

Effects of Vinyl Isocyanate Coupling Agent on the Tensile Properties of Kraft Fiber-Unsaturated Polyester Composites

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ABSTRACT: A vinyl isocyanate (VI) synthesized from toluene diisocyanate and 2-hydroxyethyl methacrylate was used as a novel coupling agent to obtain strong chemical interfacial adhesion and therefore, improve the tensile properties of Kraft fiber-reinforced unsaturated polyester (UPE) composites. Results characterized by fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), and scanning electron microscope (SEM) indicated that the novel coupling agent VI had a significant effect on the tensile properties of composites due to the formation of chemical bonds between the VI-Kraft interfaces and the VI-UPE interfaces. The tensile properties of composites modified by VI were much better than those of the control composite without VI modification. The VI-modified composites after severe hygrothermal aging exhibited lower losses of tensile properties and desirable tensile durability. The improvement in tensile properties, less interfacial separation after severe hygrothermal aging, lower damping values, and higher glass transition temperature are sufficient to show that the interfacial adhesion between the Kraft fiber and the UPE matrix was significantly improved because the coupling agent VI has both active isocyno groups which react with the Kraft fiber and vinyl groups which are copolymerizable with the UPE resin. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: composites; coupling agent; mechanical properties; polyesters; biofibers

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INTRODUCTION

In the past decade, more and more attention has been paid to using bio-based fillers such as those from wood, bamboo, cotton, hemp, sisal, kenaf, jute, and many others in the form of either fibers or flours. These inexpensive fillers can be used to reinforce polymer matrices, exhibiting properties such as low density and comparable specific strength. These fillers are low- or nonabrasive to equipment, they reduce energy consumption, and they are renewable and biodegradable.^{1–9} The renewability and biodegradability of biofillers is especially attractive with the ever-increasing environmental concerns in terms of both limiting the use of finite resources and the need to manage nondegradable waste disposal, and therefore, they are being exploited as a replacement for conventional fibers such as glass, aramid, and carbon.¹⁰ Compared with other biofillers, wood flour costs less but exhibits acceptable reinforcing properties. Consequently, wood flours are commonly used to reinforce thermoplastic polymer matrices such as polyethylene (PE), polypropylene (PP), and polyvinylchloride (PVC) to produce wood–plastic composites (WPC). WPC have many particular advantages in that they can handle additional processing but require less

maintenance than solid wood and they release no free formaldehyde. WPC materials also offer better rigidity and stiffness than plastics, they are resistant to cracking and splitting, and they can be adapted to a range of manufacturing methods.¹¹ Thus, WPC are being considered as good alternatives to solid wood and are being used not only as material for deck floors, railings, fences, handrails, cladding, and siding and windows but also for furniture and automotive components.^{2,11}

However, the use of WPC has been limited to nonload-bearing applications because of its poor mechanical properties and increased sensitivity to changes in the service environment compared with some structural composites such as glass fiber, aramid fiber, or carbon fiber-reinforced thermosetting polymers.^{12–15} This limited use can be attributed to the poor mechanical properties of wood fiber as reinforcement, the low cohesive strength of the thermoplastic matrix, and the poor wood–plastic interfacial adhesion. Of particular importance for structural applications is the importance of using materials that possess high stiffness and strength. However, wood fiber generally has a tensile strength ranging from 300 to 1000 MPa, which is much lower than that of glass fiber (2000–3500 MPa),

aramid fiber (3000–3150 MPa), and carbon fiber (about 4000 MPa).^{10,16} Also, wood flour rather than wood fiber has been generally used for molding final WPC products because it is challenging to obtain proper blends of wood fiber and the viscous melted thermoplastics. Though wood flour exhibits better dispersion in the extruded compound than wood fiber, wood flour has less reinforcing efficiency compared with wood fibers because of the smaller aspect ratio and interfacial area, resulting in poor mechanical properties of composites that have been reinforced by wood flour than by wood fiber.¹⁷ Beg and Pickering also confirmed that most mechanical properties of wood fiber-reinforced polypropylene composites decreased with decreasing fiber length.¹⁶ Also, for ease in molding, the polymer matrices for WPC are typically a thermoplastic nonpolar polyolefin that exhibits weak van der Waals force and lacks hydrogen bonds and crosslinks between polymer chains. Therefore, these thermoplastic matrices exhibited lower cohesion strength or poorer mechanical properties than thermosetting matrices such as epoxy and phenol–formaldehyde resins that are generally used to preparing modern advanced composites.

