

THERMOMECHANICAL PULP FIBER SURFACE MODIFICATION FOR ENHANCING THE INTERFACIAL ADHESION WITH POLYPROPYLENE

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ABSTRACT

Chemical coupling on the thermomechanical pulp (TMP) fiber improved tensile strength of the TMP fiber handsheet and isotactic polypropylene film laminates (TPL). For the maleic anhydride (MA) with benzoyl peroxide (BPO) as an initiator, tensile strength increased 52% with the TMP fiber treatment over untreated laminates. The optimum strength properties were obtained with an MA and BPO ratio of 2:1. Scanning electron microscopy (SEM) images also showed the effectiveness of MA loading on the surface of TMP fibers due to increased fiber failure without fiber pullout from the polypropylene matrixes. Crystallinity and heat flow from DSC, as expected, decreased with the addition of MA on the TMP fiber surface. These results were also in accordance with the morphological observations at the fracture surface, Fourier-transform infrared spectroscopy (FTIR) spectra, and thermal analysis. Based on the high correlation between tensile strength and the number of fibers counted at the point of failures, the number of fibers proved to be a sensitive measure of the effectiveness of surface treatment.

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INTRODUCTION

The potential use of thermomechanical pulp (TMP) fibers as a reinforcing component for thermoplastics opens up further possibilities for use of low-cost lignocellulosic fiber resources. Researchers have shown an increasing interest in natural fiber-reinforced polymer composites due to the inherent properties of bio-based fibers, such as low density, relatively high toughness, high strength and stiffness, and good thermal properties and biodegradability (Rowell and Clemons 1992; Rezaei and Warner 1997; Wu et al. 2000; Joseph et al. 2003). However, a main disadvantage of natural fibers is their poor compatibility with hydrophobic thermoplastics. Therefore, chemical modifications are necessary to increase interfacial adhesion at the wood fiber and semicrystalline polymer interface.

Surface modification with multifunctional monomers increases interfacial adhesion by modifying surface chemistry, surface roughness, and surface free energy of the wood fibers (Gray 1974; Liu et al. 1994; Wang and Hwang 1996). Anhydrides as a coupling agent have received a great amount of interest (Maldas et al. 1989; Maldas and Kokta 1991; Khan and Idriss Ali 1993; Bamford and Al-Lamee 1994; Lu and Chung 1998; Hill and Cetin 2000; Li et al. 2001). Anhydride groups react chemically with the hydroxyl groups of wood fibers to form ester bonds. These bonds between the treated wood fiber and PP provide a good interfacial adhesion for wood fiber and thermoplastic composites (WPC). Maleic anhydride (MA), polymethylene polyphenyl isocyanate (PMPPIC), and maleic anhydride polypropylene (MAPP) are recognized as well-known coupling agents in WPC (Lu et al. 2000). MA and MAPP have been shown to be relatively effective in improving both physical and mechanical properties of TMP fiber and PP composites. Both the chemical structure and the modification procedure improved mechanical properties of WPC through their coupling actions at the interface. The reac-

tion rate and the number of anhydride groups reacted with the lignocellulosic fibers differed from those of MA due to differences in their chemical structure which affected their reactivity (Clemons et al. 1992; Felix and Gatenholm 1993; Grell 2001; Lu et al. 2002).

Benzoyl peroxide (BPO) and dicumyl peroxide (DCP) were commonly used as initiators for the modification of wood fibers and thermoplastics to graft MA onto the wood fiber surfaces (Keener et al. 2004; Demir et al. 2005; Denac et al. 2005a; 2005b; Minisini and Tsobnang 2005). Initiators have been used to improve interfacial adhesion by adding them directly to the fiber-plastic mixture (Cousin et al. 1989; Sapiuha et al. 1990). However, the BPO impregnation was much less effective than the direct blending process with an exception of some improvement in the yield stress of low density polyethylene (LDPE) composites (Raj et al. 1990). The lower effectiveness of the impregnation method was caused by fiber surface adsorption which reduced the amount of peroxide available when the fibers were treated with MA (Bataille et al. 1990). A small amount of BPO or DCP sharply increased the yield stress of PE composites. The BPO or DCP concentration, defined as a peroxide weight fraction at which the yield stress reaches 95% of its maximum, depended on the fiber content (Sapiuha et al. 1990; Gassan and Bledzki 1997). DCP was more effective than BPO at low levels of peroxide addition due to the lower decomposition rate at high temperatures ensuring a better dispersion in the polymer. However, thermodynamic mechanical properties of polyvinyl chloride (PVC) based composites increased 20% by using 4.12% MAPP (Raj and Kokta 1995; Matuana et al. 1998; Lu et al. 2004).

