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Thermosets as compatibilizers at the isotactic polypropylene film and thermomechanical pulp fiber interphase

SANGYEOB LEE [1], TODD F. SHUPE [2,*] and CHUNG Y. HSE [3]

[1] *Department of Forest Products and Center for Advanced Vehicular System (CAVS), Mississippi State University, Mississippi State, MS 39762, USA*
[2] *Louisiana Forest Product Development Centers, School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA*
[3] *Principal Wood Scientist, USDA Forest Service, Southern Research Station, Pineville, LA 71360, USA*

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Abstract—The objective of this study was to improve interfacial adhesion properties at the interface of thermomechanical pulp (TMP) fiber and isotactic polypropylene (iPP) using thermoset adhesives such as phenol formaldehyde (PF) and urea formaldehyde (UF). This study also attempted to achieve fiber-to-fiber adhesion using thermoset adhesives before the molten iPP would flow into the fiber web. The fracture surfaces with thermoset adhesive showed identical differences in terms of fracture modes at the interface. An increased TMP fiber failure was observed with increased thermoset quantity at the interface. Using one percent resin content of weight fraction of TMP fiber handsheet, the tensile strength properties increased almost two fold higher than the strength of control samples. Additional adhesive contents of three and five percent showed gradual strength enhancement. However, the enhanced strength was statistically insignificant. UF resin showed slightly better strength performance over PF resin. This result may be caused by solid contents and additional pigments of resins.

Keywords: Thermomechanical pulp (TMP); thermoset resins; polypropylene (PP); laminates; interfacial properties.

1. INTRODUCTION

Thermosets have a wide range of applications for the bio-based composites with extensive compatibility with hydrophilic substrates. Due to the lack of polar groups in the isotactic polypropylene (iPP), thermoset compatibility to thermoplastics resins generally is very poor and has resulted in few applications in the field of wood

*To whom correspondence should be addressed. E-mail: tshupe@agcenter.lsu.edu

fiber–plastic composites (WPC). Yet the selective addition of thermosets to wood and wood fiber can yield a wide variation in the mechanical and physical properties of WPC regardless of limitations due to the inherent incompatibility at the interface and differences in the thermal histories [1, 2]. Therefore, most investigations have focused on the thermoset application at the wood fiber and thermoplastic interface [3, 4].

Relatively few studies have been made to combine iPP with thermosets such as UF (urea formaldehyde) [1, 5], PF (phenol formaldehyde) [6, 7], epoxy resin [8, 9], polyester [2] and isocyanate [10–13]. The thermosets can be used as compatibilizers to coat the surface of wood fibers and increase interfacial adhesion at the wood fiber and polyolefin interphase, but they may be less effective in enhancing WPC properties [14]. However, the thermosets combined with heat conditioning and ionomer treatment have been shown to enhance interfacial strength properties due to the increased interaction between the two materials [15–19].

The extrusion originally was used to produce WPC in a continuous process from a material inlet to the cooling system [20]. When the thermosets are applied into the process, the process faces various problems due to the cure of the thermosets before the thermoplastic reaches its melting point. However, it is proposed that this problem does virtually not exist when wood fiber handsheets are laminated with iPP film. The thermoset loading can also add strength to the handsheet and improve tensile strength properties of TMP fiber handsheets and isotactic polypropylene (iPP) film laminates (TPL). In this study, investigation focused on the loading effects of thermosets such as UF and PF on the tensile strength properties of TPL as well as factors related to handsheet preparation and evaluation technologies for quantizing the improvements in strength properties for the laminates.

2. MATERIALS AND METHODS

2.1. Materials

Thermomechanical pulp (TMP) fibers of loblolly pine (*Pinus taeda* L.) were processed at 8 bar pressure and contained 8.2% moisture content. Isotactic polypropylene (iPP) films (Co-ex biaxially oriented polypropylene; Plastic Suppliers, Inc., Columbus, OH) was used for TPL. Two thermosets — urea formaldehyde (UF; Dynea Inc., Chembond® YTT-063-02, 60% solid content) and phenol formaldehyde (PF: Dynea 13B410, 100 cps, Sp. Gr.: 1.202, 52% solid content) — were used as compatibilizers.