Due to the lack of compatibility, the polar hydrophilic wood showed poor interfacial adhesion to nonpolar hydrophobic conventional commercial polymers such as PP, PE, PVC, and unsaturated polyester, which also led to undesirable properties of the final WPC composites such as the decrease of the mechanical properties and creep resistance.^{6,9,14,17–20} However, the interfacial adhesion has a significant effect on many properties of the composites because fiber–matrix adhesion is responsible for efficient load transfer in the composite.²¹ As a result, many studies have focused on this issue and confirmed that the poor interfacial adhesion could be improved using compatibilizers or coupling agents to form bridges of chemical bonds, strong secondary interactions (such as hydrogen bonding), and/or entanglements of polymer chains between the polar wood flour or fiber and the nonpolar polymer matrices.¹⁸ Maleated polypropylene (MAPP) is the most popular coupling agent as it can economically improve the tensile strength, flexural strength, and creep resistance of a composite.^{6,9,14,16–20} However, MAPP has no functional groups that can chemically graft to nonpolar matrix but has anhydride groups that may react with hydroxyl groups of wood to form ester bonds. It was reported that silane-grafted high-density polyethylene (HDPE) as a coupling agent resulted in better mechanical improvement of wood composites than the MAPP, because silane-grafted HDPE has only one active functional group (silane) that can chemically graft to wood more effectively.^{22,23} Therefore, if a coupling agent has two kinds of functional groups, one that can chemically react with the wood and the other that can chemically react with the polymer matrix, it is expected to improve the mechanical properties of the WPC more efficiently due to the strong chemical interfacial adhesions between the wood fiber and the polymer matrix.

When preparing a wood–plastic composite that could be a candidate for load-bearing materials, some measures need to be taken into account, such as (a) substituting wood fibers for wood flour because of much better reinforcing efficiency, (b) using a thermosetting matrix instead of a thermoplastic one for improving cohesive strength, and (c) efficiently improving the wood–matrix interfacial adhesion. Therefore, a new idea was proposed in cur-

rent study to develop a high-strength WPC composite for load-bearing materials by reinforcing thermosetting unsaturated polyester (UPE) resin with higher strength Kraft wood fiber and improving the chemical interfacial adhesion between the wood fiber and the resin using vinyl isocyanate (VI).

EXPERIMENTAL

Materials

The bleached Kraft paper used in this research was a commercial product prepared from pine and fir with a basis weight of 70.2 g/m² from a local paper mill. UPE resin 191# with a solids content of 63.1% and commercial methyl ethyl ketone peroxide (MEKP) as the initiator were supplied by a local FRP mill in Harbin. Toluene 2,4-diisocyanate (TDI, with isocyanate group content or NCO content 48.2 wt %), styrene, and tetrahydrofuran were also reagent-grade and were purchased from Tianjin Kernel Chemical, China. The reagent 2-hydroxyethyl methacrylate (HEMA) stabilized by hydroquinone monomethylether was purchased from Tokyo Chemical Industry, Japan. These chemicals were used as received.

Synthesis and Characterization of VI

According to the synthetic scheme shown in Figure 1, the VI was synthesized by reacting 69.6 g TDI (0.4 mol) with 49.4 g HEMA (0.38 mol) in 51 g styrene as a diluting agent in a 250 mL four-necked flask equipped with a condenser and purged with dry nitrogen. The reaction mixture was stirred at ambient heat for 15 min and then heated gradually to 55°C, and kept at a temperature between 55 and 60°C for about 4.5 h until the NCO content in the mixture reached stability. The reaction mixture was then cooled to below 40°C and transferred to a container and sealed for storage. The resultant mixture had a solids content of 69.9 wt % and a final NCO content of 13.2 wt %. The NCO contents of the sampled reaction mixture and the final product were analyzed by back titration according to ASTM D-2572-97, “Standard test method for isocyanate groups in urethane materials or prepolymers.”

To investigate the chemical structure of the above reaction resultant, a mixture of 6.96 g TDI (0.04 mol), 4.94 g HEMA (0.038 mol), and 5.1 g tetrahydrofuran were added to a 20 mL ampule and sealed. The sealed ampule was then placed in an oven at 63°C and kept there for 5 h. The resultant liquid was then placed between two fourier transform infrared spectroscopy (FTIR) KBr windows and scanned using a Magna IR560 FTIR instrument (Nicolet). The HEMA liquid sample was directly analyzed in the same manner.

In order to confirm that whether vinyl groups of HEMA, VI, and styrene polymerized or not during the synthesis of VI, the mixture of styrene, HEMA, and TDI with the same chemical stoichiometry as that of VI synthesis was placed in a well-sealed FTIR cell for *in situ* FTIR analysis using reflecting absorption mode. The sealed FTIR cell contained reactants was put into a dry oven preheated to 60°C for various times (12, 120, and 270 min) for FTIR scanning.

Composite Preparation

In a 500 mL beaker, 220 g of UPE resin 191#, 1.65 g MEKP, and solutions with varying amounts of VI (0 g, 7.86 g, 15.71 g, 23.57 g, and 31.43 g) were added and then stirred to form clear

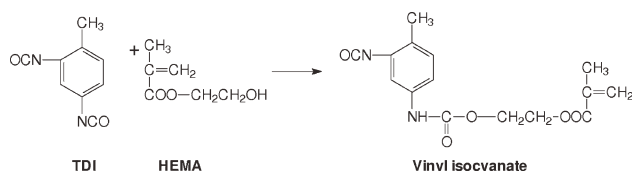


Figure 1. synthetic scheme of VI.

