

Maleated Polypropylene Film and Wood Fiber Handsheet Laminates

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The grafting effect of maleic anhydride (MA) as an interfacial bonding agent and its influence on the tensile strength properties of thermomechanical pulp handsheet-isotactic polypropylene (iPP) film laminates was studied. For the MA treated with benzoyl peroxide (BPO) as an initiator, tensile strength properties increased 76% with PP film over untreated laminates. The optimal strength properties were obtained with a MA and BPO ratio of 2:1. A strong correlation was observed between the number of fibers in the web and tensile strength properties for both handsheet drying conditions. The R^2 values were 0.95 for air-dry conditions and 0.94 from oven-dry conditions. Scanning electron microscopy images also showed the effectiveness of MA loading on the surface of thermomechanical pulp fibers due to increased fiber failure, which occurred without fiber being pulled out from the PP matrixes. Crystallinity and heat flow were determined using differential scanning calorimetry (DSC) and increased as expected as the ratio of MA and BPO increased from 0:0 to 2:1. These results were also in accordance with the morphological observations at the fracture surface, Fourier transform infrared spectra, and thermal analysis. POLYM. COMPOS., 00:000–000, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

Anhydride-based compatibilizers at the hydrophilic wood fiber and hydrophobic polypropylene (PP) interface are of growing interest to increase interfacial adhesion. Anhydride compounds can react with wood fibers to form ester linkages with the hydroxyl groups of the wood fiber and, thus, providing the fiber surfaces a certain degree of

hydrophobicity, depending on the composition of the anhydrides [1–3]. Among anhydride coupling agents, maleic anhydride (MA) as a copolymer has improved the mechanical properties of wood fiber-thermoplastic composites (WPC) [4–7]. Considerable research has been directed toward promoting interfacial interactions between polymer matrixes and wood fiber surfaces [8–11]. However, the treatment effects on the interfacial strength properties of WPC varied with the different fiber sources and polymer types.

The use of MA to graft the surface of wood fiber and polyolefins was explored as a technique to improve the physicochemical properties of thermoplastics (PP, polyethylene: PE, polystyrene: PS, and polyvinylchloride: PVC) [12, 13]. The grafting of MA on plastics can be carried out under a variety of conditions. The most frequently used technique for WPC is free radical initiation reactions [14]. When the MA reacts with the thermoplastic polymers, the C=C bond may break and new C—C bond or bonds are formed between the MA residue and the backbone of the plastics.

The concentration of MA and the initiators type and amount have a great influence on the efficiency of MA-polymer treatment of PP and fibers. Initiators, such as benzoyl peroxide (BPO) [15–17], dicumyl peroxide (DCP) [18], and *tert*-butyl peroxy benzoate [19], have been used as an initiator for MA grafting on the polymer backbone. The DCP was more effective than BPO to treat wood fibers with MA-polymer (PS or HDPE) [4]. The properties improved along with the rise in concentration of MA and initiators up to 3% MA and 0.5% initiators, and then decreased at higher concentrations [4, 20]. The extent of improvement also depended on the type of polymer matrixes.

The mechanical properties of these plastics generally decrease after MA grafting [18, 19] due to the chain

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scission during the maleation process that results in decreased average molecular weight [21], the presence of nonreacting MA [15], and the decrease in crystallization degree in the case of crystallizable polymers. However, the mechanical properties of composites with the modified plastics were enhanced as the matrix or part of the matrix, owing to the improvement of interfacial adhesion [22, 23]. Tensile strength of WPC was improved 20–30% over the untreated PP-based composites [21]. However, tensile modulus decreased 20–30%. Further increase in mechanical properties of WPC was also obtained using MA modified PP [19].

The MA grafted on the backbone of synthetic polymers such as PE and PP has been proven to form either covalent ester or hydrogen bonds when reacting with hydroxyl groups at the cellulose surface. The presence of anhydride groups was confirmed by IR spectrum. The formation of ester bonds between cellulose backbone and MA grafted polyolefins has been confirmed by fourier-transform infrared spectroscopy with the appearance or increase in the intensity of the absorption bands near 1720 cm^{-1} , which is characteristic of ester bonds [24–27]. Incompatibility between the wood fiber surface and PP interface resulted in lower interfacial strength. Interfacial failure occurred as the PP matrix began to draw, which produced voids and cracks [28–32].

In light of the aforementioned research, this study was conducted to elucidate the interfacial interaction between maleated isotactic polypropylene (iPP) film and wood fiber handsheet laminates. Using thermomechanical pulp (TMP) fibers, the effect of MA concentrations and grafted levels of MA and BPO on PP film was studied on fracture characteristics, thermal behavior, and mechanical properties of TMP fiber handsheet and iPP film laminates (TPL). Quantitative techniques were developed for measuring the effect of interfacial bonding by microscopic examination of tensile tests of the laminates.

