effects between them in the curing reactions, which led to the formation of strong matrixes for superior fiber-reinforced composites with flexural and tensile properties comparable or even superior to those with styrene-(PG-MA) as matrixes (Figure 6.2 - 6.5).

The proposed network structure of a cured MC-(PG-MA) resin is shown in Figure 6.8. Three types of linkages are proposed to exist: a) linkage I from the copolymerization of the C=C bonds of MC and the C=C bonds of PG-MA, b) linkage II from the homopolymerization of the C=C bonds of MC, and 3) linkage III from the homopolymerization of the C=C bonds of PG-MA. All these three linkages are proposed to result in strong network structures for superior mechanical properties. Because PG-MA cannot homopolymerize well, the amount of the linkage III is supposed to be low.

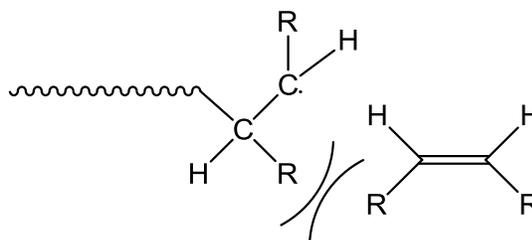
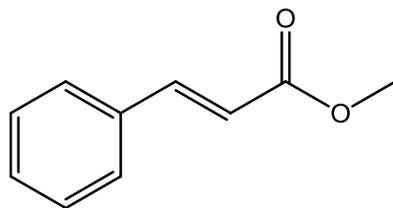
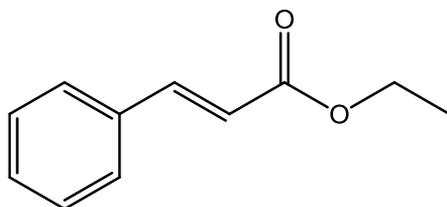


Figure 6.6 Steric hindrance making the polymerization of 1,2-disubstituted monomers difficult



Methyl cinnamate (MC)



Ethyl cinnamate (EC)

Figure 6.7 Chemical structures of MC and EC

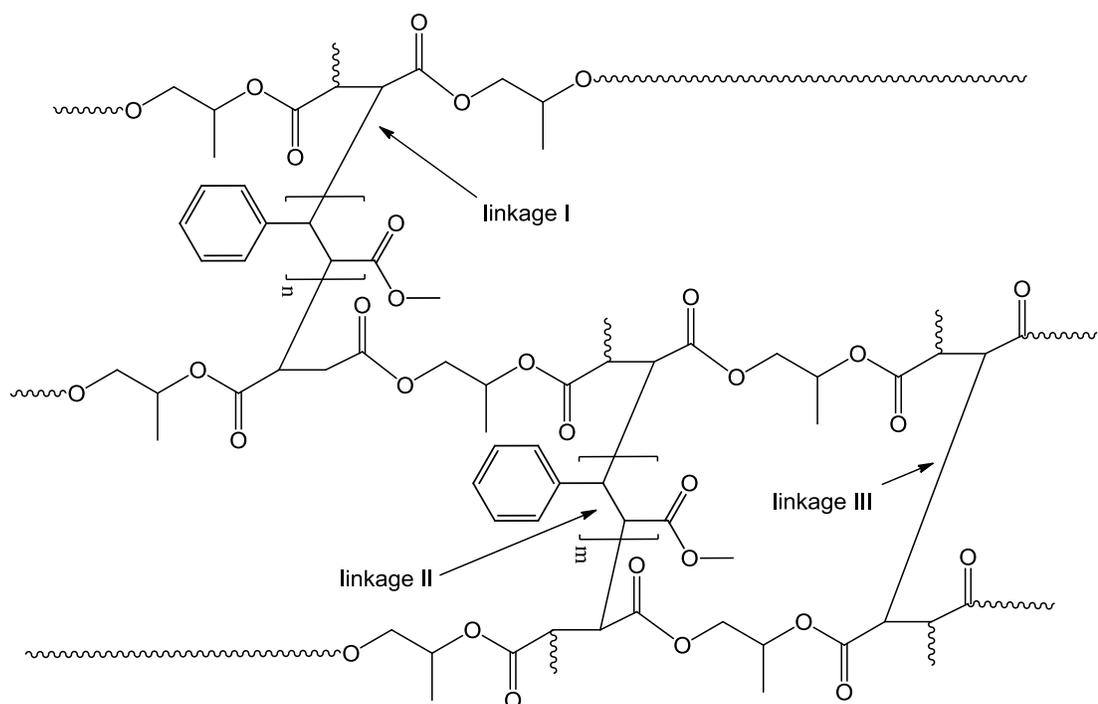


Figure 6.8 Proposed crosslinking networks of a cured MC-(PG-MA) resin

6.4.4 Glass transition temperatures (T_g)

As shown in Table 6.1, the cured MC30(PG-MA) resin had a higher T_g than the cured EC30(PG-MA) resin. The reinforcement of glass fibers increased the T_g by approximately 15 °C. The T_g of glass-fiber-MC30(PG-MA) was higher than that of glass-fiber-EC30(PG-MA); but was lower than that of glass-fiber-styrene-(PG-MA) by approximately 42 °C.

The cured styrene-(PG-MA) resin had cracking issues (Figure 6.9a). Measurements of the T_g of the cured styrene-(PG-MA) resin could not be done by DMA because no usable test specimens free of defects could be prepared. Surprisingly, the cured MC-(PG-MA) resin and the cured EC-(PG-MA) resin did not have the cracking issue (Figure 6.9b) (a piece of wood was placed underneath the cured resin board for showing the transparent, crack-free appearance of the cured resin). MC or EC was less reactive than styrene for the crosslinking reactions with PG-MA. The reduced reactivity of MC or EC is believed to lead to the reduced degree of crosslinking in the cured resin, which is speculated to be responsible for the reduced brittleness and T_g s.

The T_g of a composite is required to be higher than room temperature or a use temperature so that the composite remains rigid and has high mechanical properties in its applications. The T_g of glass-fiber-MC30(PG-MA) or glass-fiber-EC30(PG-MA) was well above normal indoor and outdoor temperatures at which the composites are

used. Because of the high strength, high modulus, and high T_g , glass-fiber-MC30(PG-MA) or glass-fiber-EC30(PG-MA) composites can be useful materials for various structural and non-structural applications

Table 6.1 T_g for non-reinforced cured resins and glass fiber-reinforced composites

Cured products	T_g (°C)
<i>Non-reinforced cured resins</i>	
MC30(PG-MA)	122.3
EC30(PG-MA)	113.6
Styrene-(PG-MA)*	/
<i>Glass fiber-reinforced composites</i>	
Glass-fiber-MC30(PG-MA)	136.5
Glass-fiber-EC30(PG-MA)	128.6
Glass-fiber-styrene-(PG-MA)	178.2

* The cured resin had a considerable amount of cracks in it (Figure 6.9a) and was not usable for DMA measurements.

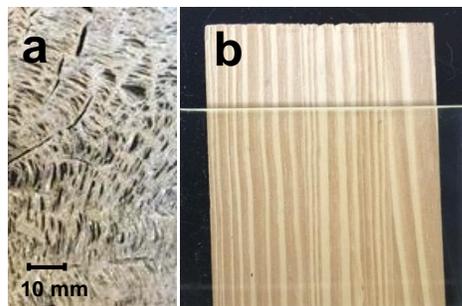


Figure 6.9 Appearance of the non-reinforced cured resins of (a) Styrene-(PG-MA) and (b) MC-(PG-MA) and EC-(PG-MA) (Picture was taken from a representative section of a 200 mm × 200 mm × 3 mm board)

6.4.5 Resin viscosity and pot life

While styrene is a liquid, MC (melting point: 33 – 38 °C) is a solid at room temperature. PG-MA is also a solid with a melting point of 110 °C. Neither MC nor PG-MA can be easily processed at room temperature for the production of composites.

That the introduction of a soluble impurity to a pure substance can lower the melting point of the pure substance is well known. The addition of MC to PG-MA indeed decreased the melting point of PG-MA, resulting in a homogenous and easily pourable liquid solution at room temperature.

As shown in Figure 6.10, the viscosity of MC30(PG-MA) was 112.7 Pa·s at room temperature. Increase in the MC content from 30 to 40% significantly decreased the viscosity of the resins to 17.8 Pa·s. EC (melting point: 6 – 8 °C) is a liquid at room temperature. EC30(PG-MA) had a lower viscosity (98.8 Pa·s) than MC30(PG-MA) at room temperature. The styrene-(PG-MA) resin used in this study had the viscosity of 1.0 Pa·s at room temperature. Although MC-(PG-MA) and EC-(PG-MA) had higher viscosities than styrene-(PG-MA), they were pourable liquids at room temperature and were fairly easy to work with during the hand lay-up application in this study.

As shown in Figure 6.10, the viscosities decreased rapidly with increasing temperatures, which mean that a low viscosity of MC-(PG-MA) and EC-(PG-MA) resins could be easily achieved through heating the resins. The viscosity of 6 Pa·s was obtained at 34 °C for MC40(PG-MA), and 53 °C for MC30(PG-MA) and EC30(PG-MA), respectively. The viscosity of 1.0 Pa·s was obtained at 48 °C for MC40(PG-

MA), and 70 °C for MC30(PG-MA) and EC30(PG-MA), respectively. The curves for MC30(PG-MA) and EC30(PG-MA) overlapped at above 38 °C..

At 70 °C, MC30(PG-MA) had the pot life of longer than 4 h (the pot life experiment was intentionally stopped at 4 h because such a pot life was considered sufficiently long for most applications.)

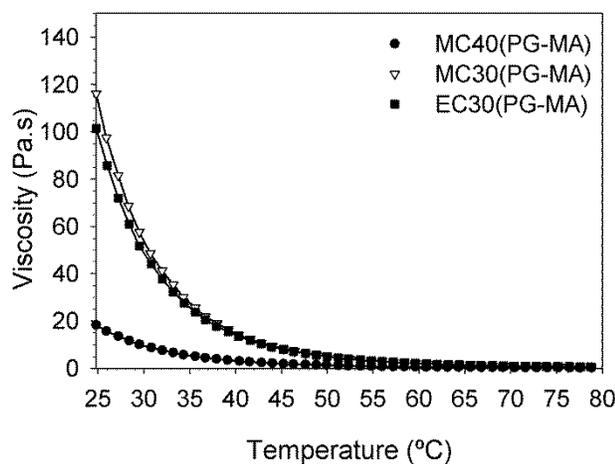


Figure 6.10 Effects of temperature on the viscosity of MC-(PG-MA) or EC-(PG-MA) resins

MC and EC are safe, renewable substances. This study demonstrated that the MC-(PG-MA) resins with the renewable material content of 30–40% could be a great replacement for the styrene-(PG-MA). MC and EC are promising styrene replacements for PG-MA.