and homogeneous UPE solutions which had VI contents of 0 wt %, 2.5 wt %, 5 wt %, 7.5 wt %, and 10 wt % (on the basis of UPE resin). Varying amounts of styrene (9.42 g, 7.06 g, 4.70 g, 2.35 g, and 0 g) were also added to the corresponding mixtures in order to obtain the same styrene content (65.2 wt %, on the solid basis of UPE resin). A total of 19 Kraft paper sheets 320 mm \times 240 mm were dried in an oven at 103°C for 6 h and then weighed (W_1 , g). The modified UPE solution was spread sufficiently onto the oven-dried Kraft papers by a rubber roller. All 19 resin-spread paper sheets were stacked regularly by hand, stood for 5 min to allow the resin to impregnate the paper, and then cold-pressed at 5 MPa for one minute to form a composite plate and to squeeze the excess resin for recycling. After that, the cold-pressed plate was placed between two Teflon films and hot pressed at 125°C and 15 MPa for 400 s to obtain composite with thickness about 2 mm. Finally, the composites were kept in a 125°C oven for 2 h for postcuring before cutting specimens for characterizations.

Density and Resin Content Determination

After trimming about 20 mm from each outside edge of composite panel, the length (a , mm), width (b , mm), thickness (c , mm), and weight (W_2 , g) of each sample were measured. The composite density (kg/m^3) was calculated using the formula $10^6 \times W_2/(a \times b \times c)$. The resin content (%) of the Kraft fiber-reinforced UPE composite was obtained by dividing the resin mass in the composite ($W_2 - W_3$) by the weight of the trimmed composite (W_2), i.e., $(W_2 - W_3)/W_2 \times 100$, in which the resin mass in the composite was obtained by subtracting the total mass of the 19 Kraft paper sheets with the same area as the composite, $W_3 = 19 \times [W_1/(320 \times 240)] \times a \times b$, from the trimmed composite weight W_2 .

Accelerated Hygrothermal Aging of the Composites

A candidate composite material for structural uses is expected to have a service life of ten years. As a result, it is quite unrealistic to evaluate the environmental responses of materials in real time. Nevertheless, it is of great importance to investigate the mechanical durability of Kraft fiber-reinforced UPE composites in an in-service state. According to some references that evaluate the mechanical durability and water resistance of composites such as Canada Standard CSA 0112.9-04 "Evaluation of adhesive for structural wood products" and Japan Industry Standard JIS K6806-2003 "Water based polymer-isocyanate adhesives for woods," an accelerated hygrothermal aging process composed of five continual cycles of "boiling in water for 4 h then drying at 63°C for 20 h" was proposed and carried out to evaluate the mechanical durability of the obtained composites. During each aging cycle, the dried specimens were put into a stainless wire cage then immersed into boiling water and kept for 4 h; after

that, the boiled specimens were immediately transferred from boiling water into a preheated oven (63°C) and kept at $63 \pm 2^\circ\text{C}$ for 20 h.

Tensile Strength and Modulus

Tensile tests for the composites were conducted according to the ASTM Standard D638 2000 using a Universal Testing Machine (SANS, Shenzhen, China) with a strain rate of 100 mm/min. Type IV tensile specimens were cut from the composites before and after accelerated hygrothermal aging, respectively, by a machining center with following dimensions: $W = 3.18$ mm, $L = 9.53$ mm, and $G = 7.62$ mm, where W is the width of the narrow section, L the length of the narrow section, and G the gage length according to ASTM D638 2000. The thickness of the composites was about 2 mm.

Dynamic Mechanical Analysis

The mechanical damping parameter ($\tan \delta$) as a function of temperature was measured in a Dynamical Mechanical Analyzer (dynamic mechanical analysis (DMA)242, Netzsch, Germany). The measurements were carried out using a three-point bending mode on rectangular samples 50 mm \times 10 mm \times ~ 2 mm over a temperature range of -20°C to 300°C at a heating rate of $5^\circ\text{C}/\text{min}$ under nitrogen flow. The samples were scanned at a fixed frequency of 10 Hz with a static force of 0.1 N, a dynamic force of 2 N and amplitude of 30 μm .

Scanning Electron Microscope (SEM) Analysis

A composite specimen 50 mm \times 10 mm \times ~ 2 mm was immersed in liquid nitrogen and kept there for 5 min for quick freezing (quenching). The quenched specimen was then immediately broke by impact force and the fractured surface was cut-off for scanning electron microscope (SEM) examination. All SEM samples were coated with approximately 10–20 nm of gold before examination with a QUANTA-200 SEM (FEI Co) with a working distance of about 10 mm at 12.5 kV.