2.2. Experimental

Laminates with five layers were fabricated for this study as shown in Fig. 1. A total of 27 handsheets was formed in 30.5 cm × 30.5 cm with 10 grams (OD wt.) of TMP fibers and dried at 60°C with 0.34 MPa pressure for 72 hours. Handsheets were cut

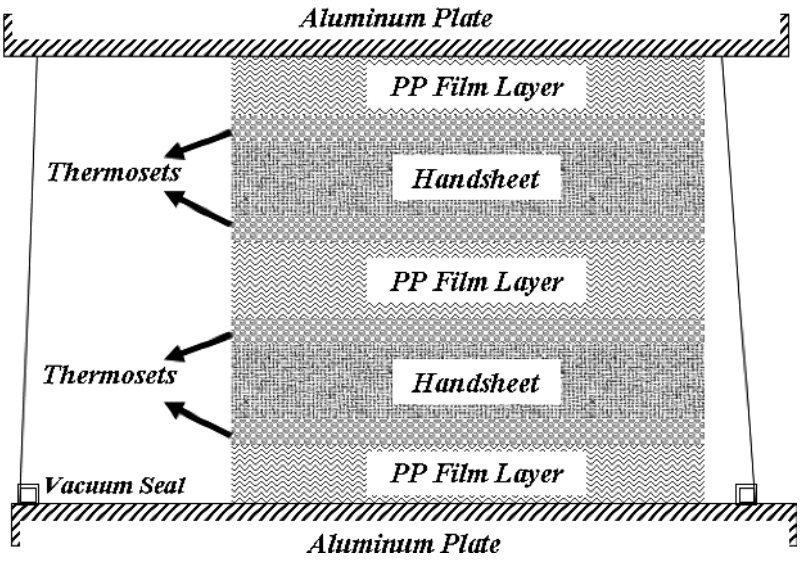

Figure 1. A schematic diagram of fabricating five-layered laminates.

into 12.7 cm × 15.2 cm and stored in a vacuum desiccator. UF and PF were sprayed on the surface of the TMP fiber handsheets at three weight fraction levels of 1%, 3% and 5%. The PF or UF loaded TPL (50/50% weight fraction) were pressed at 0.69 MPa for three min with 177 and 204°C.

Tensile strength properties were tested using an Instron 4465 mechanical testing machine at a crosshead speed of 0.13 cm/min according to ASTM D638-03. Two hundred and sixteen dog-bone tensile samples were cut in a nominal dimension of 12.7 cm × 2.03 cm × 0.03 cm with a neck width of 0.89 cm. At least 21 specimens were tested for each set of samples and the mean values as well as the standard deviations were calculated.

A DSC (Perkin-Elmer DSC 7) system was used to evaluate and confirm thermal characteristics of UF and PF-loaded TPL. The measurement was carried out with nitrogen gas flow environment at 40 sccm flow rate. The mass fraction of iPP from the laminates is w. Sample laminates were stored in vacuum desiccator for 24 h. Round disks (6 mm diameter) were prepared to fit the sample pan and placed in the pan with a lid on top. A heating rate of 5°C/min from −30°C to 200°C and a cooling rate of 5°C/min from 200°C to 50°C for DSC samples were applied for this study. Thermal characteristics of glass transition (T_g), onset (T_{om} and T_{oc}), and peak temperature (T_m and T_c) were determined by exothermic and endothermic curves during the polymer melt and crystallization process based on ASTM E793-01 and E794-01. The T_g was determined by a point of maximum slope. Percentages of crystallinity ($X_C = (\frac{\Delta H_f}{w\Delta H_f^0}) \times 100$) with three levels of UF and PF loaded fiber combinations were used to calculate X_C. The ΔH_f is the heat of fusion from DSC and ΔH_f^0 (=207.14 J/g) is 100% pure crystalline iPP.