MATERIALS AND METHODS

Materials

TMP fibers used were loblolly pine (*Pinus taeda* L.) chips which were converted into coarse TMP at the Bio Composites center, University of Wales, Bangor, Wales, UK, at a steam pressure of 8 bars. The moisture content for the fibers used for this study was 8.2%. MA (Huntman Chemical Co., Chesterfield, MO, USA) used as a modifying agent had a purity of >99% and a melting point of 52°C . BPO (Benox[®] A-80, NORAC, Azusa, CA, USA), as an initiate for MA reaction on the PP film surface, contained 20% water and 5.1% active oxygen. Toluene (Fisher Scientific, Pittsburgh, PA, USA) was used as a reagent. Sheets of iPP film (Plastic Suppliers, Columbus, OH, USA) were used to make TPL.

Polypropylene Film Modification and Laminate Fabrication

The iPP film modification with MA was accomplished by a soaking method involving the $177.8\text{ mm} \times 304.8\text{ mm}$ film sheets in a MA/BPO solution diluted in toluene. Treatment solutions were formulated based on the weight fraction of MA/BPO in toluene. Toluene (1L) was heated to 100°C and 12.5, 25, and 50 g of MA and 12.5 g BPO were used for the dilution ratios. PP films were soaked in 2L of solution for 5 min. The treated iPP films were removed from the solution and dried at ambient room conditions.

A total of 22 handsheets measuring $304.8\text{ mm} \times 304.8\text{ mm}$ were made with 10 g (OD wt) of TMP fibers and press-dried at 60°C and 0.34 MPa. Handsheets were cut into $152.4\text{ mm} \times 177.8\text{ mm}$ of 34 sheets and stored in a vacuum dessicator. Thus, two experiment designs of 2 (dry conditions) \times 3 (film locations) \times 4 (replications) to characterize the effect of fibers in the web and 3 (MA treatment conditions) \times 3 (replications) for the ratio effect were used. The TPL (50/50% weight fraction of TMP/PP) were pressed between hot plates at 0.69 MPa pressures for 3 min and 400°F to reach the flow point of the PP film. Tensile strengths of laminates were measured in each fabrication type of PP film on both sides, the top side, and the bottom side (see Fig. 1). Thus, the location effect of PP films for the polymer laminates were evaluated to address optimum PP melt flow into the TMP fiber handsheet.

Tensile Strength Properties and Image Analysis

Two hundred sixteen dog-bone tensile samples were cut with nominal dimensions of $127\text{ mm} \times 20.3\text{ mm} \times 0.3\text{ mm}$ with a neck width of 8.9 mm. Tensile properties were tested using an Instron 4465 mechanical testing machine at a crosshead speed of $1.3\text{ mm} \cdot \text{min}^{-1}$ according to ASTM D638-03. At least seven specimens were tested for each TPL and the means and the standard deviations were calculated. Failure sections of the dog-bone samples were viewed using light microscopy to generate failure section images using a Spot RT camera. The images were further processed using Image Pro Plus software (V 4.5) with a simple intensity range to count the number of TMP fibers at the fracture surface of the tensile test samples. In short, the data collection process included (1) generating original fracture images, (2) transforming images using “Edge Finder Function” to make the edges clear, and (3) collecting the number of fibers of exposed fibers (see Fig. 2).

Analysis for Grafting Effects

A confirmation of MA interaction between the TMP fiber and MA grafted PP matrix was determined by use of