6.5 Conclusions

Glass fiber- and kenaf fiber-reinforced MC-(PG-MA) and EC-(PG-MA) composites were fully cured after being pressed at 160 °C for 60 min. The flexural modulus of glass-fiber-MC30(PG-MA) was significantly higher than that of glass-fiber-styrene-(PG-MA). The flexural modulus and tensile strength of glass-fiber-MC30(PG-MA) were comparable to those of glass-fiber-styrene-(PG-MA). The flexural strength and tensile properties of kenaf-fiber-MC30(PG-MA) were not significantly different from those of kenaf-fiber-styrene-(PG-MA). The flexural strength, flexural modulus, and tensile strength of glass-fiber-EC30(PG-MA) were comparable to those of glass-fiber-styrene-(PG-MA). The cured MC30(PG-MA), the cured EC30(PG-MA), and their corresponding glass fiber-reinforced composites all had T_g s well above room temperature (>110 °C). The cured MC-(PG-MA) and EC-(PG-MA) products were crack-free. Mixtures of MC and PG-MA were homogenous and easily pourable liquids at room temperature. The viscosity of MC-(PG-MA) or EC-(PG-MA) were higher than that of styrene-(PG-MA), but decreased rapidly along with the increase in temperature. At 70 °C, MC30(PG-MA) had the same viscosity (1 Pa·s) as styrene-(PG-MA), with a sufficiently long pot life of over 4 h.

6.6 Acknowledgement

The authors are grateful to Dr. Willie E. Rochefort for his assistance on DSC experiments, viscosity measurements, and pot life measurements. This study was supported by return royalty fee income of patented wood adhesive technologies

invented by K. Li's group. We thank Ashland Inc. (Dublin, OH) for providing the commercial styrene-(PG-MA) resin, PG-MA, and glass fiber mats, and for assistance on DMA measurements.

6.7 Reference

1. Boland, D.J., Brophy, J.J., and A.P.N. House (1991). *Eucalyptus Leaf Oils*. ISBN 0-909605-69-6.
2. Viña, Amparo; Murillo, Elizabeth (2003). "Essential oil composition from twelve varieties of basil (*Ocimum* spp) grown in Colombia". *Journal of the Brazilian Chemical Society* 14 (5): 744. doi:10.1590/S0103-50532003000500008
3. Nawal Kishore Dubey, T.N. Tiwari, Danielle Mandin, Hary Andriamboavonjy, Jean-Pierre Chaumont. (2000). Antifungal properties of *Ocimum gratissimum* essential oil (ethyl cinnamate chemotype). *Fitoterapia*. 71, 567–569.
4. Wong, K. C.; et al. (2006). "Composition of the essential oil of rhizomes of *kaempferia galanga* L". *Flavour and Fragrance Journal* 7 (5): 263–266. doi:10.1002/ffj.2730070506
5. Safety data sheet of methyl cinnamate or ethyl cinnamate.
6. FDA (Food and Drug Administration). Code of Federal Regulations, 21 CFR 172.515. Title 21 – Food and Drugs, Volume 3, Chapter I – Food and Drug Administration, Department of Health and Human Services. Part-172 – Food Additives Permitted for Direct Addition to Food for Human Consumption. Subpart F – Flavoring Agents and Related Substances, 515 – Synthetic Flavoring Substances and Adjuvants.
7. Ruth Winter. *A Consumer's Dictionary of Food Additives*, 7th Edition. Three River Press. New York. 2009. p352, p225.
8. Wu, Y., Li, K. *J. Appl. Polym. Sci.* **2016**, 133, 43052.
9. Malcolm P. Stevens. *Polymer Chemistry: an introduction*. 1999. Oxford University Press. pp192
10. C. S. Marvel and G. H. McCain. *J. Am. Chem. Soc.* 1953, 75: 3272–3273
11. Li, K., Wu, Y. World Intellectual Property Organization. WO 2015143304 A1

12. Kandelbauer, A. Tondi, G. Zaske, O. C. and Goodman, S. H. Unsaturated Polyesters and Vinyl Esters. *In Handbook of Thermoset Plastics*, 3rd ed. Goodman, S. H. and Dodiuk-Kenig, H. Eds. William Andrew: San Diego, CA, 2014. Chapter 6, pp 111–172

Chapter 7 - Replacement of styrene with methyl cinnamate in an unsaturated polyester resin from propylene glycol, isophthalic acid and maleic anhydride

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7.1 Abstract

Methyl cinnamate (MC) was investigated as a styrene replacement in a commercial unsaturated polyester (UPE) resin (styrene-(PG-IPA-MA)) that is a mixture of styrene and a UPE plastic (PG-IPA-MA) derived from propylene glycol (PG), isophthalic acid (IPA), and maleic anhydride (MA). Mixtures of MC and PG-IPA-MA (MC-(PG-IPA-MA) resins) were homogenous and pourable liquids at room temperature. The MC-(PG-IPA-MA) resins were comparable or even superior to styrene-(PG-IPA-MA) in terms of the flexural and tensile properties of the resulting kenaf fiber-reinforced composites. Effects of the MC content on mechanical properties of the composites were investigated. Water absorption properties of the composites were studied. Viscosities and pot lives of the MC-(PG-IPA-MA) resins were measured. A representative crosslinked structure of the MC-(PG-IPA-MA) resins is proposed and discussed.

7.2 Introduction

Methyl cinnamate (MC) is a non-hazardous chemical and is approved by the FDA (U.S. Food and Drug Administration) for use as a food additive.^{1,2} MC has been previously investigated as a styrene replacement for a commercial unsaturated polyester (UPE) resin that was a mixture of styrene and a UPE plastic (PG-MA) derived from propylene glycol (PG) and maleic anhydride (MA).³ It has been demonstrated that MC was comparable to styrene in terms of the flexural and tensile properties of the resulting kenaf fiber-reinforced MC-(PG-MA) composites.³

Styrene-(PG-IPA-MA) resin is a commonly used specialty resin in the market^{4,5}, which is a mixture of styrene and PG-IPA-MA that is derived from PG, isophthalic acid (IPA), and MA. Styrene-(PG-IPA-MA) is used particularly for applications that require high strength properties.^{4,5} AESO has been investigated as a styrene replacement in styrene-(PG-IPA-MA) in our previous study.⁶ The study demonstrated that AESO was comparable or even superior to styrene in terms of the flexural and tensile properties of the composites.⁶ However, the resulting resins from AESO and PG-IPA-MA were not pourable at room temperature, which makes the resins less convenient to use than styrene-(PG-IPA-MA).⁶ Because of the commercial importance of PG-IPA-MA, it is of particular interest for us to develop non-hazardous, styrene-free resins based on PG-IPA-MA that are i) easily pourable at room temperature for typical hand lay-up applications and ii) comparable to styrene-(PG-IPA-MA) in terms of the mechanical properties of the resulting composites.

In this study, we found that MC could fully replace styrene for styrene-(PG-IPA-MA) for formation of pourable liquid resins that served as strong matrixes for kenaf fiber-reinforced composites.

7.3 Experimental

7.3.1 Materials

MC was purchased from Sigma-Aldrich (St. Louis, MO). *tert*-Butyl peroxybenzoate (TBPB) was purchased from Composite One (Vancouver, WA). Kenaf fibers were obtained from Kenaf Industries Ltd (Raymondville, TX). PG-IPA-MA and styrene-(PG-IPA-MA) were provided by Ashland Inc. (Dublin, OH). PG-IPA-MA was slowly ground into powder before use.

7.3.2 Preparation of MC-(PG-IPA-MA) resins

MC (40.3 g) was heated to 85 °C in a 250-mL beaker equipped with a mechanical stirrer and an oil bath. PG-IPA-MA (60.5 g) was slowly added into MC over 3 min. The mixture was stirred for 10 min to generate a colorless, clear, homogenous, and pourable solution. The solution was purged with nitrogen for 15 min and was cooled to 60 °C. Subsequently, TBPB (3 g, 3 wt% based on the total weight of the solution) was added into the solution. The solution was stirred for 3 min. The resulting solution had a MC/(PG-IPA-MA) weight ratio of 40/60 and was designated as MC40(PG-IPA-MA). MC30(PG-IPA-MA) and MC50(PG-IPA-MA) with the MC/(PG-IPA-MA) weight ratios of 30/70 and 50/50, respectively, were prepared with

the same procedure as described for MC40(PG-IPA-MA). A mixture of styrene-(PG-IPA-MA) and TBPB (3 wt% based on MC) was prepared and used as a control. A mixture of MC and TBPB (3 wt% based on MC) was prepared and used as a control.

7.3.3 Preparation of kenaf fiber-reinforced MC-(PG-IPA-MA) composites

Kenaf fiber mats were prepared with the procedure reported previously.⁶ The MC40(PG-IPA-MA) resin (7.8 g) was evenly poured onto the upper surface of a kenaf fiber mat that was placed in a stainless steel mold with the dimension of the chamber being 200 mm × 200 mm × 3 mm. The mat was flipped and applied with the same amount of resin on the opposite surface. Afterwards, a second fiber mat was stacked above the first mat with the fiber direction parallel to each other, and subsequently applied with MC40(PG-IPA-MA) on both surfaces with the same procedure as described previously. The same procedure was repeated until five fiber mats were applied with the resin. A stack of the five fiber mats in the mold was covered by a stainless steel plate on top, was pressed at 3.5 MPa with an automatic Benchtop Carver press (Carver Inc., Wabash, IN) for 10 min at room temperature, and subsequently pressed at 4.5 MPa for 60 min with the temperature being raised to 160 °C at about 10 °C/min. The mold was then placed between two plywood boards, pressed under a pressure of 4.5 MPa, and slowly cooled down for 100 min. The resulting composite board was removed from the mold, designated as kenaf-fiber-MC40(PG-IPA-MA), and stored at room temperature overnight before being evaluated for its mechanical properties and water resistance. Kenaf-fiber-MC30(PG-

IPA-MA) and kenaf-fiber-MC50(PG-IPA-MA), kenaf-fiber-MC50(PG-IPA-MA), kenaf-fiber-MC, and kenaf-fiber-styrene-(PG-IPA-MA) were prepared with the same procedure. Two boards were made and tested for each resin composition.