Morphological characteristics of the fracture surfaces of UF and PF loaded TPL were observed by using scanning electron microscopy (SEM; Hitachi S-3600N) to confirm the loading effect at the TMP fiber and iPP interface. The fracture sections were obtained from tensile test specimens after failure occurred. Mounted laminates were coated with an approximately 15-nm thin gold layer using an ion sputter apparatus (Technics Hummer V). Images were generated at 15 kV and 1000×.

3. RESULTS AND DISCUSSION

3.1. Tensile strength properties

The effect of the method used for thermoset loading and the two pressing conditions on the tensile strength of PF loaded TPL is shown in Fig. 2. Phenol formaldehyde was loaded on the TMP fiber surface in two ways in the wet and dry fiber conditions. Five percent PF (solid basis) was added to the TMP fiber slurry for the wet loading. For the dry loading, an equal amount of PF was sprayed on the surface of TMP fiber handsheets. In general, the dry condition increased the strength properties regardless of the pressing temperatures of 177°C for PF resin and 204°C for iPP melt flow. PF sprayed on the dry handsheet and pressed at 204°C resulted in the highest tensile strength properties of laminates due to iPP melt flow on the fiber surface. The tensile strength was increased by 63% over the control samples. This result clearly related to the penetration of low-molecular weight fractions of the PF resin into the wood fiber structure as well as to the gross capillary openings in the fiber mat, leaving less PF on the surface than was sprayed on the dried surface [21–23].

The handsheet drying conditions also influenced the strength properties of laminates (Fig. 3). Applying the thermoset on the surface of TMP fiber handsheets, tensile strength properties were increased 92% with UF and 88% with PF for the

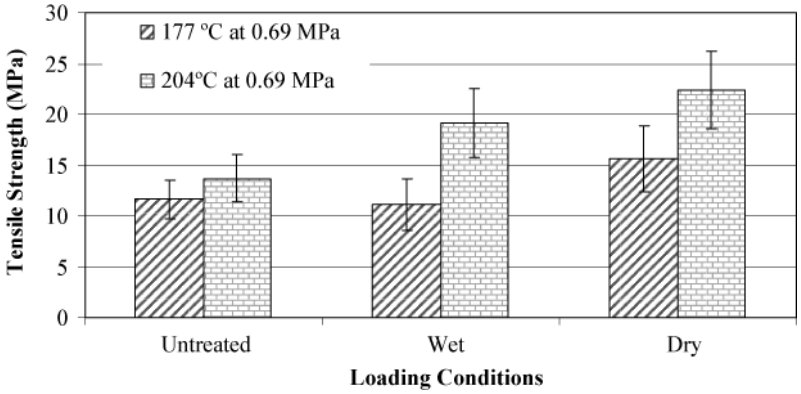

Figure 2. Tensile strength of phenol-formaldehyde resin as a compatibilizer at the thermomechanical pulp fiber and polypropylene interface as a function of phenol-formaldehyde loading conditions and pressing temperatures at 0.69 MPa.