The MA has two different functional groups, an unsaturated carbon-carbon double bond and an anhydride group. Both groups attack wood fiber surfaces and build crosslinking reactions via hydroxyl groups. This characteristic makes

MA an attractive coupling agent in WPC. Esterification reactions between wood fiber and MAPP also proved to be beneficial in increasing strength properties (Marcovich et al. 2001). The esterification reaction can be optimized by using catalysts, sodium hypophosphite hydrate, for esterification between the MA and the bleached wood fibers (Kazayawoko et al. 1997). However, little effect on the esterification of chemical-thermomechanical pulp (CTMP) fibers was reported. Tensile strength properties of PP based composites were improved with 2–5% MA addition (Mohanakrishnan et al. 1993).

With regard to mechanical properties of WPC, interfacial property enhancement is important at the TMP fiber-thermoplastic interface. The maleation of the wood fiber surfaces provided a high variation on the mechanical properties of WPC depending on the wood or plastic materials, copolymer types, and processing conditions. Therefore, this study was conducted to evaluate the effects of MA-grafted TMP fiber surfaces in contact with PP melts. It also evaluated the porosity of TMP fiber handsheets and number of fibers exposed on the fracture surfaces to determine its relationship to tensile strength properties of TMP fiber handsheets and isotactic polypropylene laminates (TPL).

MATERIALS AND METHODS

Materials

Wood fiber samples used in this study were loblolly pine chips (*Pinus taeda* L.) converted to thermomechanical pulp fibers at 8 bar steam pressure conditions and 8.2% moisture content. Maleic anhydride (Huhtman Chemical Co., Chesterfield, MO) was used as a modifying agent with a purity >99% and a melting point of 52°C. Benzoyl peroxide (BPO; Benox® A-80; NORAC, Inc. Azusa, CA) was used as an additive component to initiate MA reaction on the TMP fiber surface. It contained 20% water and 5.1% active oxygen. Toluene (Fisher Scientific Inc., Pittsburgh, PA) was used as a reagent. Sheets of isotactic polypropylene film (Plastic

Suppliers, Inc., Columbus, OH) were used to fabricate TPL.

Thermomechanical pulp fiber modification

Table 1 shows the conditions of the TMP fiber surface modification. The modification with MA was carried out by soaking the fibers in an MA/BPO solution. Treatment solutions were formulated based on the weight fraction of MA (12.5, 25, and 50 grams)/BPO (12.5 grams) in toluene (1 L) which was heated to 100 °C. The final total solution was 2 L. Fifty-eight grams of TMP fibers were soaked for 10 minutes. The treated fibers were removed from the treatment solution, and excess chemicals on the surface of the TMP fibers were washed out with distilled water. The fibers were oven-dried at 60°C for 38 hours.

Fabrication of handsheet and polypropylene film laminates

A total of 36 handsheets were formed with 2 grams (OD wt.) of treated TMP fibers and were press-dried at 25°C and 60°C with 0.34 MPa pressure to evaluate the effect of drying conditions on the handsheet porosity and tensile strength properties of TPL. Handsheets were stored in a vacuum dessicator until laminates were fabricated. The TPL (50/50% weight fraction) were pressed under 0.69 MPa pressures for three minutes at 400°F.

Image analysis

A SPOT RT Color "F" mounted digital camera (Diagnostic Instruments Inc., 1520 × 1080 resolution and Spot Adventure—Ver. 3,2,4) was

TABLE 1. Maleic anhydride grafting conditions for the thermomechanical pulp fiber surface modification.