7.3.4 Determination of flexural properties of the composites

Test specimens with the dimension of 65 mm × 12.7 mm × 3 mm and with the fibers aligning along the lengthwise direction of the specimens were evaluated for the flexural strength and flexural modulus through a three-point bending test that was performed in accordance with ASTM D790, with a span of 48 mm and a rate of crosshead motion of 1.30 mm/min. At least nine specimens were tested.

7.3.5 Determination of tensile properties of the composites

The tensile strength and tensile modulus were obtained from a tensile test according to ASTM D3039. For the preparation of the dumbbell shape specimen for the tensile test, the composite board was first cut into rectangular shape with the dimension of 58 mm × 14.5 mm × 3 mm and with the fibers aligning along the lengthwise direction of the specimen. The rectangular specimen was further cut into the dumbbell shape with the gripping length of 11 mm on each end, the width of the narrow section of 8.5 mm, and the length of the narrow section of 30 mm. The distance between two grips was 36 mm, the rate of crosshead motion was 0.5 mm/min. At least six specimens were tested.

7.3.6 Statistical analysis

Data from the flexural and the tensile tests were statistically analyzed by the method of one-way ANOVA with SAS software (SAS Institute, Cary, NC). Comparisons were based on a 95% confidence interval.

7.3.7 Measurements of water absorption of the composites

The water absorption tests were performed in accordance with ASTM D570. Test specimens with the dimension of 76.2 mm × 25.4 mm × 3 mm were dried in an oven for 24 h at 50 °C, cooled in a desiccator, and weighed for the dried weight. The specimens were then immersed in distilled water. At predetermined intervals, the specimens were removed from water, wiped with dry tissue papers, weighed, and put back in the water. The water absorption of the specimen was calculated by the ratio of the weight gain to the dry weight. Three specimens were tested.

7.3.8 Differential scanning calorimetry (DSC) analysis

DSC experiments were conducted on a TA Q2000 analyzer (TA Instruments, Inc., New Castle, DE). The analyzer was calibrated in three steps: the first with nothing in the chamber to get a baseline correction, the second with sapphire to calibrate the heat capacity, and the third with indium for temperature calibration. The specimen chamber was purged with nitrogen gas with a flow rate of 75 mL/min during the experiments. The test specimen (13.5 mg) in hermetic aluminum pan with a lid was

heated from room temperature to 250 °C at the rate of 10 °C/min. An empty hermetic aluminum pan with a lid was used as a reference.

7.3.9 Measurements of resin viscosity

The resin viscosity was measured with an AR 2000ex rheometer (TA Instruments, Inc., New Castle, DE) with parallel plate geometry (25 mm in diameter). The gap between two plates was 400 µm. Test specimens (0.20 g) were steady-sheared at a shear rate of 5 Hz from 25 to 75 °C at the rate of 10 °C/min. Sampling delay time was 10 s.

7.4 Results and discussion

7.4.1 Determination of curing conditions

As shown in Figure 7.1, the curing of MC40(PG-IPA-MA) started at around 110 °C and ended at around 210 °C, with an exothermal peak at 162 °C. The curing condition of 160 °C for 60 min was expected to be capable of fully curing the MC-(PG-IPA-MA) resins and styrene-(PG-IPA-MA) in the preparation of kenaf fiber-reinforced composites. The characterization of the resulting composites with DSC did not reveal any residual exothermal peaks in the temperature range of 25 to 250 °C, confirming that the resins in the composites were completely cured (DSC graph not shown).

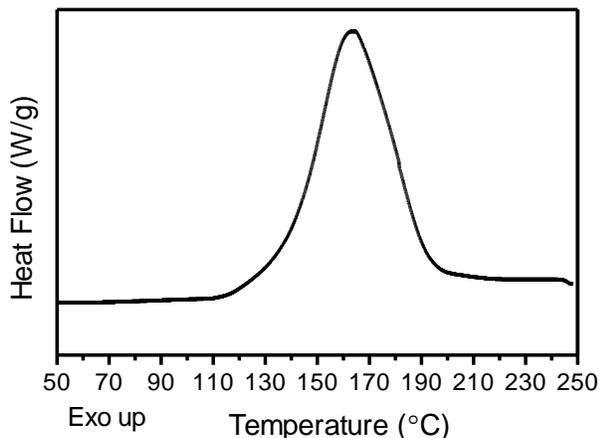


Figure 7.1 DSC curve for the course of curing of MC40(PG-IPA-MA) (ramp rate: 10 °C/min)

7.4.2 Effects of the MC content on the mechanical properties of the composites

As shown in Figure 7.2 and 7.3, kenaf-fiber-MC had very low flexural and tensile properties, indicating that MC alone could not be cured well for formation of good matrixes for kenaf fiber-reinforced composites. Mixtures of MC and PG-IPA-MA, however, could serve as strong matrixes for kenaf fiber-reinforced composites, as demonstrated by the significantly higher flexural and tensile properties of the resulting kenaf-fiber-MC-(PG-IPA-MA) composites.

As shown in Figure 7.2 and 7.3, the flexural and tensile strength did not significantly change, but the flexural and tensile modulus significantly increased when the MC content increased from 30 to 40%. The flexural and tensile properties significantly decrease when the MC content increased from 40 to 50%. Kenaf-fiber-MC40(PG-IPA-MA) had significantly higher flexural strength and modulus than kenaf-fiber-

styrene-(PG-IPA-MA). The tensile strength and modulus of kenaf-fiber-MC40(PG-IPA-MA) were not significantly different from those of kenaf-fiber-styrene-(PG-IPA-MA).

The chemical structure of MC, the representative structure of PG-IPA-MA, and a representative crosslinked network of MC-(PG-IPA-MA) are shown in Figure 6.7, 3.6, and 7.4, respectively. Three types of reactions are proposed to exist for formation of three types of chemical linkages in the crosslinking network: 1) the copolymerization of C=C bonds of MC with C=C bonds of PG-IPA-MA (linkage I); 2) the homopolymerization of the C=C bonds of PG-IPA-MA (linkage II); and 3) the homopolymerization of the C=C bonds of MC. We proposed that these reactions together generated the rigid crosslinking network in the cured products so that superior mechanical strength and modulus were obtained.

MC is a crosslinking agent for PG-IPA-MA. If the amount of MC is not sufficient, the complete crosslinking of PG-IPA-MA cannot be achieved (insufficient amounts of the linkage I), which can result in low mechanical properties of the composites. MC cannot homopolymerize well, as evidenced by the very low mechanical properties of kenaf-fiber-MC (Figure 7.2 and 7.3). If the amount of MC is too high, there will be a correspondingly high amount unreacted MC or oligomers from polymerization of MC in the resulting matrix, which can lower the mechanical properties of the composites. Results from Figure 7.2 and 7.3 demonstrate that the MC content of around 40% in the

MC-(PG-IPA-MA) resins was optimum in terms of flexural and tensile properties of the kenaf fiber-reinforced composites.

The C=C bonds in PG-IPA-MA are 1, 2-disubstituted and cannot freely move around for reactions because they are distributed along the polyester chains, which makes the homopolymerization of PG-IPA-MA difficult. The amount of the linkage II is supposed to be low. Because MC cannot homopolymerize well, it is believed that the chain length of the linkage III is not long.

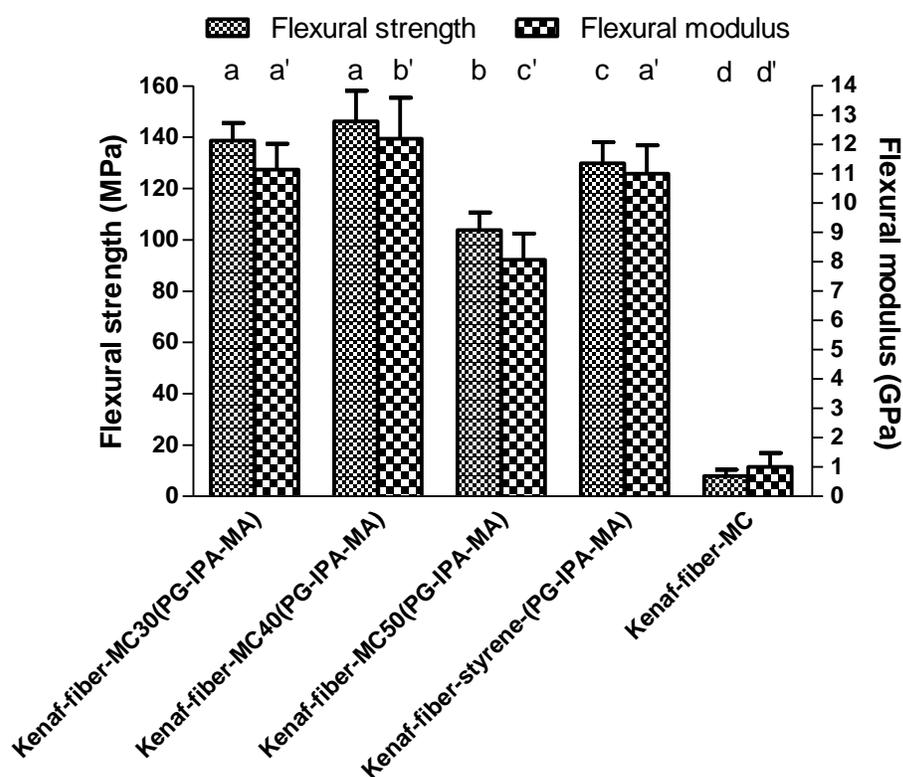


Figure 7.2 Effects of the MC content on the flexural properties of the composites.
 (The means between two groups significantly differ if the letters on top of error bars
 are different)