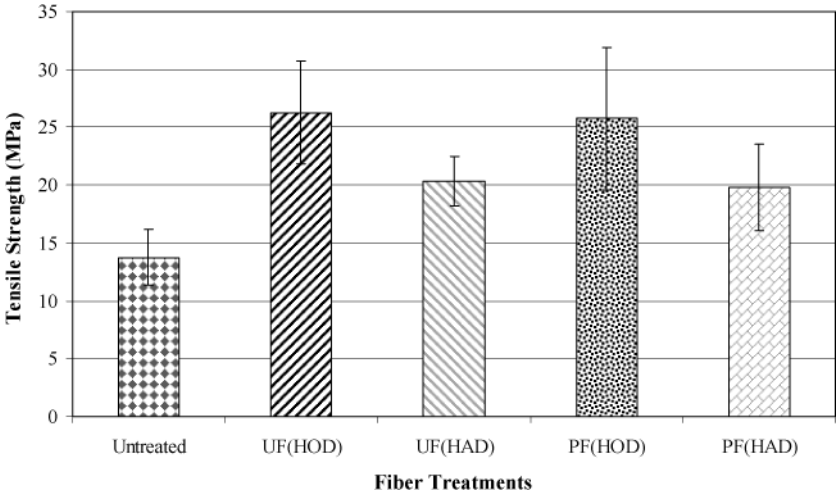

Figure 3. Preconditioning effect of handsheets on the tensile strength of laminates with sprayed 5% thermosets as compatibilizers. UF = Urea-formaldehyde, PF = Phenol-formaldehyde, HOD = Handsheet (oven-dry) and HAD = Handsheet (air-dry).

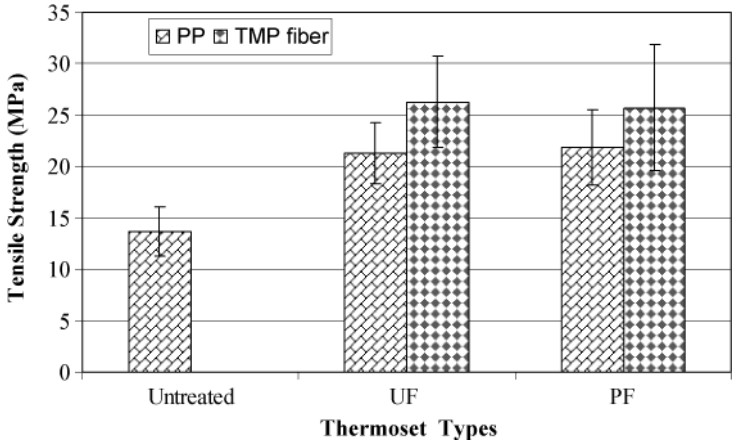

Figure 4. The effect on tensile strength of 5% thermosets when applied on a single side of thermomechanical pulp fiber handsheets or polypropylene film. UF = Urea-formaldehyde and PF = Phenol-formaldehyde.

oven dried conditions over oven-dried untreated samples. In both cases, the result reflects the fact that the OD handsheets (0% moisture content) absorbed more water from the resins than did the air-dried specimens (6.3% moisture content). Thus, moisture content of the handsheet influenced the resin penetration and the tensile strength of TPL, when the UF and PF resin used in this study were promoted to enhance interfacial bonding with iPP film laminates.

Figure 4 shows tensile strength properties of laminates when 5% UF and PF were applied to one side of the TMP fiber handsheets or iPP film as compatibilizers.

The data collected from UF and PF applied on the iPP film were compared with resins applied on the TMP fiber handsheet. Confirming the results shown in Fig. 3, the UF applied on the handsheet surfaces yielded slightly higher mean tensile properties than PF resin and insignificant differences were observed. The strength property enhancement (92% over untreated) significantly differed from that for the PF and UF applied on the iPP film surface; but the tensile strength values between resin types were not statistically significant. However, thermoset applied on the surface of handsheets provided higher mean values than on the PP film. This result indicates that thermosets on the hydrophobic surface nature of TMP fibers provided interconnection among the fibers and resulted in an increase in the property enhancement. Thermoset loading on the handsheet surfaces provided strength enhancement for TLP. Furthermore, the tensile strength properties of UF and PF loaded laminates were significantly different compared with unloaded laminates.

The effect of the levels of application of UF and PF resin to TMP fiber handsheets is shown in Fig. 5. It shows how three levels (1, 3 and 5%) of thermoset adhesives used as compatibilizers at the TMP fiber and iPP interface improved tensile strength properties of the laminates compared with the untreated specimens. The investigation showed that the strength properties of both resin types improved with increased resin content on the surface of the handsheets with the PF resin being more influenced by the treatment level than the UF. Thus, UF generally was more compatible at the TMP fiber and iPP interface, confirming the observation made earlier. It is obvious that both thermosets positively influenced the tensile strength properties of TPL.