TMP Fibers	7.5 grams (each load)
MA and BPO ratios	0:0, 1:1, 2:1, and 4:1
Reagent Chemicals	Toluene
Reaction Temperature	100°C
Treatment Time	10 minutes

employed for microphotographing handsheet porosity and number of fiber measurements. Pores created from a fiber network are important to address handsheet characteristics and provide polymer melt flow. In this study, the porosity was void spaces among the fibers in handsheets and expressed as a unit area. The porosity was also used to address ratio differences between wood fibers and void spaces as a percentage. The images for the handsheets were transformed into gray scale images, and data were collected using light intensity selection with 146 to 255 intensity range (Fig. 1). The number of fibers at the section of tension failure contributes strength properties of fiber reinforced composites. Therefore, measurement of the number of TMP fibers in the tension break, using the fracture mode images (Fig. 2), was performed with image transformation. The images were transformed using an edge finder function to count the fibers exposed at the fracture surface. For the image analysis and data collection, Image-Pro® plus software (Media Cybernetics—Ver. 5,0) was used to collect quantitative measurements of porosity, porous (%), and number of fibers in the tensile failure section of the dog-bone samples.

Tensile strength

Two hundred and sixteen dog-bone tensile samples were cut in a nominal dimension of $12.7 \times 2.03 \times 0.03 \text{ cm}^3$ with a neck width of 0.89 cm. Tensile strength properties were tested using an Instron 4465 mechanical testing machine at a

crosshead speed of 0.13 cm min^{-1} according to ASTM D638-03 (ASTM 2003). At least 21 specimens were tested for each set of samples and the mean values as well as the standard deviations were calculated.

Thermal characteristics

A DSC (Perkin-Elmer DSC 7) system was used to evaluate and confirm thermal characteristics of surface modified TMP fiber and polypropylene laminates at levels of MA fraction. 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 curves during the polymer melt and crystallization process based on ASTM E793-01 and E794-01 (ASTM 2001). The X_c (Eq. 1) with polypropylene and 4 levels of MA-treated fiber combinations was used to calculate parameters of interest. 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 applied for this study.

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

where: X_c = % of crystallinity

ΔH_f = Heat of fusion from DSC

ΔH_f^0 = 100% Crystalline PP

w = Mass fraction of PP

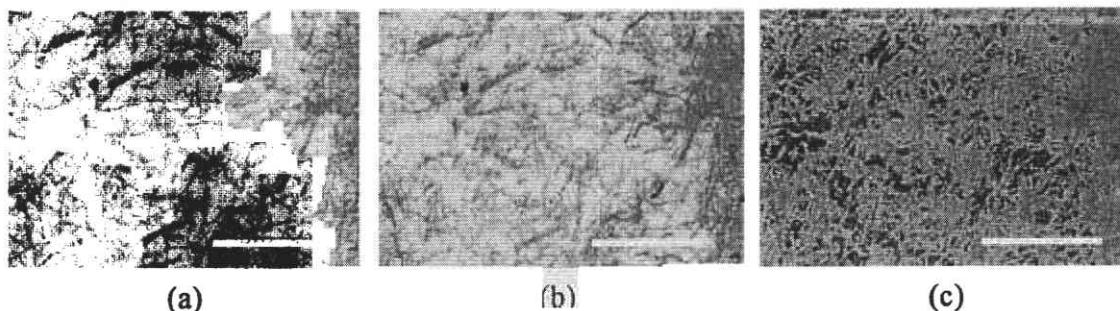


FIG. 1. Porosity of wood fiber handsheet and polypropylene laminates using image analysis; (a) Stage I. Original images, (b) Stage II. Gray transformation, and (c) Stage III. Intensity range selection. ($16 \times 11 \text{ mm}^2$). (Scale bar on each image represents 5 mm).