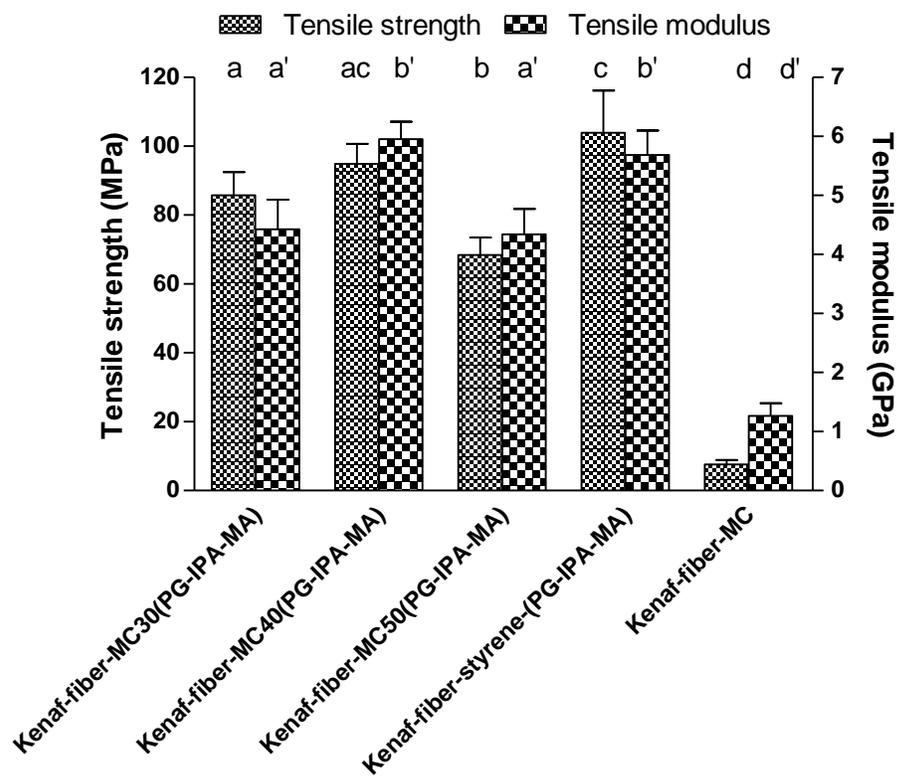


Figure 7.3 Effects of the MC content on the tensile properties of the composites.
 (The means between two groups significantly differ if the letters on top of error bars
 are different)

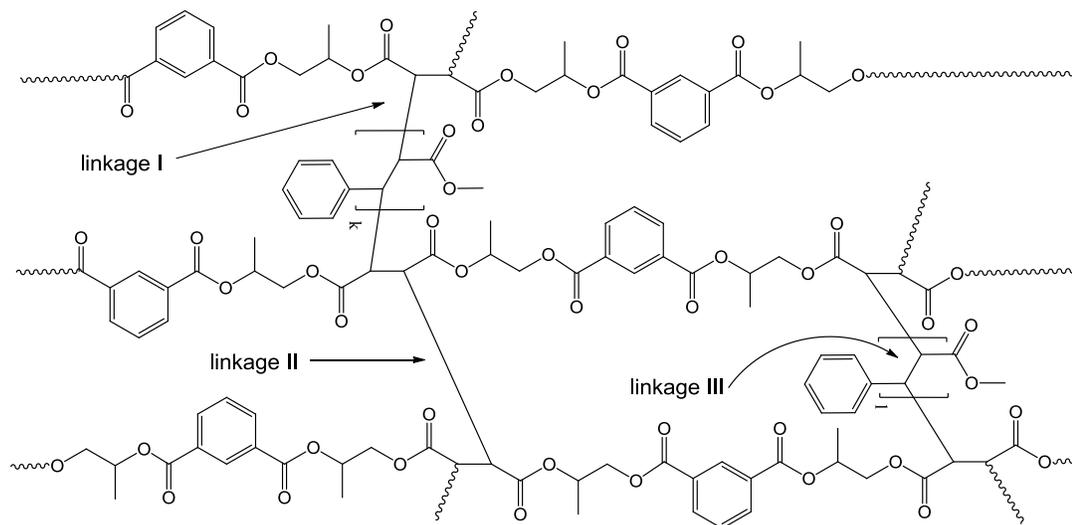


Figure 7.4 Proposed crosslinking networks of MC-(PG-IPA-MA)

7.4.3 Effects of the MC content on the water absorption properties of the composites

As shown in Figure 7.5, kenaf-fiber-MC-(PG-IPA-MA) composites had higher water absorption than kenaf-fiber-styrene-(PG-IPA-MA) at any immersion time. The water absorption increased when the immersion time increased and then gradually leveled out. The water absorption increased when the MC content increased. Kenaf-fiber-MC50(DCPD-UPE) delaminated after the immersion time reached 28 days. The low water resistance of kenaf-fiber-MC50(PG-IPA-MA) indicated that cured MC50(DCPD-UPE) did not bind the kenaf fibers well, which is consistent with its low flexural and tensile properties (Figure 7.2 and 7.3). The low water resistance of kenaf-fiber-MC50(PG-IPA-MA) is mostly probably due to excessive MC in the MC-(PG-IPA-MA) resins, which results in a weakened polymeric matrix with a substantial

amount of unreacted MC or oligomers of MC in it. These results indicated that kenaf-MC40(PG-IPA-MA) might not be suitable for applications where the water uptake of the composites must be lower. These results also demonstrated that kenaf-MC50(PG-IPA-MA) may not be used in applications where the composites are required to be submerged in water for a long period of time.

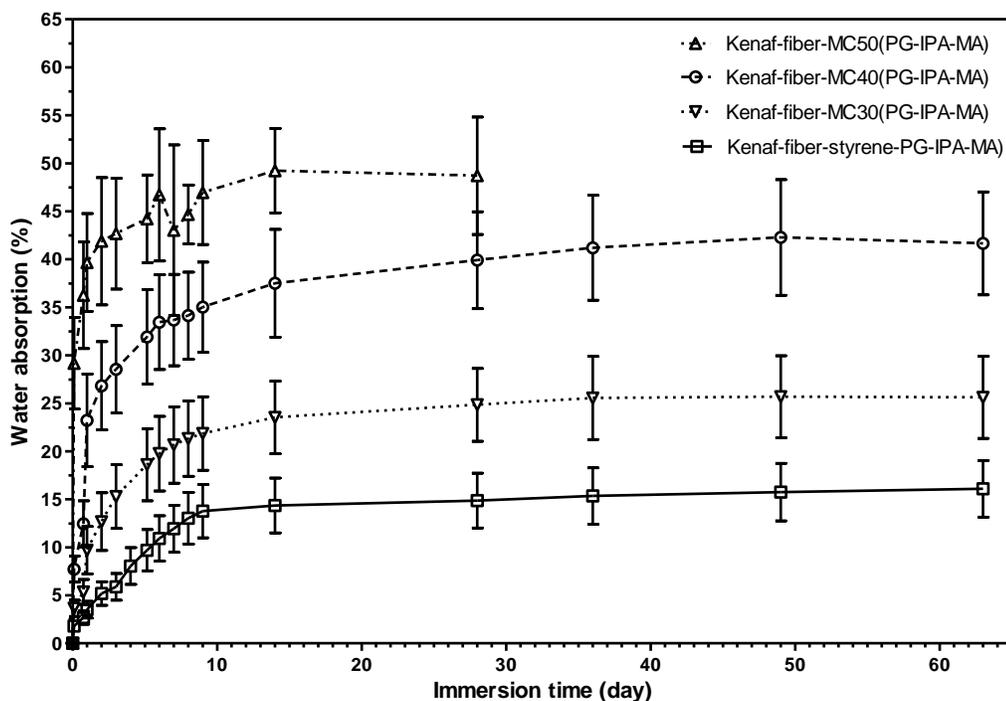


Figure 7.5 Effects of the MC content on the water absorption of the composites

7.4.4 Resin viscosity and pot life

The mixtures of the MC and PG-IPA-MA at weight ratios studied here were pourable liquids although they are both solid at room temperature. For example, the viscosity of the MC40(PG-IPA-MA) was 57 Pa·s at room temperature (Figure 7.6). The

MC40(PG-UPA-MA) was fairly easy to work with for the hand lay-up resin application in this study. For many applications, the viscosity of MC40(PG-IPA-MA) does not have to be as low as 1.7 Pa·s that is the viscosity of styrene-(PG-IPA-MA) at room temperature. If a lower viscosity is required for certain applications, it can be easily lowered by raising the temperature of the resin. As shown in Figure 7.6, the viscosity decreased dramatically when the temperature increased. The viscosity of 1.7 Pa·s was obtained at 62 °C. The pot life of MC40(PG-IPA-MA) was longer than 5 h at 62 °C (the measurement was intentionally stopped at 5 h because we considered such a pot life is sufficiently long for most composite fabrication processes).

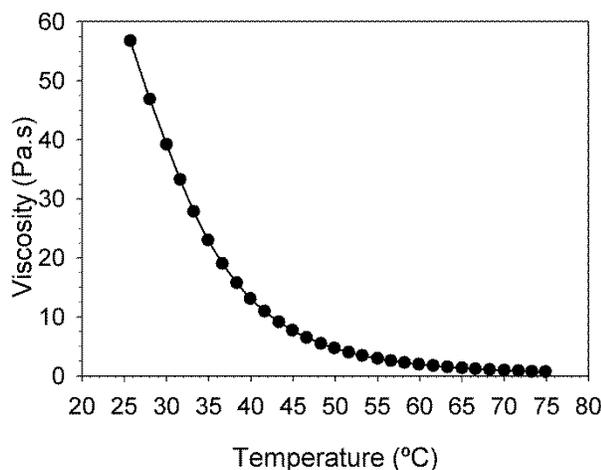


Figure 7.6 Effects of temperature on the viscosity of MC40(PG-IPA-MA)

7.5 Conclusions

Kenaf fiber-reinforced MC-(PG-IPA-MA) composites were completely cured after pressed at 160 °C for 60 min. The MC content of 40% in the MC-(PG-IPA-MA)

resins resulted in the highest flexural and tensile properties of the composites. The flexural strength and modulus of kenaf-fiber-MC40(PG-IPA-MA) were significantly higher than those of kenaf-fiber-styrene(PG-IPA-MA). The tensile strength and modulus of kenaf-fiber-MC40(PG-IPA-MA) were not significantly different from those of kenaf-fiber-styrene(PG-IPA-MA). Kenaf-fiber-MC40(PG-IPA-MA) had higher water absorption than kenaf-fiber-styrene-(PG-IPA-MA). MC40(PG-IPA-MA) had a sufficiently low viscosity of 57 Pa·s at room temperature for most of UPE applications. MC40(PG-IPA-MA) at 62 °C had the same viscosity of 1.7 Pa·s as the styrene(PG-IPA-MA) at room temperature and had a pot life of longer than 5 h. MC is a promising alternative to styrene for PG-IPA-MA.

7.6 Acknowledgement

The authors are grateful to Dr. Willie E. Rochefort for his assistance on the DSC analysis and measurements of the viscosity and the pot life. This study was supported by return royalty fee income of patented wood adhesive technologies invented by K. Li's group. We thank Ashland Inc. (Dublin, OH) for providing the commercial styrene-(PG-IPA-MA) resin and the PG-IPA-MA plastic.

7.7 Reference

1. Safety data sheet of methyl cinnamate. Available at Sigma-Aldrich.com.
2. FDA (Food and Drug Administration). Code of Federal Regulations, 21 CFR 172.515. Title 21 – Food and Drugs, Volume 3, Chapter I – Food and Drug Administration, Department of Health and Human Services. Part-172 – Food Additives Permitted for Direct Addition to Food for Human Consumption. Subpart F –

Flavoring Agents and Related Substances, 515 – Synthetic Flavoring Substances and Adjuvants.