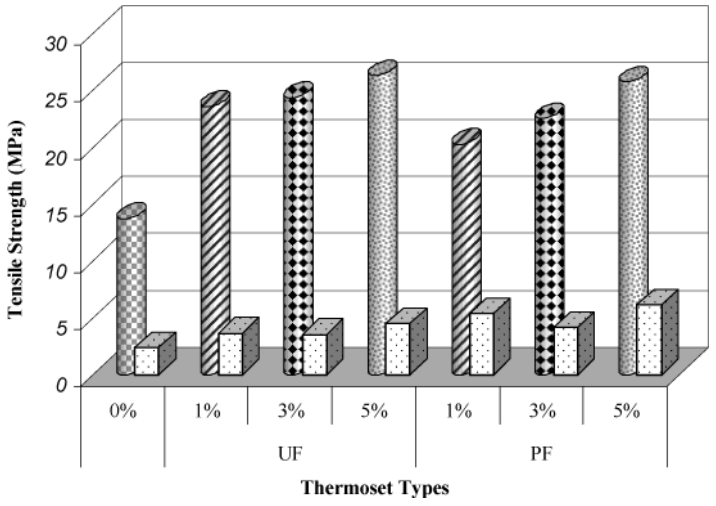

Figure 5. The effect of thermoset levels on tensile strength at the thermomechanical pulp fiber and polypropylene interface. UF = Urea-formaldehyde and PF = Phenol-formaldehyde. (The columns represent one standard deviation.)

3.2. Thermal analysis

The thermodynamic quantities of the resins sprayed on the TMP fiber handsheets laminated with iPP film are summarized in Table 1. Treatment effect at three levels of each thermoset resin on the thermal behavior was pronounced with percentages of iPP crystallinity (X_C). The X_C of both resin types, generally, increased the tensile strength with the exception of 1% PF loading which had a high standard deviation (Fig. 5). This result is conclusively confirmed by the heat flow (ΔH) from both the endothermic and exothermic curves. It shows that higher levels of resin application improved resin penetration into the fiber network. Thus, the reinforced fiber network obtained the inherent tensile properties of the fibers which improved the tensile strength properties of the laminates. The thermodynamic quantities of thermoset loaded laminates showed that onset (T_O), melting (T_m) and crystallization peaks (T_C) from the endothermic and exothermic curves were increased with additional thermoset put into the handsheets compared to pure iPP. However, the glass transition (T_g) was decreased with an increased in resin content. This result indicates that the thermoset may provide interfacial interaction at the TMP fiber surface and iPP matrix interphase and yield increased iPP crystallinity.

3.3. Fracture surface

Figure 6 shows SEM micrographs of the fracture surface of TPL which were loaded with UF and PF. The fracture surface of unloaded laminates showed that TMP fibers were pulled out without surface damage and fiber failure and could not improve significantly in tensile strength of TPL. However, when thermosets were applied on the surfaces, fiber and iPP bonding improved as indicated by the brittle failure of the laminates. The iPP matrix also covered fiber surfaces in both resin micrographs (Fig. 6(b) and 6(c)). This result clearly shows that the thermoset adhesive provided interaction at the fiber surface and iPP interface as well as added handsheet strength.

Table 1.
Thermodynamic quantities of urea-formaldehyde and phenol-formaldehyde sprayed on thermomechanical pulp fiber handsheets laminated with polypropylene film

Resin type	Density	Endothermic curve				Exothermic curve			
	(g/cm^3)	T_g (°C)	T_O (°C)	T_m (°C)	ΔH (J/g)	T_O (°C)	T_C (°C)	ΔH (J/g)	X_C (%)
Control	0.89	−21.5	153	162	62.4	121	117	103	50.0
UF 1%	1.05	−23.8	154	163	61.8	122	118	106	51.2
3%	1.09	−24.4	154	163	63.6	122	118	111	53.7
5%	1.10	−24.4	154	163	64.4	122	118	108	52.1
PF 1%	1.01	−24.4	154	163	58.9	122	118	100	48.1
3%	1.09	−24.5	154	163	60.7	122	118	110	53.1
5%	1.08	−24.6	153	163	71.2	122	118	111	53.8

Note: UF = Urea-formaldehyde, PF = Phenol-formaldehyde.