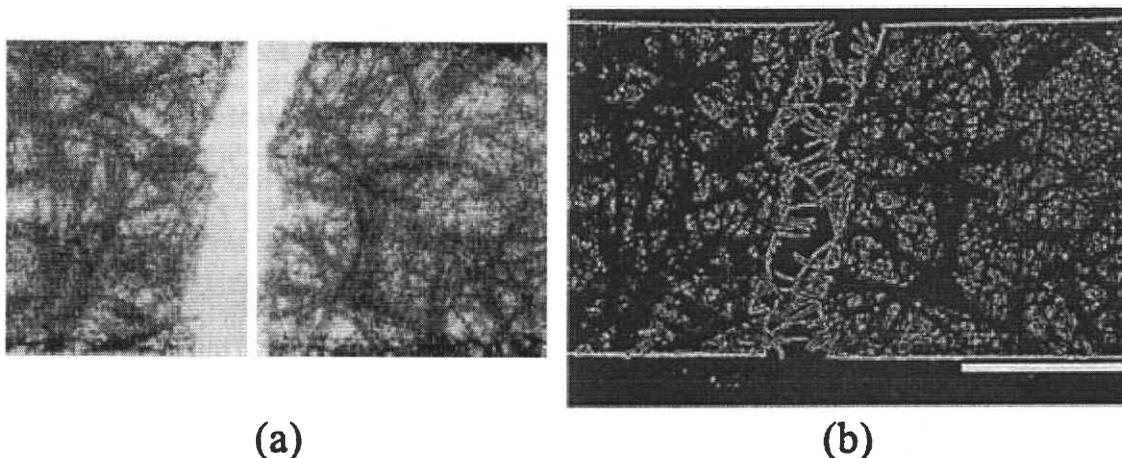


FIG. 2. Photomicrographs of handsheet and fibers from failure section of the tensile strength test (a) Stage I. Original fracture image, and (b) Stage II. Image transformation. (Scale bar on each image represents 5 mm).

Fracture surface

Scanning electron microscopy (SEM: Hitachi S-3600N) observations of the fracture surfaces of MA-grafted TMP fiber handsheet and PP film laminates were used to study the MA treatment effect at the treated fiber and PP interfaces. Mounted fibers were coated with an approximately 15-nm thin gold layer using an ion sputter (Technics Hummer V). Morphological characteristics were analyzed from photomicrographic images to study the fiber surface conditions. Images were generated at 15 kV and 1,000 \times .

RESULTS AND DISCUSSION

Porosity of thermomechanical pulp fiber handsheet

Figure 3 shows the influence of a handsheet porosity and porous percentage on tensile strength properties. Prepressing conditions for the TMP fiber handsheets were 0.34 MPa pressure at 25°C and 60°C. The handsheet porosity and porous percentage between the two temperature pressing conditions were significantly different from each other. The higher porosity and porous percentage lowered the tensile strength of laminates. The relationship between tensile

strength and void spaces indicated that lower porosity resulted in higher tensile strength due to the increased fiber reinforcement materials. The strength of TPL pressed at 60°C showed slightly higher mean values.

Number of fibers at the fracture surface

Figure 4 shows the tensile strength properties of treated TMP fiber handsheets (MA and BPO ratio = 2:1) and PP film laminates as a function of the number of fibers exposed on the fracture surface. Prepressing handsheets at both 25°C and = 60°C provided a high correlation with the number of fibers and tensile strength properties ($R^2 = 0.89$ and 0.90). Prepressing temperature at 25°C showed slightly higher tensile strength. This result indicated that fibers dried at ambient temperature were less compressed and provided a better thermoplastic melt flow. In general, the tensile strength of WPC decreases with an increasing percentage of wood flour, due to the poor stress transfer at the material interface. However, TMP fiber handsheet characteristic and fiber geometries such as fiber width, length, structure, and number of fibers contributed to the tensile strength enhancement of TPL (Thwe and Liao 2002; Bledzki et al. 2005).