RESULTS AND DISCUSSION

Mechanism of Interfacial Adhesion for VI Coupling Agent

Prior to this study, some Kraft fiber-reinforced UPE composites were prepared with various molding pressures and initiator contents to obtain a high-strength composite for load-bearing applications.^{24,25} Due to the better reinforcing efficiency of Kraft fibers than wood flour and the improved cohesive strength of thermosetting UPE as matrix, the optimized Kraft fiber-reinforced UPE composite had much higher tensile strength (83.26–111.97 MPa) than the control wood flour-reinforced polypropylene composites (39.63 MPa).^{24,25} The results showed great potential of Kraft-reinforced UPE composites for the load-bearing applications because the tensile strength was comparable to that of some chopped glass fiber-reinforced unsaturated composites (76.8–117.3 MPa).²⁶ However, when the Kraft-reinforced UPE composites subjected to a hygrothermal aging that contained five continual cycles of "boiling in water for 4 h then drying at 63°C for 20 h," the tensile strengths showed great losses up to 41.4%, showing poor mechanical durability or service safety. The great tensile losses might be attributed to the poor interfacial adhesion between polar Kraft fiber and weakly polar UPE resin.

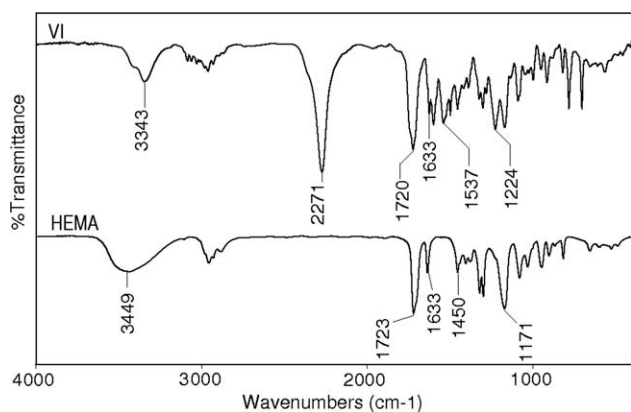


Figure 2. FTIR spectra of HEMA and synthesized VI.

Therefore, a VI was proposed in current study to further improve the mechanical properties and mechanical stabilities of Kraft-reinforced UPE composites via the formations of chemical adhesions between the interfaces of Kraft fiber and UPE resin. Isocyanate is a highly reactive compound that can react with most materials composed of active hydrogen, and therefore, polyisocyanates have been used to prepare polyurethane resin for both bonding and impregnation-modifying wood.^{27,28} Karmar-kar et al. have successfully grafted an isocyanate called m-TMI (m-isopropenyl-*a*, *a*-dimethylbenzylisocyanate) onto polypropylene as a compatibilizer, which resulted in significant improvement in the tensile and flexural strength of wood-PP composites.²⁹ The improvement should be attributed to the formation of a urethane linkage between the coupling agent and the wood via the reaction of the isocyanate groups with the hydroxyl groups of the wood. Unsaturated polyester resins are low-molecular-weight products obtained by copolymerization of both saturated acids/anhydrides (such as phthalic anhydride) with unsaturated acids/anhydrides (such as maleic anhydride) with a diol. Therefore, low molecular weight unsaturated polyesters contain carbon-carbon double bonds that are able to

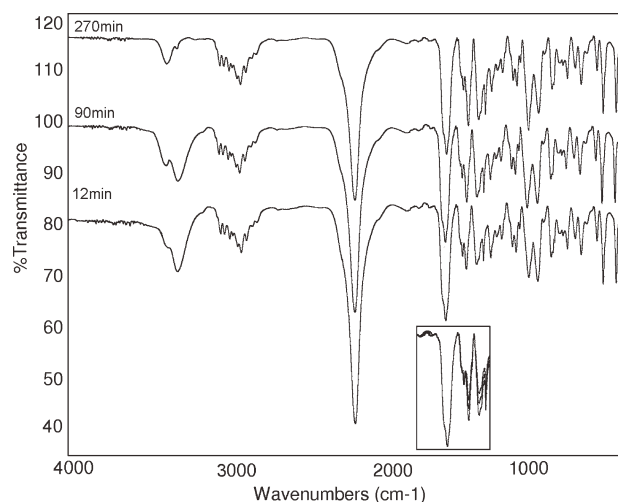


Figure 3. *In situ* FTIR spectra of the mixture of TDI, HEMA, and styrene at 60°C for various times.

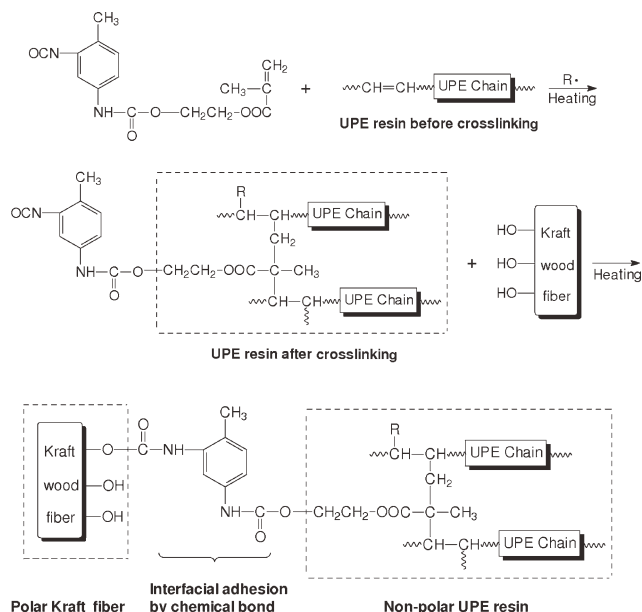


Figure 4. Schemes for the formation of interfacial adhesion by chemical bonds between UPE and Kraft wood fiber.

undergo free-radical crosslinking reactions with styrene and other vinyl monomers.