 : *Metal Plate*
  : *Handsheet*
  : *PP Film Layer*

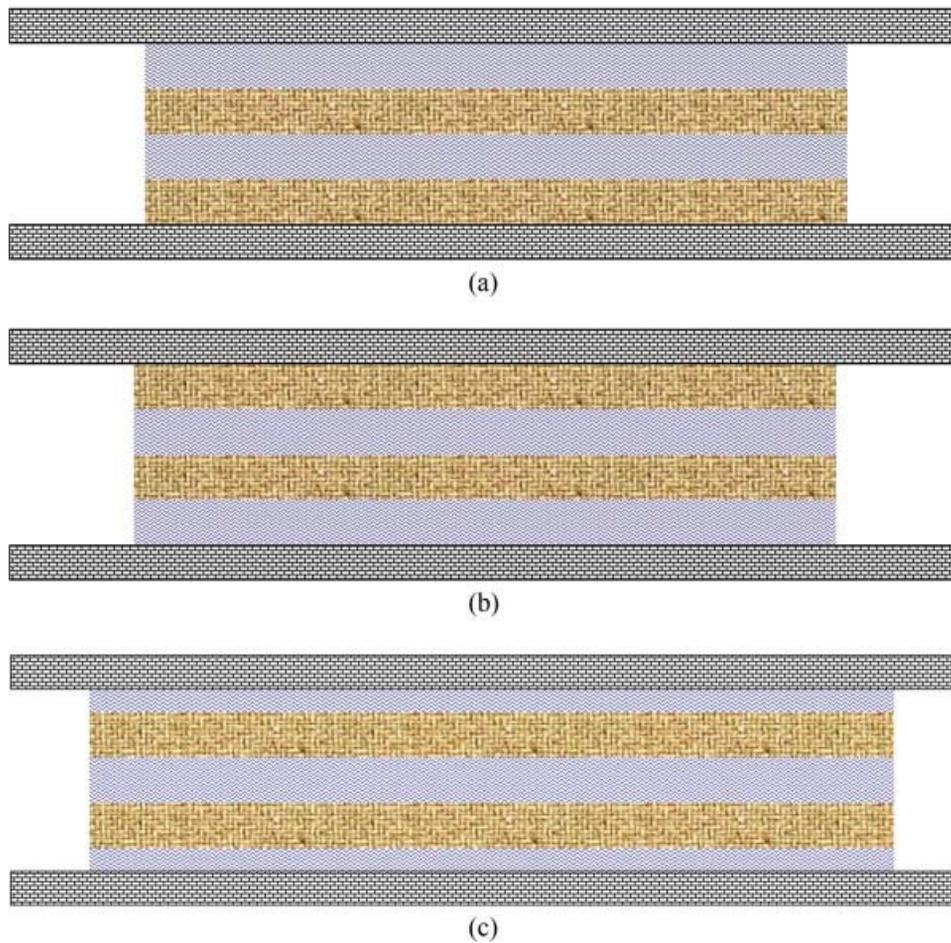


FIG. 1. Laminate fabrication with polypropylene film sheets to optimize matrix flow into TMP fiber hand-sheets. PP film sheets were laminated on the top side (a), the bottom side (b), and both sides (c) of the hand-sheets. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the FT-IR (NEXUSTM 670 FT-IR E.S.P.; Thermo Nicolet). The FT-IR is equipped with “Smart Golden Gate” and mid-range (4000–650 cm^{-1}) capabilities. The data acquisition software was OMNIC 5.2. Treated PP films were scanned at the mid-IR range to study the multi-functional monomer retention on the surface of iPP films. Most of the grafted MA on the films showed a cyclic form with a peak from 1690 to 1760 cm^{-1} , which should be assigned to the carboxylic acid of cyclic anhydride with broad band width. The BPO peak was expected to appear from 675 to 760 cm^{-1} .

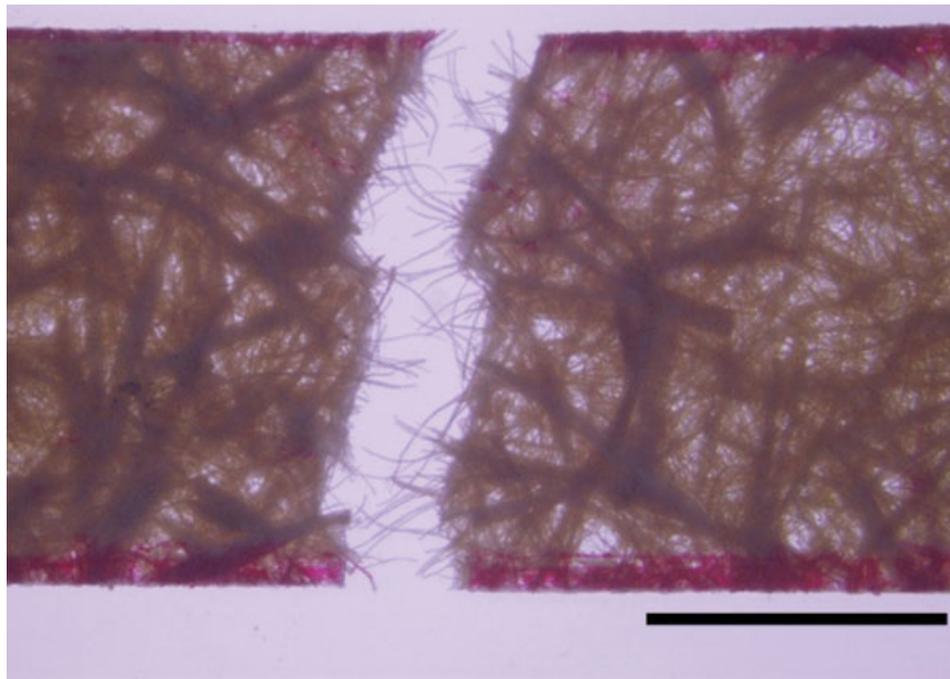
Thermal characteristics of the surface-polymer interphase were evaluated using a differential scanning calorimetry (DSC; Perkin-Elmer DSC 7) system to confirm iPP melt flow and crystallization parameters in the presence of different levels of MA treatment. Thermal characteristics of T_o and T_c were determined by exothermic curves during the polymer crystallization process from the

melt, based on ASTM E793-01 and E794-01. A heating rate of 5°C min^{-1} from -30°C to 200°C and a cooling rate of 5°C min^{-1} from 200°C to 50°C for DSC samples were used for this study. The X_c with levels of MA treatment on iPP surface and TMP fiber combinations was also calculated with the following equation.