3. Chapter 6 - Replacement of styrene with methyl cinnamate or ethyl cinnamate in an unsaturated polyester resin from propylene glycol and maleic anhydride
4. Strong, A. B. *Fundamentals of Composites Manufacturing: Materials, Methods and Applications*, 2nd ed. Society of Manufacturing Engineers: Dearborn, MI, **2008**. Chapter 3, pp 47–83
5. Kandelbauer, A. Tondi, G. Zaske, O. C. and Goodman, S. H. Unsaturated Polyesters and Vinyl Esters. *In Handbook of Thermoset Plastics*, 3rd ed. Goodman, S. H. and Dodiuk-Kenig, H. Eds. William Andrew: San Diego, CA, 2014. Chapter 6, pp 111–172
6. Chapter 3 - Replacement of styrene with acrylated epoxidized soybean oil in an unsaturated polyester resin from propylene glycol, isophthalic acid and maleic anhydride

Chapter 8 - Replacement of styrene with methyl cinnamate in a dicyclopentadiene-modified unsaturated polyester resin

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8.1 Abstract

Non-hazardous methyl cinnamate (MC) was investigated as an alternative to styrene in a commercial unsaturated polyester (UPE) resin (styrene-(DCPD-UPE)), a mixture of styrene and a UPE (DCPD-UPE) that was derived from ethylene glycol, diethylene glycol, maleic anhydride, and dicyclopentadiene (DCPD). Mixtures of MC and DCPD-UPE (MC-(DCPD-UPE) resins) were found to have fairly low viscosities at room temperature. The resulting glass fiber-reinforced MC-(DCPD-UPE) composites had higher flexural modulus and tensile strength than the styrenated counterparts. The resulting kenaf fiber-reinforced composites had comparable flexural and tensile properties to the styrenated counterparts. Glass transition temperatures of cured MC-(DCPD-UPE) resins and the resulting composites were well above room temperature. The pot life of the MC-(DCPD-UPE) resins was long enough for most of their applications. Effects of the MC content on the mechanical properties of the

composites and on viscosities of the resins were investigated. A crosslinked network structure of the cured MC-(PG-MA) resins was proposed and discussed.

8.2 Introduction

Methyl cinnamate (MC) is non-hazardous and is widely used as a food additive.¹⁻³ MC has been found to be a superior alternative to styrene in two different types of commercial unsaturated polyester (UPE) resins in our previous studies.^{4,5} One was styrene-(PG-MA) that was a mixture of styrene and PG-MA prepared from propylene glycol (PG) and maleic anhydride (MA).⁴ The other UPE resin was styrene-(PG-IPA-MA) that was a mixture of styrene and PG-IPA-MA prepared from PG, isophthalic acid (IPA), and MA.⁵ Styrene-(DCPD-UPE) is another widely used UPE resins in the market, which is a mixture of styrene and a DCPD-modified UPE (DCPD-UPE) prepared from ethylene glycol, diethylene glycol, MA, and dicyclopentadiene (DCPD). DCPD-UPE has different properties from the PG-MA and PG-IPA-MA. For example, DCPD-UPE has a lower polarity and a lower molecular weight than PG-MA and PG-IPA-MA. The styrene-(DCPD-UPE) resins thus have different applications from the styrene-(PG-MA) and styrene-(PG-IPA-MA) resins. In this study, MC was investigated as a styrene replacement in the styrene-(DCPD-UPE).

It was found that the MC-(DCPD-UPE) resins had a very low viscosity at room temperature. The resulting glass fiber- and kenaf fiber-reinforced MC-(DCPD-UPE) composites displayed superior flexural and tensile properties.

8.3 Experimental

8.3.1 Materials

MC was purchased from Sigma-Aldrich (St. Louis, MO). *tert*-Butyl peroxybenzoate (TBPB) was obtained from Composite One (Vancouver, WA). DCPD-UPE, styrene-(DCPD-UPE), and glass fiber mats with randomly oriented glass fibers were obtained from Ashland Inc. (Dublin, OH). The glass fiber mats were cut into the dimension of 200 mm × 200 mm with a paper cutter before use. Each glass fiber mat had the weight of about 17 g. Kenaf fibers were purchased from Kenaf Industries Ltd (Raymondville, TX).

8.3.2 Preparation of MC-(DCPD-UPE) resins

MC (105.2 g) and DCPD-UPE (420 g) were added in a 600-mL beaker equipped with a mechanical stirrer and an oil bath. The mixture was heated to 60 °C and stirred for 10 min to generate a clear, homogenous, and easily pourable solution. The solution was purged with nitrogen for 10 min. Subsequently, TBPB (15.7 g, 3 wt% based on the total weight of the solution) was added into the solution and then stirred for 3 min. The resulting solution was poured into a container. The container was placed in a centrifuge (Labofuge 400, Heraeus Instrument, Germany) and was centrifuged at 3000 rpm for 3 min for the removal of air bubbles in the solution. The resulting MC-(DCPD-UPE) resin had the MC/(DCPD-UPE) weight ratio of 20/80 and was designated as MC20(DCPD-UPE). MC30(DCPD-UPE) and MC25(DCPD-UPE) with

the MC/(DCPD-UPE) weight ratios of 30/70 and 25/75, respectively, were prepared with the same procedure as described previously for MC20(DCPD-UPE). The styrene-(DCPD-UPE) resin was mixed with TBPB (3 wt% based on styrene-(DCPD-UPE)) and used as a control.

8.3.3 Preparation of glass fiber-reinforced MC-(DCPD-UPE) composites

The MC20(DCPD-UPE) resin (18 g) was evenly poured onto the surface of a glass fiber mat that was placed in the chamber of a stainless steel mold with the dimension of 200 mm × 200 mm × 3 mm. Subsequently, the mat was flipped over and applied with 30 g of the resin on the surface. A second glass fiber mat was stacked above the first mat and was applied with 30 g of resin on the surface. A third glass fiber mat was stacked above the second mat and was applied with 30 g of resin on the surface. A fourth glass fiber mat was stacked above the third mat and was applied with 18 g of resin on the surface. After the resin application, the mats were placed onto a hot plate (50 °C) and rolled by a rubber roller by hand for about 5 min for removing air inside the resin-saturated glass fiber mats. Afterwards, the mats in the stainless steel mold was covered by a stainless steel plate on top and was first pressed at 3 MPa by an automatic Benchtop Carver press (Carver Inc., Wabash, IN) for 10 min, and subsequently pressed at the same pressure for 60 min with the temperature rising to 160 °C at about 10 °C/min. The mold was then taken out of the press and cooled down at room temperature. The resulting composite board was designated as glass-fiber-MC20(DCPD-UPE). Glass-fiber-MC30(DCPD-UPE) and glass-fiber-

MC25(DCPD) were prepared with the same procedure as described previously for the preparation of glass-fiber-MC20(DCPD-UPE). Glass-fiber-styrene-(DCPD-UPE) was prepared with the same procedure as described previously for glass-fiber-MC20(DCPD-UPE), except that the resin was kept at room temperature during the rolling for air removal. All resulting composite boards had a weight of about 151 g (excessive resins flowed out of the mold during the pressing process) and a dimension of 200 mm × 200 mm × 2.5 mm. The fiber content was calculated to be about 45% by weight. At least two boards were made and tested for each composition.

8.3.4 Preparation of kenaf fiber-reinforced MC-(DCPD-UPE) composites

Kenaf fiber mats were prepared according to the procedure reported in our previous study.⁶ MC20(DCPD-UPE) (9.0 g) was slowly poured onto the upper surface of a kenaf fiber mat that was placed in the chamber of the stainless steel mold with the dimension of 200 mm × 200 mm × 3 mm. The mat was flipped and subsequently applied with the same amount of resin on the opposite surface. A second fiber mat was stacked above the first mat with the fiber direction parallel to each other, and subsequently applied with MC20(DCPD-UPE) on both surfaces with the same procedure as described previously. The same procedure was repeated until five fiber mats were coated with the resin. A stack of the five resin-coated fiber mats in the mold was covered by the stainless steel plate on top and was pressed at 3.8 MPa with the Benchtop Carver press for 10 min at room temperature, and subsequently for 60 min under the same pressure with the temperature being raised to 160 °C at about 10

°C/min. Afterwards, the mold was taken out from the press and cooled down at room temperature. The resulting kenaf fiber-reinforced composite board was designated as kenaf-fiber-MC20(DCPD-UPE). Kenaf-fiber-MC30(DCPD-UPE) was prepared with the same procedure as previously described for Kenaf-fiber-MC20(DCPD-UPE). The resulting composite boards had a weight of about 121 g (excessive resins flowed out of the mold during the pressing process) and a dimension of 200 mm × 200 mm × 2.8 mm. The fiber content was calculated to be about 65% by weight for all composite boards. At least two boards were made and tested for each composition.

8.3.5 Determination of flexural properties of the composites

For glass fiber-reinforced composites, test specimens with the dimension of 65 mm × 12.7 mm × 2.5 mm were prepared and evaluated for the flexural strength and flexural modulus through a three-point bending test in accordance with ASTM D790, with a span of 40 mm and a rate of crosshead motion of 1.28 mm/min. Eighteen specimens were tested and averaged values were reported.

For kenaf fiber-reinforced composites, test specimens with the dimension of 65 mm × 12.7 mm × 2.8 mm and with the fibers aligning along the lengthwise direction of the specimens were prepared and evaluated for the flexural strength and flexural modulus through a three-point bending test in accordance with ASTM D790, with a span of 42 mm and a rate of crosshead motion of 1.11 mm/min. Eighteen specimens were tested and averaged values were reported.

8.3.6 Determination of tensile properties of the composites

For glass fiber-reinforced composites, the tensile strength and tensile modulus were obtained from a tensile test in accordance with ASTM D638. For the preparation of type I dumbbell-shaped specimens, the composite boards were first cut into rectangular specimens with the dimension of 180 mm × 19 mm × 2.5 mm. The rectangular specimens were further cut to dumbbell-shaped specimens that had a width of narrow section of 13 mm and a length of narrow section of 57 mm. The distance between grips was 115 mm and the rate of crosshead motion was 5 mm/min. At least five specimens were tested and averaged values were reported.

For kenaf fiber-reinforced composites, the same procedure previously described were used, except that test specimens with the thickness of 2.8 mm and with the fibers aligning along the lengthwise direction of the specimens were used, and the rate of crosshead motion was 2 mm/min. At least five specimens were tested and averaged values were reported.