Based on these facts, a VI was synthesized by incorporating 2-hydroxyethyl methacrylate into toluene 2,4-diisocyanate with the reaction scheme illustrated in Figure 1. The FTIR spectra in Figure 2 confirmed the above synthetic mechanism. The FTIR spectrum of HEMA had the following typical IR identifications: a band at about 3449 cm^{-1} is attributed to the OH stretching mode; the stretching modes of C=O and C=C were detected at 1723 cm^{-1} and 1633 cm^{-1} , respectively; the C—O—C asymmetric stretching modes of the ester group was detected at about 1171 cm^{-1} . After HEMA reacted with TDI that resulted in a urethane linkage, some new bands were detected at 3343, 2271, and 1537 cm^{-1} that were attributed to the NH stretching modes of urethane, the N=C=O stretching modes of free isocyanate group, and the N—H bending deformation modes of urethane (accompanied the C—N asymmetric stretching modes), respectively. The OH stretching mode of HEMA at about 3449 cm^{-1} vanished and was transformed into NH stretching modes of urethane at about 3343 cm^{-1} , indicating the reaction of the OH groups of HEMA with the N=C=O groups of TDI and the formation of a urethane linkage. After the reaction, the vinyl groups of HEMA still existed in the resultant VI, and no polymerization between styrene and the HEMA or VI occurred as evidenced by the consistent shapes and intensities of the bands at about 1633 cm^{-1} in the *in situ* FTIR spectra in Figure 3 that simulated the VI synthesis.

The resultant VI was expected to result in more effective interfacial adhesion when it was used as a coupling agent because it contained active NCO groups and C=C bonds that could form stronger interfacial adhesion via chemical bonds to both the Kraft wood fiber and the UPE resin. As the adhesion mechanisms illustrate in Figure 4, the C=C bond of VI copolymerized

Table I. Tensile Properties of Various Kraft Fiber-Reinforced UPE Composites Before and After Hygrothermal Aging

VI content (%)	Density (kg/m ³)	Resin content (%)	Tensile strength			Tensile modulus		
			Without aging (MPa)	After aging (MPa)	strength loss (%)	Without aging (MPa)	After aging (MPa)	Modulus loss (%)
0 (Control)	1371	34.0	102.7 (4.7)	59.8 (1.3)	41.8	390.3 (49.2)	181.5 (29.4)	53.5
2.5	1463	34.2	159.3 (7.0)	114.8 (4.1)	27.9	583.4 (28.4)	413.9 (29.9)	29.1
5	1465	34.1	167.6 (4.7)	125.4 (5.7)	25.2	559.6 (25.3)	452.9 (16.3)	19.1
7.5	1439	34.4	174.1 (11.0)	130.3 (7.3)	25.2	595.6 (28.8)	444.5 (37.0)	25.4
10	1445	34.3	175.1 (7.3)	133.6 (2.5)	23.7	585.9 (57.2)	436.6 (15.9)	25.5

Note: values in parenthesis are standard derivations.

with the C=C bonds of the UPE resin via a free-radical mechanism and incorporated covalent VI into the crosslinked UPE network. Meanwhile, the NCO groups of the VI reacted with the hydroxyl groups of the wood and were chemically joined to the wood fiber by the formation of a urethane linkage. According to modern adhesion theories, adhesion by chemical bonding is much stronger than adhesion by mechanical interlocking, physical adsorption, or molecular interlocking (chain entanglement).³⁰

Basic Physical and Tensile Properties of Kraft Fiber-Reinforced UPE Composites

The basic physical and tensile properties of Kraft fiber-reinforced UPE composites modified by varying amounts of VI are summarized in Table I. Using the same forming technology, i.e., hot pressing at 125°C and 15 MPa for 400 s, all the composites resulted in very similar resin contents, ranging from 34.0% to 34.4%. In one of our previous studies, it was confirmed that the resin contents of the UPE-based composites were determined by the molding pressure when both prepressing time and molding time were the same because the UPE resin before curing is liquid and thus the excessive liquid resin can be squeezed out by the force of the molding pressure.²⁴ However, the density of the control composite without VI modification was 1371 kg/m³, 5.0–6.8% less than those composites modified by varying amounts of VI. The density increase of the composites after modification by VI should be attributed to the compacter volume of the composites because of quite similar resin contents, indicating that the Kraft fibers were adhered and consolidated more tightly by the cured UPE resin in the presence of active VI as a coupling agent.