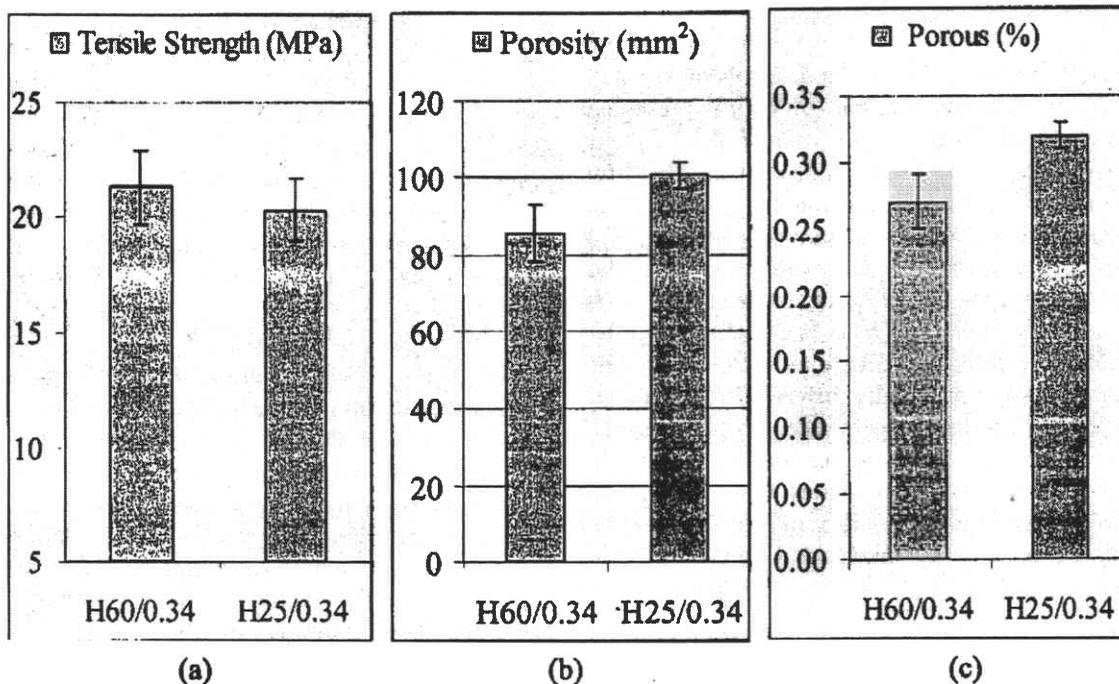


FIG. 3. Test sample laminate conditions on the (a) tensile strength, (b) porosity, and (c) porous (The error bars represent one standard deviation). H60/0.34 = handsheet pressed with 0.34 MPa at 60°C and H25/0.34 = handsheet pressed with 0.34 MPa pressure at 25°C. (21 samples per each condition).

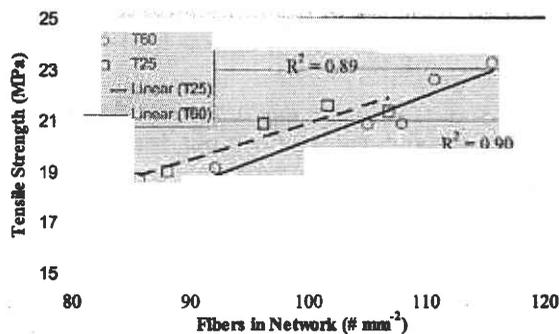


FIG. 4. Tensile strength of sample laminates as a function of the number of fibers exposed on the fracture surface. (T60 = prepressed at 60°C and T25 = prepressed at 25°C).

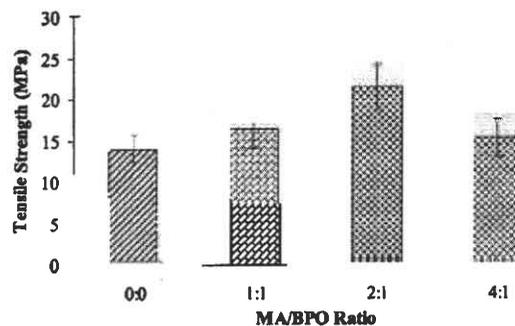


FIG. 5. Effect of weight fractions between maleic anhydride (MA) and benzoyl peroxide (BPO) in toluene on tensile strength properties of thermomechanical pulp fiber handsheet and polypropylene film laminates. (The error bars represent one standard deviation).