8.3.7 Statistical analysis

Data from the flexural and the tensile tests were statistically analyzed by permutation test using RStudio (RStudio, Inc., Boston, MA). All comparisons were based on a 95% confidence interval.

8.3.8 Dynamic Mechanical Analysis (DMA)

Both non-reinforced cured resins and glass fiber-reinforced composites were characterized with DMA. For the preparation of the non-reinforced cured resins, uncured resins were poured into the chamber that was created by putting a 3-mm thick rubber cord in between two glass plates with the dimension of 200 mm × 200 mm × 3 mm. The resins were subsequently cured in an air-circulating oven at 135 °C for 1 h, followed by a post cure at 160 °C for one more hour. Glass fiber-reinforced composite specimens were cut from the same boards as those used for the flexural and tensile tests.

The DMA experiments were conducted by Ashland Inc. (Dublin, OH) with a TA Q800 analyzer (TA Instruments, Inc., New Castle, DE) using the 35-mm single cantilever clamp. Test specimens were surface ground to achieve the thickness of 1.75 mm. Test specimens with the dimension of 17.8 mm × 12.5 mm × 1.75 mm were tested at a constant frequency of 1 Hz. The specimens were first cooled to -100 °C, tested from -100 to 200 °C (first scan), cooled to -100 °C again, and retested from -100 to 200°C (second scan), with a ramp rate of 2 °C/min. Data from the second scan were used. The temperature at $\text{Tan } \delta$ maximum (i.e., peak value) was considered the glass transition temperature (T_g).

8.3.9 Differential scanning calorimetry (DSC) analysis

DSC experiments were performed on a TA Q2000 analyzer (TA Instruments, Inc., New Castle, DE). The analyzer was calibrated in three steps: the first with nothing in

the chamber to get a baseline correction, the second with sapphire to calibrate the heat capacity, and the third with indium for temperature calibration. The specimen chamber was purged with nitrogen during the experiments with a flow rate of 50 mL/min. For temperature sweep, test specimen (10 mg) in hermetic aluminum pan with a lid was heated from room temperature to 250 °C at a rate of 10 °C/min. An empty hermetic aluminum pan with a lid was used as a reference.

8.3.10 Measurements of resin viscosity

The resin viscosity was measured with an AR G2 Rheometer (TA Instruments, Inc., New Castle, DE) with a cone-and-plate geometry (cone angle: 1 degree 59 min 46 sec; cone diameter: 40 mm; truncation gap 56 micro m). For the temperature sweep, test specimens were steady-sheared at the shear rate 1 Hz, from 25 to 90 °C at the rate of 5 °C/min.

8.3.11 The measurement of a resin pot life

For the measurement of a resin pot life at use temperatures, an oscillatory time sweep was performed with an AR 2000ex rheometer (TA Instruments, Inc., New Castle, DE) as described previously with a parallel-plate geometry (25 mm in diameter). The gap between two plates was 400 µm. Sampling delay time was set at 10 s. At t_0 , test specimens were started to be oscillatorily sheared at 5 Hz with a strain amplitude of 50% at the temperature of 46 °C. As the curing began, the shear storage modulus (G') increased rapidly. At t_1 , G' was equal to the shear loss modulus (G''). The time

between t_0 and t_1 was defined as the pot life for the resin in this study. Two specimens were tested and averaged values were reported.

8.4 Results and discussion

8.4.1 Determination of curing conditions

As shown in Figure 8.1, the curing of styrene-(DCPD-UPE) started at 110 °C and ended at 195 °C, with a higher exothermal peak at 134.7 °C and a lower exothermal peak at 165.8 °C. The curing of MC20(DPCD-UPE) started at 120 °C and ended at 195 °C, with an exothermal peak at 169.4 °C. The curing of MC30(DCPD-UPE) started at 135 and ended at 190 °C, with an exothermal peak at 169.8 °C. The hot press condition of 160 °C for 60 min was expected to fully cure the MC-(DCPD-UPE) resins and the styrene-(DCPD-UPE) resin in the preparation of glass fiber-reinforced composites and kenaf fiber-reinforced composites. No exothermal peaks on a DSC graph of the cured composites were found at 25 to 250 °C, which indicated that the resins in the composites were completely cured (DSC graph not shown). The resulting glass fiber-reinforced composites and kenaf fiber-reinforced composites had hard and smooth surfaces. No visually detectable defects such as cracks, warpage, and delamination were found.

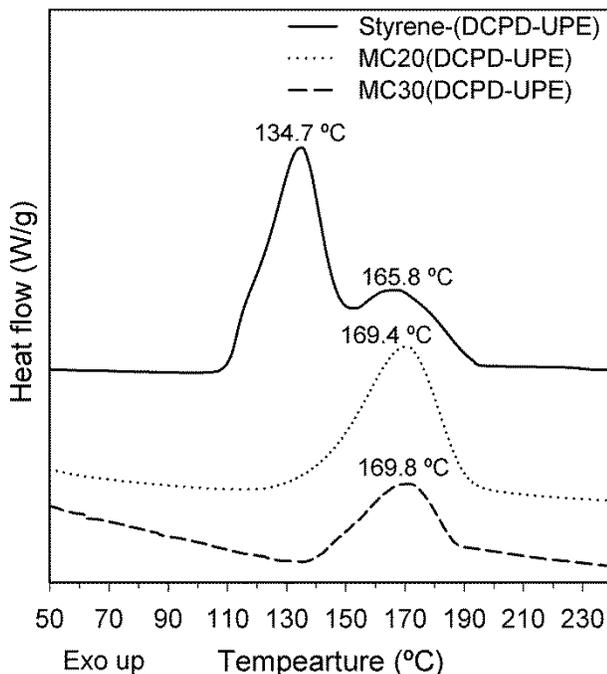


Figure 8.1 DSC curves for the course of curing of MC-(DCPD-UPE) and styrene-(DCPD-UPE) (ramp rate: 10 °C/min)

8.4.2 Effects of the MC content on the flexural and tensile properties of the glass fiber-reinforced composites

As shown in Figure 8.2, the flexural strength and flexural modulus of the glass fiber-reinforced MC-(DCPD-UPE) composites increased when the MC content decreased. Glass-fiber-MC20(DCPD-UPE) had significantly higher flexural strength and flexural modulus than glass-fiber-MC25(DCPD-UPE), both of which had significantly higher flexural strength and flexural modulus than glass-fiber-MC30(DCPD-UPE). The flexural modulus of glass-fiber-MC20(DCPD-UPE) was significantly higher than that

of glass-fiber-styrene-(DCPD-UPE), with the flexural strength being not significantly different. The flexural modulus of glass-fiber-MC25(DCPD-UPE) was not significantly different from that of glass-fiber-styrene-(DCPD-UPE); but the flexural strength of the former was lower than that of the latter.

As shown in Figure 8.3, the tensile strength and tensile modulus increased significantly when the MC content decreased from 30 to 25%. The reduction of the MC content from 25 to 20% did not significantly change the tensile strength and modulus of the glass fiber-reinforced composites. The tensile strength of glass-fiber-MC20(DCPD-UPE) was significantly higher than that of glass-fiber-styrene-(DCPD-UPE), with the tensile modulus being not significantly different. The tensile strength of glass-fiber-MC25(DCPD-UPE) was not significantly different from that of glass-fiber-styrene-(DCPD-UPE); but the tensile modulus of the former was lower than that of the latter.

It has been demonstrated that MC does not homopolymerize well.⁷ Excessive amount of MC may not participate in the crosslinking reactions and become weak parts of the cured MC-(DCPD-UPE) matrix, thus lowering the strengths and moduli of the resulting composites. If the amount of MC is not enough for the full crosslinking of the DCPD-UPE, the maximum strengths and moduli of the resulting composites cannot be realized. Results from Figure 8.2 and 8.3 suggest that MC content of above 25% is too high, and the optimum MC content is around 20%.

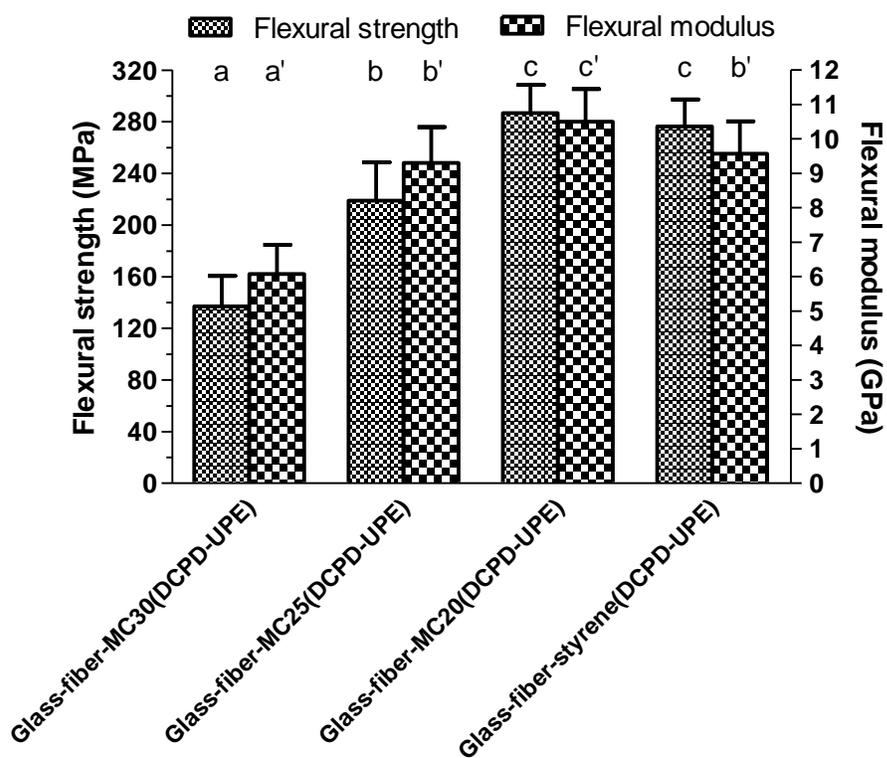


Figure 8.2 Effects of the MC content on the flexural properties of the glass fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