Tensile results in Table I indicated that the tensile strength of the composites showed ever-increasing tendency with VI content increased from 0% to 10%. And the VI-modified composites before hygrothermal aging had tensile strengths 55.1–70.5% higher than that of the control composite without VI modification (102.7 MPa). Attributing to the higher content of rigid Kraft fiber with fiber loading about 59.8%, this control composite had much higher tensile strength than some reported biofiber-UPE composites that had tensile strengths ranged from 25 MPa to 65 MPa and fiber loadings ranged from 20% to 40%.^{7,31} The tensile moduli showed a similar tendency as the tensile strength. These results indicate that using the VI as a coupling agent had a significant effect on the mechanical properties of the resultant composites. Tensile results in Table I also

indicated that there is no significant variation in elongation at break, ranged from 11.4% to 13.3%, for composites with various VI coupling agent due to similar contents of Kraft wood fiber. It has been reported by many researchers that elongations at break of wood-polymer composites are predominantly determined by the content of wood fiber because the fiber has lower elongation at break than the polymer matrix.^{29,32,33}

The tensile strengths of VI-modified composites, 159.3–175.1 MPa, were much higher than that of wood flour-reinforced thermoplastic polymer composites (34.5–52.1 MPa),^{20,24,29} which were also comparable to that of some woven glass fiber-reinforced unsaturated polyester composites at maximum load (181.8–233.4 MPa),²⁶ showing good potential of the VI-modified composites for load-bearing applications.

Effects of Hygrothermal Aging on Tensile Properties of Composites

Numerous studies have indicated that hygrothermal aging is inclined to have detrimental effects on fiber-reinforced polymeric composite materials, such as degradation due to moisture-induced swelling and thermal expansion, mechanical and physicochemical changes in the polymeric matrix because of water uptake, and deterioration of the matrix–fiber interface by debonding or microcracking.³⁴ Especially in current case in which the highly hydrophilic Kraft wood fibers with strong water absorption were used as reinforcements and a severe hygrothermal process composed of five cycles of “boiling in water for 4 h then drying at 63°C for 20 h” was applied, the mechanical properties of the aged composites were notably reduced, as shown in Table I. After the hygrothermal aging, the tensile strength of the control composite without VI modification decreased from an initial 102.7 MPa to 59.8 MPa (41.8% strength loss) while the tensile modulus was reduced from 390.3 MPa to 181.5 MPa (53.5% modulus loss). The composites modified by varying amounts of VI after the same hygrothermal aging process showed considerably higher tensile strengths (ranging from 114.8 MPa to 133.6 MPa) and moduli (ranging from 413.9 MPa to 452.9 MPa), lower strength losses (ranging from 23.7% to 27.9%), and lower moduli losses (ranging from 19.1% to 29.1%) than that of the control composite without VI modification. For instance, their tensile strengths were 1.92–2.23 times as much as that of the aged control composite and even 12–30% more than that of control composite without hygrothermal aging.

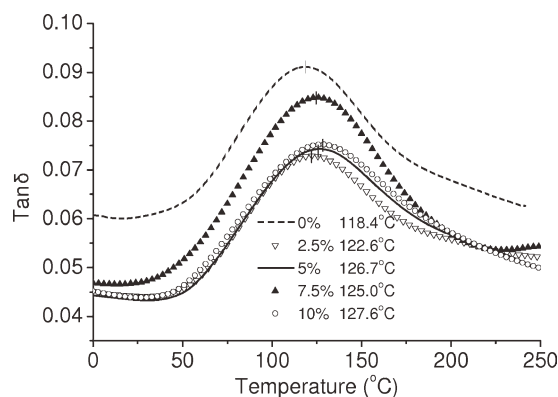


Figure 5. Effect of temperature on the $\tan \delta$ value of the composites with various VI contents (without hygrothermal aging).

All the above results strongly confirmed that the addition of VI as coupling agent could significantly improve the tensile properties and the durability of the Kraft fiber-reinforced UPE composites as a result of the improved interface adhesion between the UPE matrix and the Kraft fiber via the formation of strong chemical bonds (Figure 4). The improvement of interfacial adhesion can be evidenced by the DMA analysis shown in Figure 5. The DMA peak of the $\tan \delta$ - T curve is also called a damping peak that is responding to the glass transition where the movements of polymer chains start to be triggered from an initial frozen state. The glass transition leads to the changes in the polymer from a rigid state to an elastic state. In a fiber-reinforced composite system, the glass transition of the polymer component is affected through the incorporation of rigid fibers with the polymer matrix due to the stress concentrations at the fiber ends in association with the additional viscoelastic energy dissipation in the matrix material and the restricted movements of the polymer chains on the interface with incorporated rigid fibers. In addition, the incorporation of rigid fibers with the polymer matrix will improve the rigidity or reduce the viscosity of interface layer, resulting in lower $\tan \delta$ value that is the ratio of loss modulus (associated with the viscosity) to storage modulus (associated with the rigidity). As a result, the composite with improved interfacial adhesion had a lower $\tan \delta$ value and a higher peak temperature of DMA peak (associated with the glass transition temperature).³⁵ The DMA analyses in Figure 5 shows that the control composite without VI modification had not only the highest $\tan \delta$ (0.091) but also the lowest peak temperature (118.4°C), while all VI-modified composites had lower $\tan \delta$ (ranging from 0.073 to 0.085) but also the higher peak temperature (ranged from 122.6°C to 127.6°C), indicating that the chemical interfacial adhesion resulted from the VI strongly incorporated the rigid Kraft fibers to the UPE resin and restricted the movements of the UPE chains. As a result, the composites modified by the VI showed higher storage moduli than that without VI modification, as shown in Figure 6, due to the formation of interfacial adhesions.^{35,36} And the tendency of storage moduli at lower scanning temperature (<100°C) against VI content was corresponding with that of tensile strength against VI content showed in Table I.