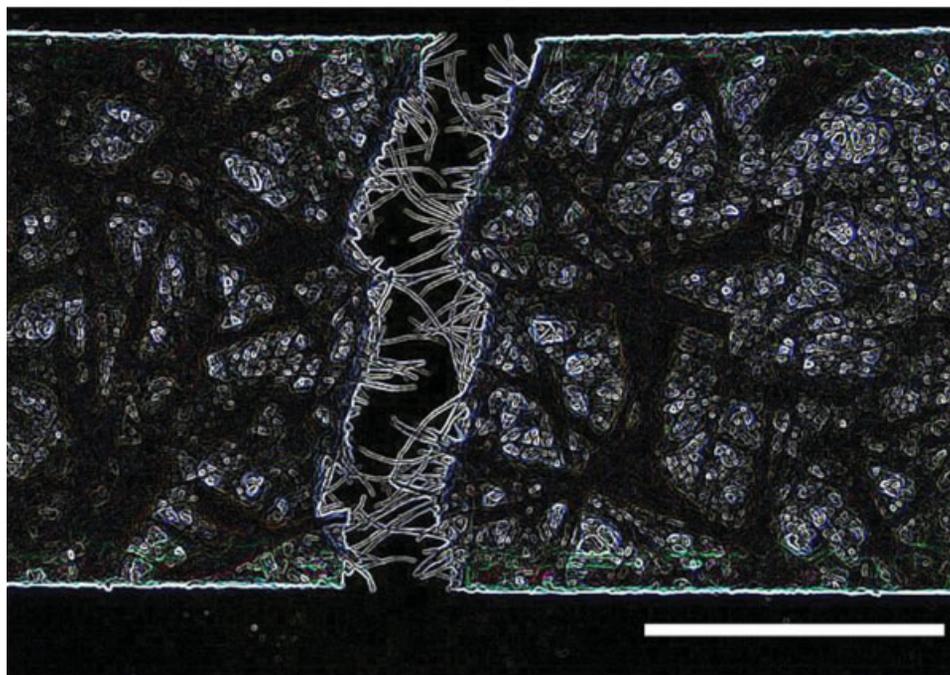
$$X_c = \left(\frac{\Delta H_f}{w \Delta H_f^0} \right) \times 100 \quad (1)$$

where X_c = % of crystallinity; ΔH_f = heat of fusion from DSC; ΔH_f^0 = 100% crystalline PP; w = mass fraction of PP.

Morphological observations on the fracture surfaces of the tensile test specimen were sputtered coated with gold and observed using a scanning electron microscope (Hitachi S-3600N) at 15 kV and 1000 \times . The fracture



(a)



(b)

FIG. 2. Photomicrographs of failure sections from the tensile strength test (a) Stage I- Original fracture image, and (b) Stage II- Image transformation. (Scale bar on each image represents 5 mm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surfaces of the TMP fiber handsheets and MA grafted PP film laminates were studied to confirm the MA treatment effect at the TMP fiber and MA grafted iPP interface. Mounted fracture sections were coated with an approximately 15-nm thin gold layer using an ion sputter (Technics Hummer V) apparatus.

RESULTS AND REMARKS

Number of Fibers at Fracture Surface

Figure 3 shows tensile strength of TPL as a function of the number of fibers exposed at the fracture surface of

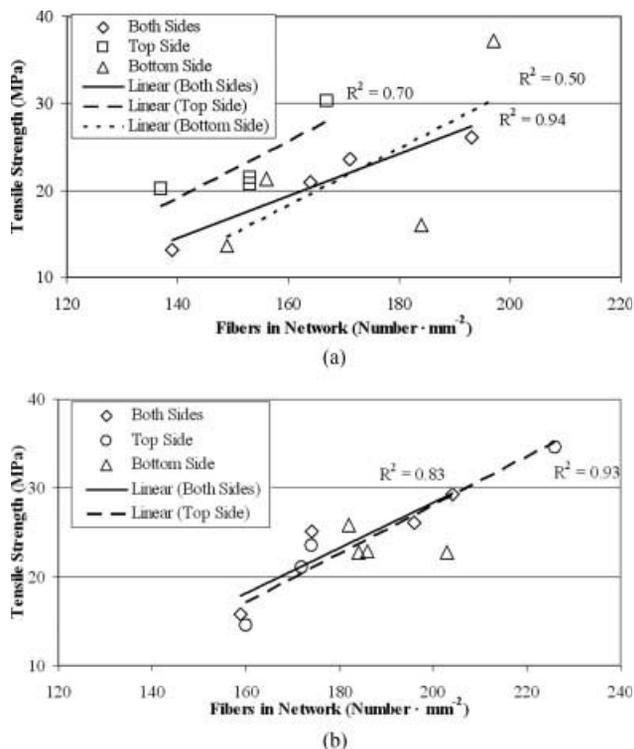


FIG. 3. Tensile strength of laminates as a function of the number of fibers shown at the tension break with two handsheet press drying conditions of (a) air-dry at 22°C, and (b) oven-dry at 60°C. (Each data point represents the average of seven tensile specimens).