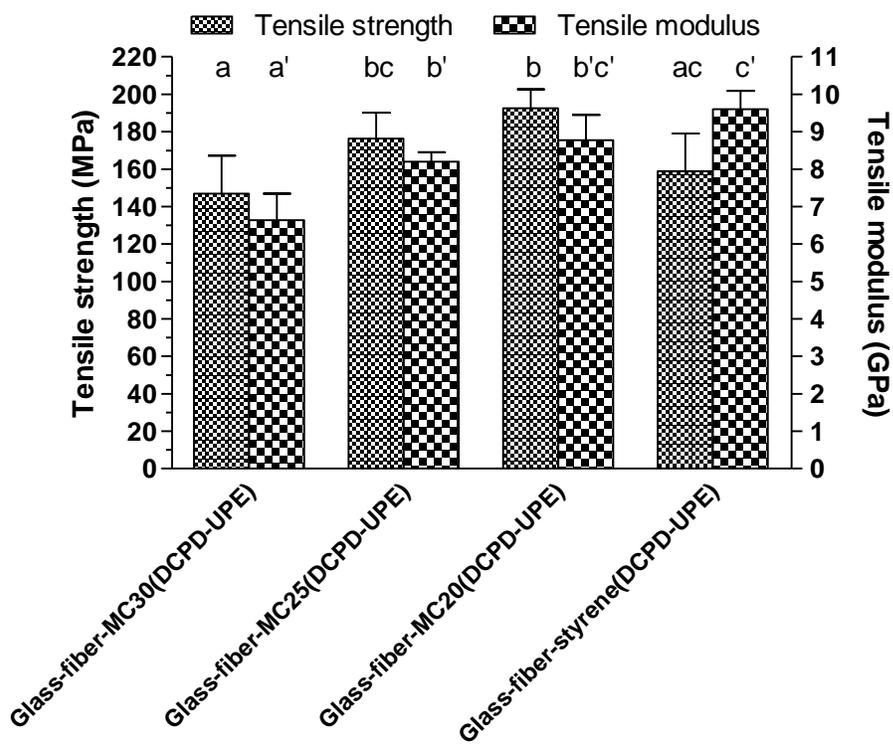


Figure 8.3 Effects of the MC content on the tensile properties of the glass fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

8.4.3 Effects of the MC content on the flexural and tensile properties of the kenaf fiber-reinforced composites

As shown in Figure 8.4, the flexural strength and flexural modulus of the kenaf fiber-reinforced composites increased significantly when the MC content decreased from 30 to 20%. The flexural strength and flexural modulus of kenaf-fiber-MC20(DCPD-UPE) were not significantly different from those of kenaf-fiber-styrene-(DCPD-UPE). As shown in Figure 8.5, the tensile strength and tensile modulus of the kenaf fiber-

reinforced composites increased significantly when the MC content was reduced from 30 to 20%. The tensile strength and tensile modulus of kenaf-fiber-MC20(DCPD-UPE) were not significantly different from those of kenaf-fiber-styrene(DCPD-UPE). As discussed previously, the MC content of 30% appears to be too high to form a superior MC-(DCPD-UPE) matrix. The change of the reinforcing fibers from glass fibers to kenaf fibers does not appear to change the effects of the MC content on the strengths and moduli of the resulting composites.

The flexural strength of glass-fiber-MC20(DCPD-UPE) was about 86% higher than that of kenaf fiber-MC20(DCPD-UPE) (Figure 8.2 and 8.4). The flexural modulus, tensile strength, and tensile modulus of glass fiber-MC20(DCPD-UPE) are correspondingly much higher than those of kenaf fiber-MC20(DCPD-UPE). The higher strengths and moduli of glass fiber-MC20(DCPD-UPE) are believed to be mainly due to the fact that glass fibers are much stronger than kenaf fibers.

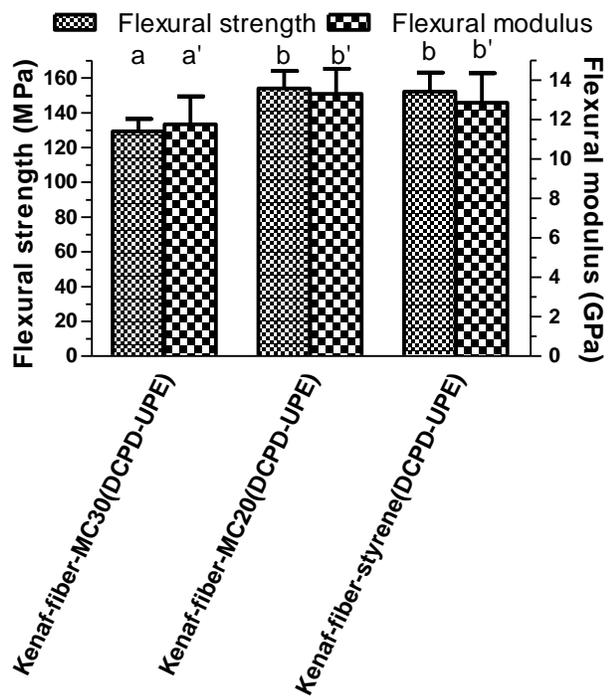


Figure 8.4 Effects of the MC content on the flexural properties of the kenaf fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

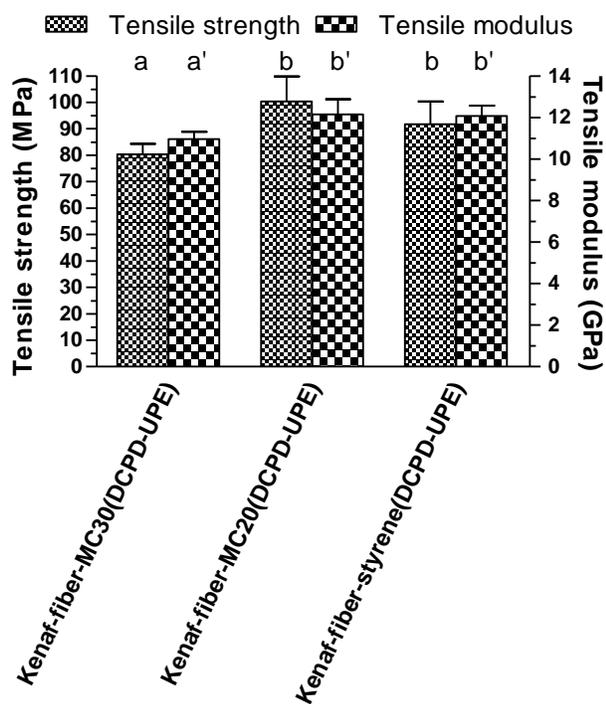


Figure 8.5 Effects of the MC content on the tensile properties of the kenaf fiber-reinforced composites. (The means between two groups significantly differ if the letters on top of error bars are different)

8.4.4 A proposed network structure

The chemical structure of MC, the representative structure of DCPD-UPE, and a proposed network structure of cured MC-(PG-MA) resins are shown in Figure 6.7, 5.7, and 8.6, respectively. Three types of linkages are proposed to exist in the network structure: 1) the linkage I from the homopolymerization of C=C bonds of MC, 2) the linkage II from the homopolymerization of C=C bonds on the backbone chains of DCPD-UPE, and 3) the linkage III from the comopolymerization of the C=C bonds of

MC with the C=C bonds on the backbone chains of DCPD-UPE. We proposed that all these linkages contributed to the formation of a rigid polymer network structure which resulted in high mechanical properties. The chain lengths of the linkage I are expected to be short because the MC does not homopolymerize well. The C=C bonds in DCPD-UPE are all 1,2-disubstituted, and thus have high steric hindrance for their reactions. The C=C bonds are inside the long polymeric chains of DCPD-UPE, which significantly lower the mobility of the C=C bonds and thus significantly lower their chances to react with each other. Therefore, the content or density of the linkage II is expected to be low.

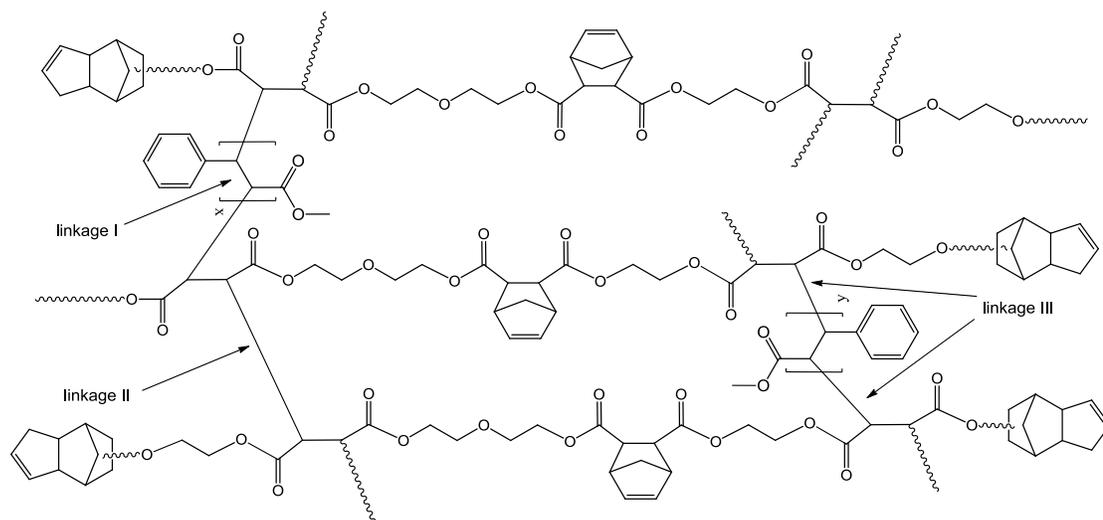


Figure 8.6 Proposed network structure of a cured MC-(DCPD-UPE) resin

8.4.5 Glass transition temperatures (T_g)

As shown in Table 8.1, the T_g s of cured MC20(DCPD-UPE) and glass-fiber-MC20(DCPD-UPE) were 125.4 °C and 100.6 °C, respectively, which indicated that

The reinforcement of the MC-(DCPD-UPE) matrix with glass fibers lowered the T_g . The fiber-reinforced composites may lose their rigidity and strengths at a temperature of above their T_g s. Therefore, the T_g s for any fiber-reinforced composites have to be higher than the highest temperature to which the composites may be exposed in their actual applications. The T_g s of cured styrene-(DCPD-UPE) and glass-fiber-styrene-(DCPD-UPE) were 168.3 °C and 164.7 °C, respectively, that were correspondingly higher than those of cured MC20(DCPD-UPE) and glass-fiber-MC20(DCPD-UPE) (Table 8.1). These results indicated that the applicable range of use temperature for glass-fiber-MC20(DCPD-UPE) was narrower than that for glass-fiber-styrene-(DCPD-UPE). Considering that fiber-reinforced UPE composites are never exposed to a temperature of 100 °C in many of their applications, the glass-fiber-MC20(DCPD-UPE) composites are expected to be very useful materials in various structural and non-structural applications.