The SEM photographs of the Kraft fiber-reinforced UPE composites before and after hygrothermal aging more apparently

evidenced the improvement of interfacial adhesion between the Kraft fiber and the UPE matrix, as shown in Figure 7. Before hygrothermal aging, all composites including the control composite modified by 0% VI showed good interfacial adhesion without apparent separation between the Kraft fiber-UPE interfaces, as shown by the SEM photographs of Figure 7(A) and Figure 7(C) that represent the composite samples modified by 0% and 2.5% VI, respectively. The good interfacial adhesion of control composite A was attributed to the many polar ester groups in the UPE resin and the high molding pressure that forced liquid UPE resin to compactly contact with Kraft fibers and then fastened the contact by the UPE solidification (cross-linking) during hot-press molding process, resulting in an acceptable compatibility of the UPE with the polar Kraft fiber and a good tensile strength of 102.7 MPa for the control composite. However, the interfacial adhesion of the control composite was not as strong as we expected. After hygrothermal aging, the SEM in Figure 7(B) displayed interfacial separation (marked by the arrows) due to the destruction of the interface during the water boiling cycles of the hygrothermal aging process. When 2.5% VI was added and served as a coupling agent, the resultant composite had very strong interfacial adhesion that could endure five cycles of "boiling in water for 4 h then drying at 63°C for 20 h" without obvious interface separations, as shown by the arrows in Figure 7(D). Further increase of VI content from 5% to 10%, the composites showed quite similar SEM micrographs before and after hygrothermal aging with the composites with 2.5% VI. Therefore, strong interfacial adhesion is the key reason why aged composites modified by VI had much higher tensile strengths than the aged control composite and even higher than the control composite without hygrothermal aging, as shown in Table I.

Effects of VI Content on the Tensile Strength

The tensile strengths of Kraft fiber-reinforced UPE composites without hygrothermal aging consistently increased from 102.7 MPa to 175.1 MPa as the content of VI increased gradually from 0% to 10%. However, it is interesting to note that there was a sharp increase of tensile strength (55.1%) when the VI level increased from 0% to 2.5%, while further increase of the amount of VI from 2.5% to 10% only resulted in a 15.4%

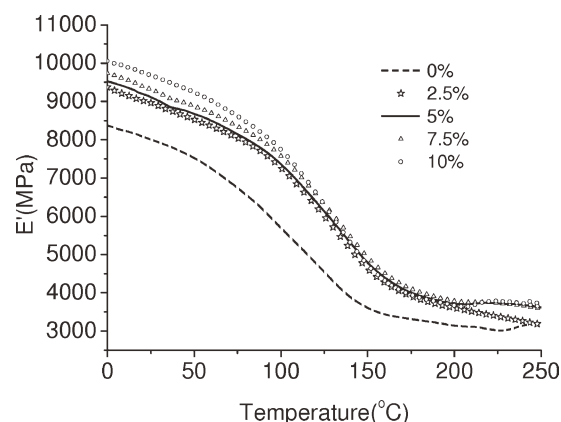


Figure 6. Effect of temperature on the storage modulus of the composites with various VI contents (without hygrothermal aging).