the tensile test specimens for each experimental condition of iPP film loading and handsheet drying. The iPP film loading conditions were 100% on the top (Fig. 1a), bottom (Fig. 1b), and 50% both sides (Fig. 1c) of the TMP fiber handsheets by weight. The two handsheet drying conditions were air dried at 22°C and oven dried at 60°C with 0.34 MPa press loading. The laminates were fabricated using treated PP film sheets with a MA and BPO ratio of 2:1. The PP film sheets loaded on both sides provided a uniform and greater volume of PP melt flow into the TMP handsheets compared to the other two pressing conditions. The uniform melt flow resulted in higher correlation between the number of fibers in the web and tensile strength. This result was observed for both handsheet drying conditions. The R^2 values for loading on both sides were 0.95 for air-dry and 0.94 from oven-dry. This result shows that the greater volume of melt flow characteristics of the thermoplastic matrix resulted in a better fiber reinforced composite material than the other two hot pressing conditions. Further, it shows the effect of gravity (iPP film on the top side) improves the melt flow of iPP. Additionally, the results show that the technique of counting the numbers of TMP fibers at the tension failure provides a sensitive measure of wood fiber-PP interfacial bonding.

Effects of the MA and BPO Ratios

MA and BPO ratios on tensile strength properties of TMP fiber handsheet and MA treated iPP film laminates

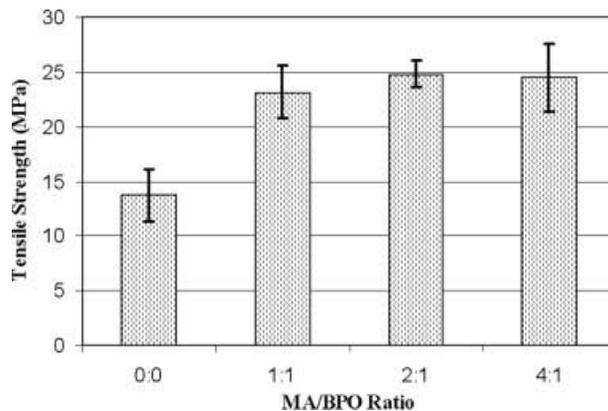


FIG. 4. Tensile strength properties of maleic anhydride grafted polypropylene film laminated with thermomechanical pulp fiber handsheets. (The error bars represent one standard deviation).

are shown in Fig. 4. It is obvious that MA is generally an effective modifier in increasing the tensile strength regardless of the levels of MA and BPO ratios used. The highest mean tensile strengths were obtained from the iPP film treated at the 2:1 ratio, which was 76% greater than the untreated laminates. It is well known that addition of MA to wood fiber and PP composites increases the tensile properties of composites [9, 33–35]. Although all of the MA grafted laminates were significantly better than test samples without MA treatment, there was no statistically significant difference among the tensile strength of the MA loaded samples. The fracture surface of TPL in tension failure proved that counting the number of fibers at the tension break is a better method of measuring the effect of MA grafting at the TMP fiber and PP interface.

Fourier-Transform Infrared Spectroscopy

Absorbance of FTIR spectra from the MA modified PP film with BPO as a catalyst is shown in Fig. 5. In general, anhydride grafted PP had slightly shifted wave number at 1788 cm^{-1} and the lower wave number is the