Table 8.1 T_g for non-reinforced cured resins and glass fiber-reinforced composites

Cured products	T_g (°C)
<i>Non-reinforced cured resins</i>	
MC20(DCPD-UPE)	125.4
Styrene-(DCPD-UPE)	168.3
<i>Glass fiber-reinforced composites</i>	
Glass-fiber-MC20(DCPD-UPE)	100.6
Glass-fiber-styrene-(DCPD-UPE)	164.7

8.4.6 Resin viscosity and pot life

As shown in Figure 8.7, the viscosities of MC20(DCPD-UPE), MC25(DCPD-UPE), and MC30(DCPD-UPE) were 17.2 Pa·s, 7.2 Pa·s and 3.6 Pa·s, respectively, at room temperature (25 °C). MC20(DCPD-UPE), MC25(DCPD-UPE), and MC30(DCPD-UPE) could be easily poured onto reinforcing fibers and penetrated fibers by their gravity very well at room temperature. We believe the viscosity of MC20(DCPD-UPE) is sufficiently low that it can be used for almost all applications of UPE resins, although commercial styrenated UPE resins have viscosities of 0.05 to 6 Pa·s.² The styrene-(DCPD-UPE) used in this study had the viscosity of 1.7 Pa·s at room temperature. As shown in the Figure 8.7, the viscosity of the MC20(DCPD-UPE) decreased rapidly when the temperature was raised from 25 °C to 40 °C and then gradually flattened out when the temperature was further raised. If a lower viscosity is indeed required for some applications, the 1.7 Pa·s could be easily achieved at 46 °C for MC20(DCPD-UPE), 41 °C for MC25(DCPD-UPE), and 34 °C for MC30(DCPD-UPE).

At 46 °C, MC20(DCPD-UPE) had the pot life of larger than 9 h (we intentionally stopped the test at 9 h because such a pot life was expected to be sufficiently long for most fabrication processes). Maintaining the temperature of MC20(DCPD-UPE) at 46 °C should not be a difficult thing to do.

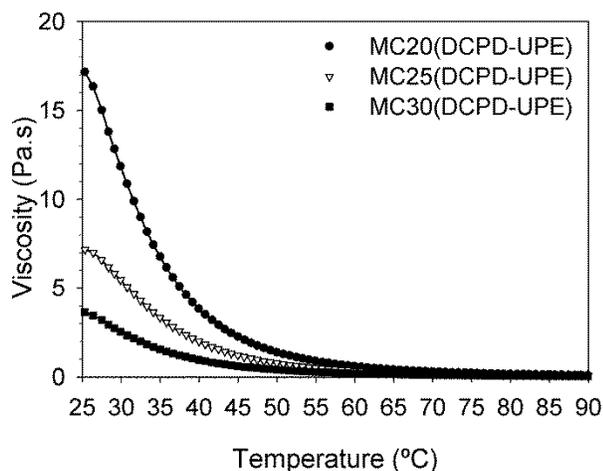


Figure 8.7 Effects of temperature on the viscosity of MC-(DCPD-UPE) resins

8.5 Conclusions

The MC-(DCPD-UPE) resins and the resulting glass fiber- and kenaf fiber-reinforced composites were completely cured at 160 °C for 60 min. The flexural modulus and tensile strength of glass-fiber-MC20(DCPD-UPE) were significantly higher than those of glass-fiber-styrene-(DCPD-UPE). The flexural strength and tensile modulus of glass-fiber-MC20(DCPD-UPE) or the flexural and tensile strength and modulus of kenaf-fiber-MC20(DCPD-UPE) were not significantly different than those of glass-fiber-styrene-(DCPD-UPE) or kenaf-fiber-styrene-(DCPD-UPE), respectively. The T_g of glass-fiber-MC20-(DCPD-UPE) was 100.6 °C which is higher than the highest temperature that fiber-reinforced UPE composites may be exposed to in their applications. MC20(DCPD-UPE) and MC30(DCPD-UPE) had sufficiently low viscosities and sufficiently long pot lives for most of their applications at room temperature. The viscosities of MC20(DCPD-UPE) could be lowered to 1.7 Pa·s at 46

°C (the same viscosity as styrene-(DCPD-UPE)) and still had its pot life of more than 9 h.

8.6 Acknowledgement

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8.7 Reference

1. Safety data sheet of methyl cinnamate. Available at Sigma-Aldrich.com.
2. FDA (Food and Drug Administration). Code of Federal Regulations, 21 CFR 172.515. Title 21 – Food and Drugs, Volume 3, Chapter I – Food and Drug Administration, Department of Health and Human Services. Part-172 – Food Additives Permitted for Direct Addition to Food for Human Consumption. Subpart F – Flavoring Agents and Related Substances, 515 – Synthetic Flavoring Substances and Adjuvants.
3. Ruth Winter. A Consumer's Dictionary of Food Additives, 7th Edition. Three River Press. New York. 2009. p352
4. Chapter 6 - Replacement of styrene with methyl cinnamate or ethyl cinnamate in an unsaturated polyester resin from propylene glycol and maleic anhydride
5. Chapter 7 - Replacement of styrene with methyl cinnamate in an unsaturated polyester resin from propylene glycol, isophthalic acid and maleic anhydride

6. Chapter 3 - Replacement of styrene with acrylated epoxidized soybean oil in an unsaturated polyester resin from propylene glycol, isophthalic acid and maleic anhydride
7. C. S. Marvel and G. H. McCain. *J. Am. Chem. Soc.* 1953, 75, 3272–3273

Chapter 9 - Conclusions

AESO and MC were investigated as alternatives to styrene in UPE resins, respectively. Three commercial UPEs (PG-IPA-MA, PG-MA, and DCPD-UPE) with very different structures and properties were used as UPEs. Two different fibers (glass fibers and kenaf fibers) were used as reinforcing fibers. Combinations of each UPE with either AESO or MC were investigated for their curing conditions, viscosities, and pot-lives. These combinations were used as styrene-free UPE resins for the preparation and evaluation of fiber-reinforced UPE composites.

AESO60(PG-IPA-MA) was superior to styrene-(PG-IPA-MA) in terms of the flexural strength and tensile modulus of the kenaf fiber-reinforced composites; and was comparable to styrene in terms of the flexural modulus and tensile strength of the kenaf fiber-reinforced composites.

The cured AESO-(PG-MA) resins did not have cracks, whereas the cured styrene-(PG-MA) had numerous cracks. AESO60(PG-MA) was superior to AESO50(PG-MA) and AESO40(PG-MA) in terms of the mechanical properties of the glass fiber-reinforced composites. The flexural strength and flexural modulus of glass fiber-AESO60(PG-MA) were higher than those of glass-fiber-styrene-(PG-MA). The tensile strength and tensile modulus of glass-fiber-AESO60(PG-MA) were comparable to those of glass-fiber-styrene-(PG-MA).

Glass-fiber-AESO40(DCPD-UPE) had comparable flexural strength, flexural modulus, and tensile strength to glass-fiber-styrene-(DCPD-UPE). Kenaf-fiber-AESO40(DCPD-UPE) had comparable flexural strength and flexural modulus to kenaf-fiber-styrene-(DCPD-UPE). Kenaf-fiber-AESO40(DCPD-UPE) had high tensile strength than kenaf-fiber-styrene-(DCPD-UPE). The increase in the AESO content from 40% to 50% did not significantly change the mechanical properties of the resulting fiber-reinforced composites.

The cured MC-(PG-MA) resins were crack-free. Glass-fiber-MC30(PG-MA) had higher flexural modulus than glass-fiber-styrene-(PG-MA). Glass-fiber-MC30(PG-MA) had comparable flexural strength and tensile strength to glass-fiber-styrene-(PG-MA). Kenaf-fiber-MC30(PG-MA) had comparable flexural strength, tensile strength, and tensile modulus to kenaf-fiber-styrene-(PG-MA). The increase in the MC content from 30% to 40% or the replacement of MC with EC in MC30(PG-MA) reduced the mechanical properties of the resulting fiber-reinforced composites.

Kenaf-fiber-MC40(PG-IPA-MA) had higher flexural strength and flexural modulus than kenaf-fiber-styrene(PG-IPA-MA). Kenaf-fiber-MC40(PG-IPA-MA) had comparable tensile strength and tensile modulus to kenaf-fiber-styrene(PG-IPA-MA).

MC20(DCPD-UPE) was superior to styrene-(DCPD-UPE) in terms of the flexural modulus and tensile strength of the glass fiber-reinforced composites. MC20(DCPD-UPE) was comparable to styrene-(DCPD-UPE) in terms of the flexural strength and tensile modulus of the glass fiber-reinforced composites, and in terms of the flexural

and tensile strength and modulus of the kenaf fiber-reinforced composites. The increase in the MC content from 20% to 30% reduced the mechanical properties of the fiber-reinforced composites.

The T_g s of glass-fiber-AESO60(PG-MA), glass-fiber-AESO40(DCPD-UPE), glass-fiber-MC30(PG-MA), and glass-fiber-MC20(DCPD-UPE) were 104.0, 107.2, 136.5, and 100.6 °C, respectively. These T_g s were much higher than normal indoor and outdoor temperatures at which fiber-reinforced UPE composites may be used.

AESO60(PG-IPA-MA) at 70 °C had the viscosity of 3 Pa·s and the pot life of 134 min. AESO60(PG-MA) at 70 °C had the viscosity of 1.7 Pa·s and the pot life of longer than 10 h. AESO50(DCPD-UPE) at 62 °C had the viscosities of 1.7 Pa·s and the pot life of 5.2 h. MC30(PG-MA) at 70 °C had the viscosities of 1 Pa·s and the pot life of longer than 4 h. MC40(PG-IPA-MA) at 62 °C had the viscosities of 1.7 Pa·s and the pot life of longer than 5 h. MC20(DCPD-UPE) at 46 °C had the viscosities of 1.7 Pa·s and the pot life of longer than 9 h. At the temperatures previously described, all styrene-free UPE resins had sufficiently low viscosities and sufficiently long pot lives for their easy applications.

AESO is non-volatile and has negligible toxicity. AESO is hydrophobic and is more compatible with less polar UPEs such as DCPD-UPE. MC is a non-hazardous chemical and is safe for human consumption. MC dissolves all three UPEs very well, leading to the formation of easily pourable styrene-free resins at room temperature.

AESO and MC are both bio-based chemicals, and are more sustainable than the petroleum-based styrene. The AESO-UPE or MC-UPE resins can be safely handled on an open bench without a fume hood. AESO and MC are promising safe alternatives to styrene in UPE resins.