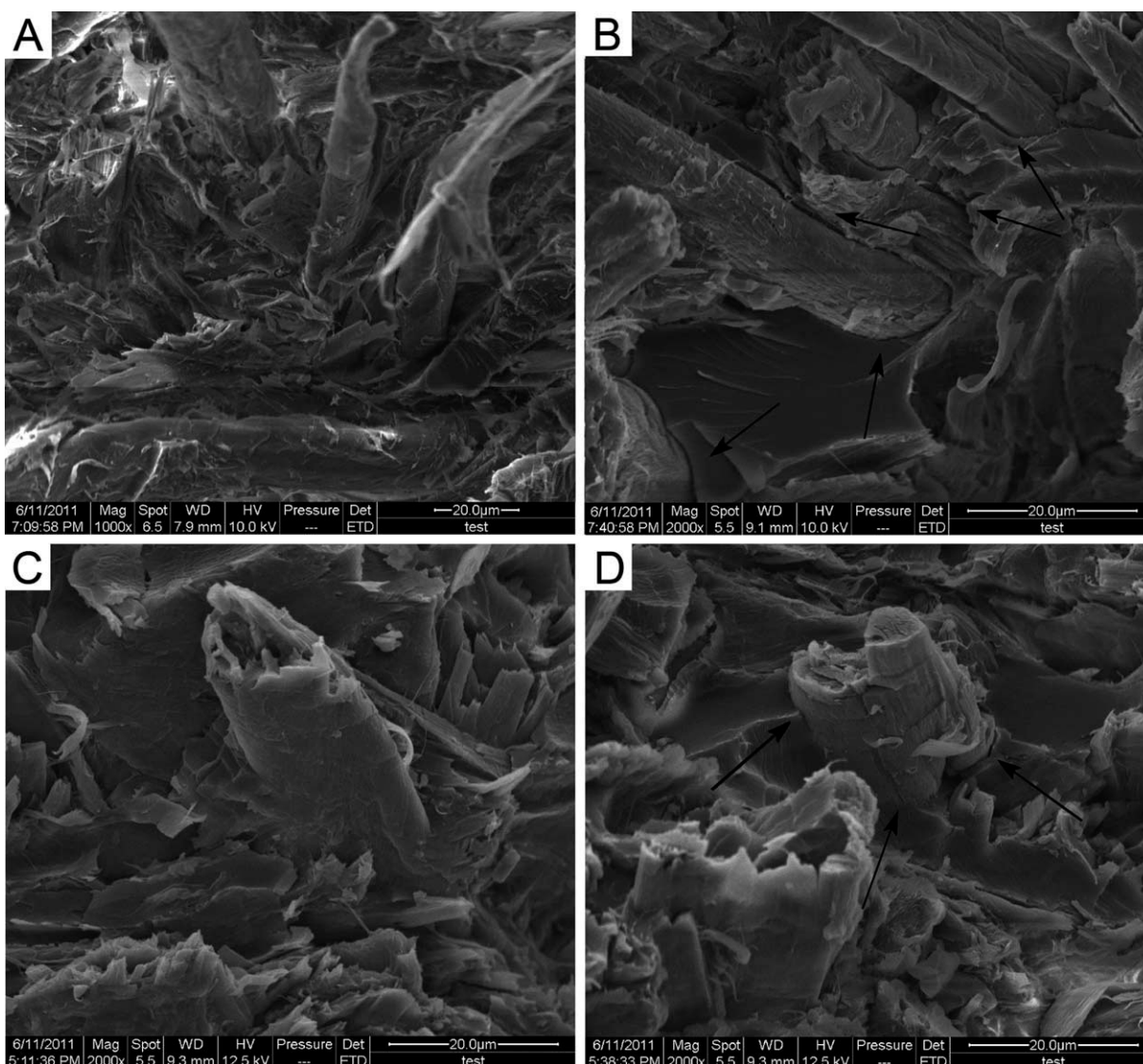


Figure 7. SEM photographs of Kraft fiber-UPE composites with 0% (A and B) and 2.5% (C and D) VI as coupling agent A and B were samples before hygrothermal aging while C and D were after hygrothermal aging.

increase of tensile strength. Meanwhile, the peak temperature of damping curve in Figure 5 also showed similar tendency with that of tensile strength, indicating that the interfacial adhesions resulted from VI were not consistent with VI content introduced. In other words, the addition of 2.5% VI as a coupling agent could result in satisfactory increases in the tensile properties and glass transition temperature of the composite, while a further increase of VI content does not bring about any more significant improvements, a result that may be attributed to a saturation of the coupling efficiency of VI in the Kraft fiber-UPE interfaces. As shown in Figure 4, the formation of a urethane linkage between the Kraft fiber and the VI and a C—C covalent linkage between UPE and VI are indispensable for ideal interfacial adhesion by chemical bonding created by a molecule of VI as the coupling agent. And the improving efficiency of the interfacial adhesion is determined by the chemical bond (the urethane linkage or the C—C covalent linkage) with the smaller quantity, or the efficiency is equivalently determined by the

quantity of available OH groups on the Kraft fiber surface or the available C=C groups on the UPE surface that are capable of reacting with VI to form chemical adhesion between the interfaces. It is uncertain which species of groups decided the coupling efficiency of VI in the Kraft fiber-UPE interfaces. But the tensile test results in Table I confirmed that 2.5% VI on the basis of UPE resin by mass was almost sufficient for a total reaction with one of the active groups on the Kraft fiber-UPE interface with less quantity, reaching a saturated status of coupling efficiency. As a result, the addition of more than a 2.5% VI content would not result in additional improvement of tensile properties.

CONCLUSIONS

The synthesized VI as a novel coupling agent had a significant effect on the tensile properties and durability of the resultant Kraft fiber-reinforced UPE composites because VI is composed

of both an isocyanate group and a vinyl group that react with the Kraft fiber and the UPE resin, respectively, thereby resulting in a strong chemical interfacial adhesion between the Kraft fiber and the UPE matrix. The VI-modified composites had a tensile strength up to 70.5% more than that of the control composite without VI modification, and a tensile modulus up to 52.6% more than that of the control composite. After severe hygrothermal aging, the VI-modified composites had a tensile strength up to 123.4% more and a strength loss up to 66.7% lower than the control composite. DMA analysis showed that the VI-modified composite had a lower $\tan \delta$ value and a higher glass transition temperature. SEM observation confirmed that 2.5% VI added as a coupling agent could result in a very strong chemical interface adhesion between the Kraft fiber and the UPE matrix that could endure five cycles of "boiling in water for 4 h then drying at 63°C for 20 h" without obvious interfacial separation.

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