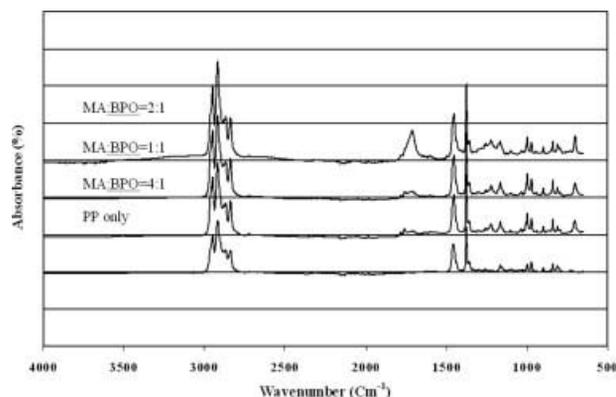
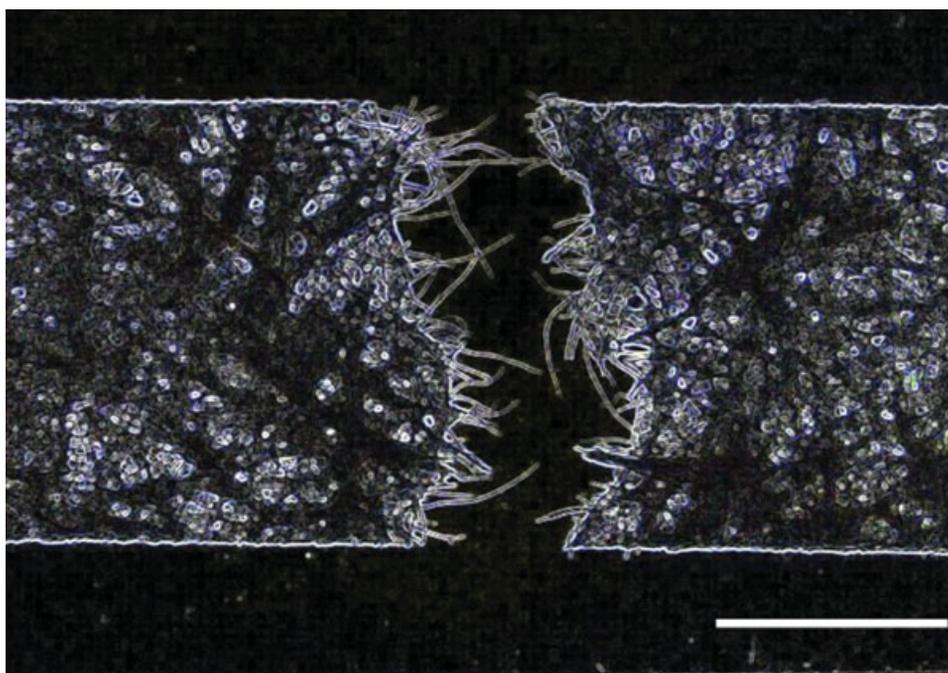


FIG. 5. Absorbance of Fourier-transform infrared spectroscopy spectra from maleic anhydride modified polypropylene film with benzoyl peroxide as a catalyst. (MA = maleic anhydride, BPO = benzoyl peroxide).

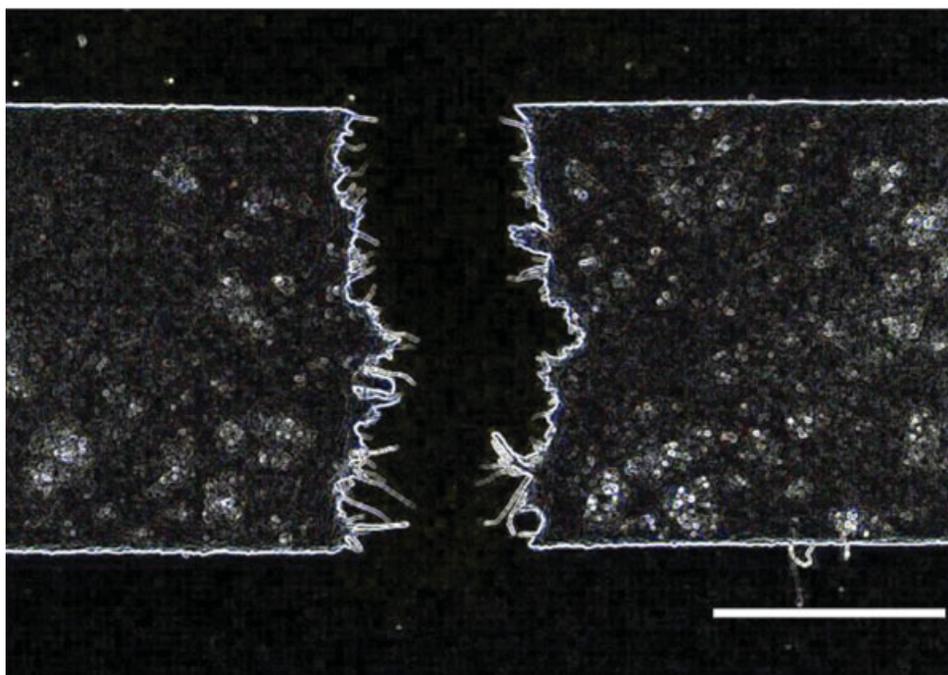
TABLE 1. Thermodynamic quantities of maleic anhydride treated polypropylene films laminated with wood fiber handsheets.

MA/BPO ratio	Density (g cm^{-3})	Endothermic curve				Exothermic curve			
		T_g ($^{\circ}\text{C}$)	T_O ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH (J g^{-1})	T_O ($^{\circ}\text{C}$)	T_C ($^{\circ}\text{C}$)	ΔH (J g^{-1})	X_C (%)
0:0	0.89	-21.5	153	162	62.4	121	117	103.5	50.0
1:1	0.88	-22.1	150	157	48.6	130	122	91.7	44.3
2:1	0.76	-22.5	150	157	64.4	123	118	106.1	51.2
4:1	0.79	-22.3	152	160	57.4	126	120	93.1	44.9

Note: MA = maleic anhydride, BPO = benzoyl peroxide.