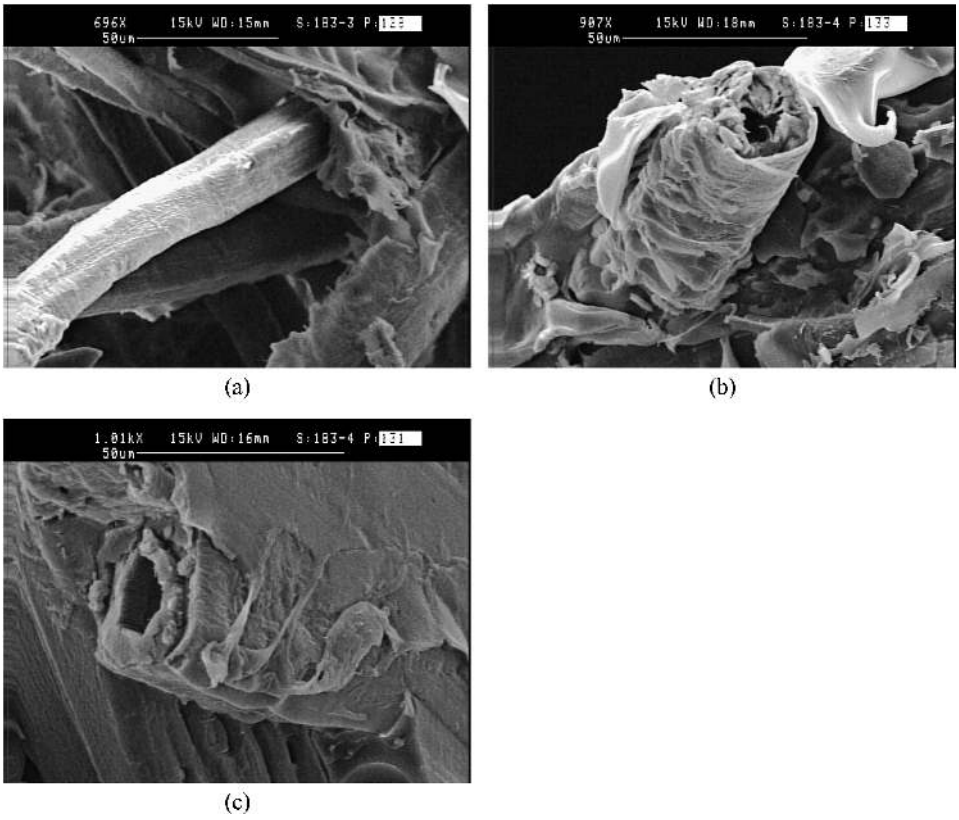

Figure 6. Scanning electron microscopy micrographs of fracture surfaces of phenol-formaldehyde (PF) and urea-formaldehyde (UF) sprayed on wood fiber handsheets and polypropylene laminates; (a) Untreated, (b) PF sprayed and (c) UF sprayed.

Additionally, there were slight differences on the iPP failure between applied resins. The PF loading micrograph (Fig. 6(b)) showed that iPP failure was mixed with brittle and stretching modes while only a brittle mode was represented with UF loaded surfaces (Fig. 6(c)).

4. CONCLUSIONS

This study investigated thermoset adhesives as interfacial compatibilizers to improve interfacial adhesion properties at the interface of thermomechanical pulp (TMP) fiber and isotactic polypropylene (iPP). Thermoset adhesives such as phenol formaldehyde (PF) and urea formaldehyde (UF) provided statistically significant improvement in tensile strength properties and played an important role at the interface. This result was also demonstrated on the thermal characteristics and SEM micrographs. It should be noticed that preconditioning of the TMP handsheets and

pressing temperature of 204°C led to optimization of the tensile strength properties of TMP fiber handsheet and iPP film laminates.

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