(a)



(b)

FIG. 6. Fracture surface from tensile strength test of thermomechanical pulp fiber handsheet and maleic anhydride treated polypropylene film laminates. (a) untreated, and (b) MA:BPO = 2:1. (Scale bar on each image represents 5 mm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

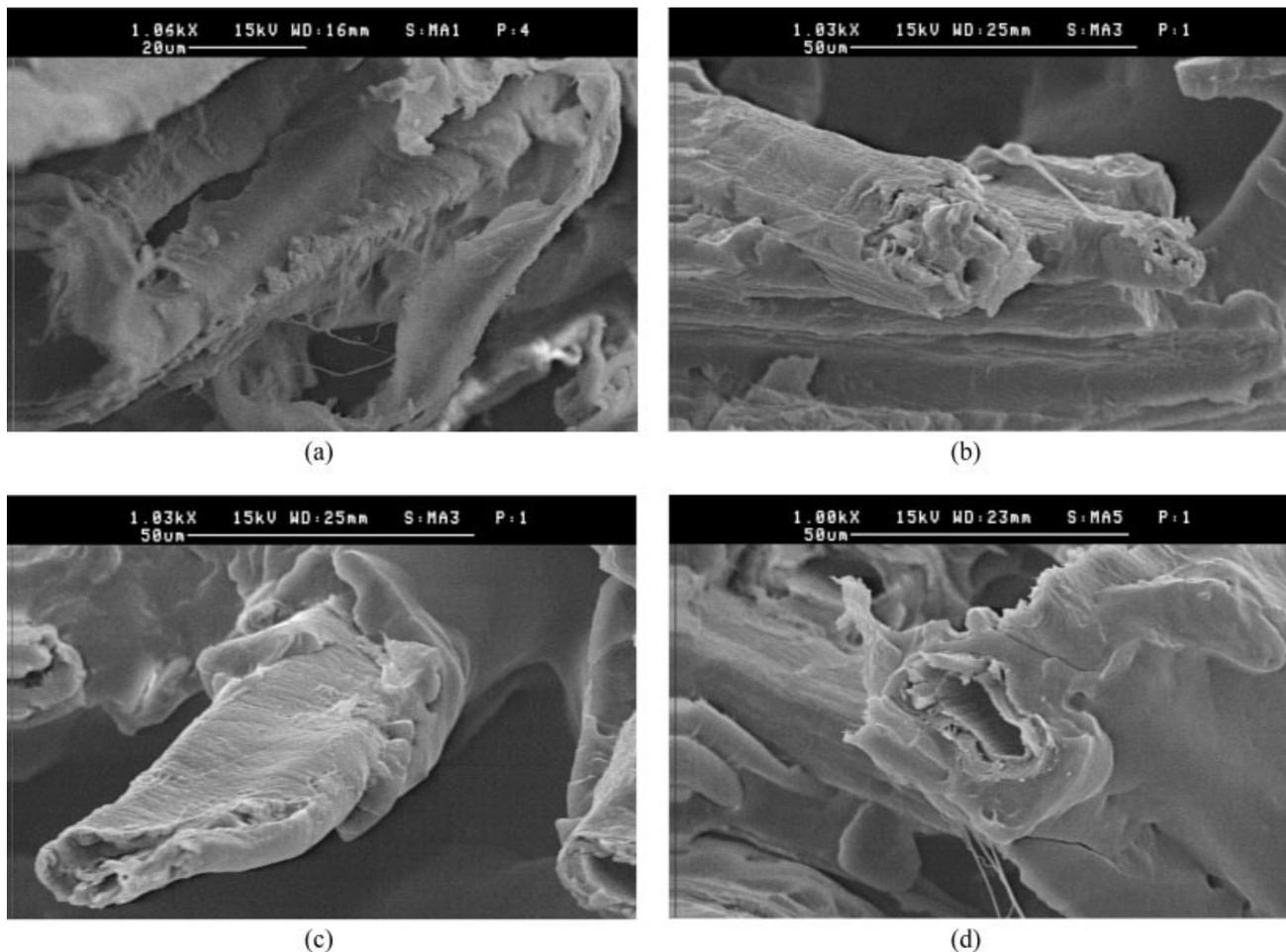


FIG. 7. Scanning electron microscopy micrographs of fracture surfaces of wood fiber handsheet and polypropylene laminates; polypropylene film grafted with maleic anhydride. (a) untreated, (b) MA:BPO = 1:1, (c) MA:BPO = 2:1, and (d) MA:BPO = 4:1.

hydrolyzed form at 1714 cm^{-1} . The hydrolyzed form generally reduces the adhesive benefit and renders it unable to produce a covalent ester bond between the matrixes. In the cases of the MA grafted iPP, absorption bands at 1780 , 1760 , 1720 , and 706 cm^{-1} were observed, which can be assigned to the absorption of the carboxylic acid ($\text{C}=\text{O}$) of anhydride in a cyclic form [24–26]. The absorptions from 2850 to 2970 cm^{-1} and from 1350 to 1480 cm^{-1} represent the characteristic absorption of the PP skeleton. The absorption band at 706 cm^{-1} also indicates evidence of BPO on the PP film. Therefore, the absorption bands at 1760 , 1720 , and 706 cm^{-1} were assigned MA loading on the wood fiber and PP film. When using MA, BPO, and toluene to treat iPP film, the MA and BPO ratios of two-to-one appeared to be an optimum ratio with an evidence of a strong, sharp, and well-defined absorption band near 1720 cm^{-1} from the digital subtraction spectra of the treated and untreated PP films. The number of anhydride groups reacted with iPP may differ greatly due to the difference in chemical ratios.

Thermal Analysis

Table 1 shows the treatment effect of four levels of MA and BPO on the thermal behavior of MA-treated PP film surfaces. The thermodynamic behaviors of TMP fiber handsheet and MA-treated PP film laminates on glass transition (T_g), onset (T_O), heat flow (ΔH), melting and crystallization peaks (T_m , T_C), and crystallinity (X_C) from the endothermic and exothermic curve are presented. The thermal quantities of T_g , T_O , and T_m from the endothermic curve generally decreased with increased MA and BPO ratios. The ratio 4:1 showed an initial increase although the thermal quantity was lower than untreated PP films. In contrast, the quantities of T_O and T_m decreased in the endothermic curve but increased in the exothermic curve. This result indicates that introducing MA into the PP matrix may alter the PP nucleation ability and lead to a decrease in the thermal quantities. The ΔH and X_C of the treated PP films also decreased with MA treatment ratios of 1:1 and 4:1. The table shows that the ratio 2:1 may be the optimum treatment condition used in this experiment, but no definite conclusions can be drawn.

Fracture Surface

Fracture mode differences from tensile samples of TMP fiber handsheets and MA-treated PP film laminates are presented in Fig. 6. The figure compares the untreated and MA:BPO (2:1)-treated dog-bone samples. Untreated samples showed that the TMP fiber pulled out from the PP matrix due to the weak interfacial interaction at the TMP fiber and PP interface (Fig. 6a). This result led to poor tensile strength performance. However, the fibers in the treated samples were broken and fewer fibers were pulled out from the PP matrix (Fig. 6b). The broken fibers indicate that there was a strong interaction at the TMP fiber and PP interface resulting from MA loading on the PP film surface. There was no difference found in the fracture mode of the modified laminates from the images generated from an edge finder function of the image analysis system.

Scanning electron microscopy micrographs of the fracture surfaces of TMP fiber handsheet and MA-treated PP film laminates showed the effectiveness of MA loading on the PP film surface (see Fig. 7). The failure mode of MA loading levels under tension load slightly differed from each other. Untreated samples showed an evidence of interfacial isolation between TMP fiber and the PP matrix. It was also observed that the fibers pulled out without surface damage and the samples failed in a brittle wood fiber failure mode due to the possible thermal degradation of the cellulose in the fibers. However, improved interfacial adhesion of MA-treated PP laminates was observed in the micrographs. The PP matrix held the TMP fiber surface without interfacial failure. The failure of both TMP fiber and the PP matrix was in a brittle mode due to the improved interfacial interaction at the TMP fiber and PP interface. Therefore, the interfacial bond between the PP and TMP fiber surface was strong and resulted in fracture of the TMP fibers rather than being pulled out of the matrix. Additionally, it should be noted that the PP melt flow into the lumen structure of the TMP fibers was observed in only a few specimens.

CONCLUSIONS

The effects of MA, material preparation, and number of fibers on the tensile strength enhancement of TMP fiber handsheet and iPP film laminates were investigated. The tensile strength properties of MA modified iPP laminates increased as the number of fibers on the fracture surface increased. The uniform iPP melt flow into the TMP fiber handsheet was also an important factor to obtain satisfactory interfacial strength properties of laminates. The poorer mechanical properties of the unmodified iPP and TMP fiber laminates were due to poor adhesion between the TMP fiber surface and iPP matrix. However, the tensile strength was improved with MA treatment on the surface of iPP film. There is a level of MA grafting on the iPP surface for the tensile strength of laminates.

The optimum MA and BPO ratio was 2:1. As the increased ratio to 2:1, the tensile strength became almost 76% higher than the strength of unmodified iPP film and TMP fiber handsheet laminates. The MA treatment as a copolymer was found to have a significant effect on the tensile strength properties and MA played an important role at the interface.

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