Effects of the maleic anhydride and benzoyl peroxide ratios

The effect of MA and BPO ratios on tensile strength properties of TMP fiber handsheet and PP laminates is shown in Fig. 5. TMP fibers treated with MA and BPO ratio 2:1 yielded the highest tensile strength properties. Treatment ef-

fects of ratios 1:1 and 4:1 were less effective on the strength enhancement than ratio 2:1. The result clearly shows that the MA and BPO ratio 2:1 is an optimum condition for the TMP fiber treatment used in this experiment. It showed 52% tensile strength enhancement over untreated laminates.

Thermal analysis

The treatment effect of four levels of MA and BPO ratios on the thermal behavior is presented in Table 2. The thermodynamic behavior of MA-treated TMP fiber handsheets and PP film laminates on glass transition (T_g), onset (T_o), and melting and crystallization peaks (T_m , T_c) from the endothermic and exothermic curve did not influence behavior except for heat flow (ΔH) and PP crystallinity (X_c). The ΔH and X_c decreased with increased MA and BPO ratios. The ratio 4:1 showed slightly different thermal quantities and resulted in poor strength performance due to excessive copolymer loading effects. In general, this result indicates that introducing TMP fiber to the PP matrix improves the semi-crystalline polymer nucleation and crystallization (Joseph et al. 2003; Lee et al. 2006).

Scanning electron microscopy

Fracture surfaces of MA-treated TMP fiber handsheets and PP film laminates show the effectiveness of MA loading at the TMP fibers and PP interface (Fig. 6). The failure mode of MA loading levels under tension differed substantially from each other. Untreated samples (Fig. 6a) show that the fiber was pulled out without surface damage and the brittle wood fiber failure mode was hardly observed in the tensile tests. The PP matrix showed an evidence of interfacial isolation between the TMP fiber and PP. However, improved interfacial adhesion in the case of MA-treated laminates (Fig. 6b, c, and d) also evidenced apparent TMP fiber and PP matrix failure. TMP fibers failed in a brittle mode, and

the PP matrix remained on the TMP fiber surface. The PP failure also indicates that the properties of PP may have changed due to the MA treatment on the TMP fiber surface. The improved interfacial interaction is due to the coupling agent acting as a true bridge polymer at the interface and led to additional fiber interlocking from the melting and flowing characteristics of the thermoplastics on the surface of TMP fibers.

CONCLUSIONS

Chemical coupling generally plays an important role in improving tensile strength enhancement in WPC. In this study, the effects of MA treatment on the surface of TMP fiber and handsheet properties on the tensile strength properties were evaluated. Based on the higher correlation between tensile strength of laminates and number of fibers on the fracture surface on both pre-press conditions, numbers of fibers contributed tensile strength properties of laminates. Copolymer treatment using MA and BPO as an initiator increased 52% tensile strength properties over untreated laminates. This study results addressed that MA and BPO ratio (= 2:1) is an optimum ratio to treat TMP fibers to increase tensile strength properties. SEM images also represented the effectiveness of MA loading on the surface of TMP fibers due to the increased fiber failure without pulled fiber out from PP matrixes. Crystallinity and heat flow from DSC, as we expected, decreased with addition of MA on the TMP fiber surface.

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TABLE 2. Thermodynamic quantities of maleic anhydride-treated thermomechanical pulp fiber handsheets laminated with polypropylene film.

MA/BPO ratio	Density (g cm ⁻³)	Endothermic curve				Exothermic curve			
		T_g (°C)	T_o (°C)	T_m (°C)	ΔH (J g ⁻¹)	T_c (°C)	T_o (°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	0.95	-21.8	153	162	61.7	121	117	98.6	47.6
2:1	1.00	-21.6	153	162	55.9	121	118	91.1	44.0
4:1	0.72	-22.4	152	161	56.4	122	118	94.9	45.8

Note: MA = Maleic anhydride; BPO = Benzoyl peroxide.

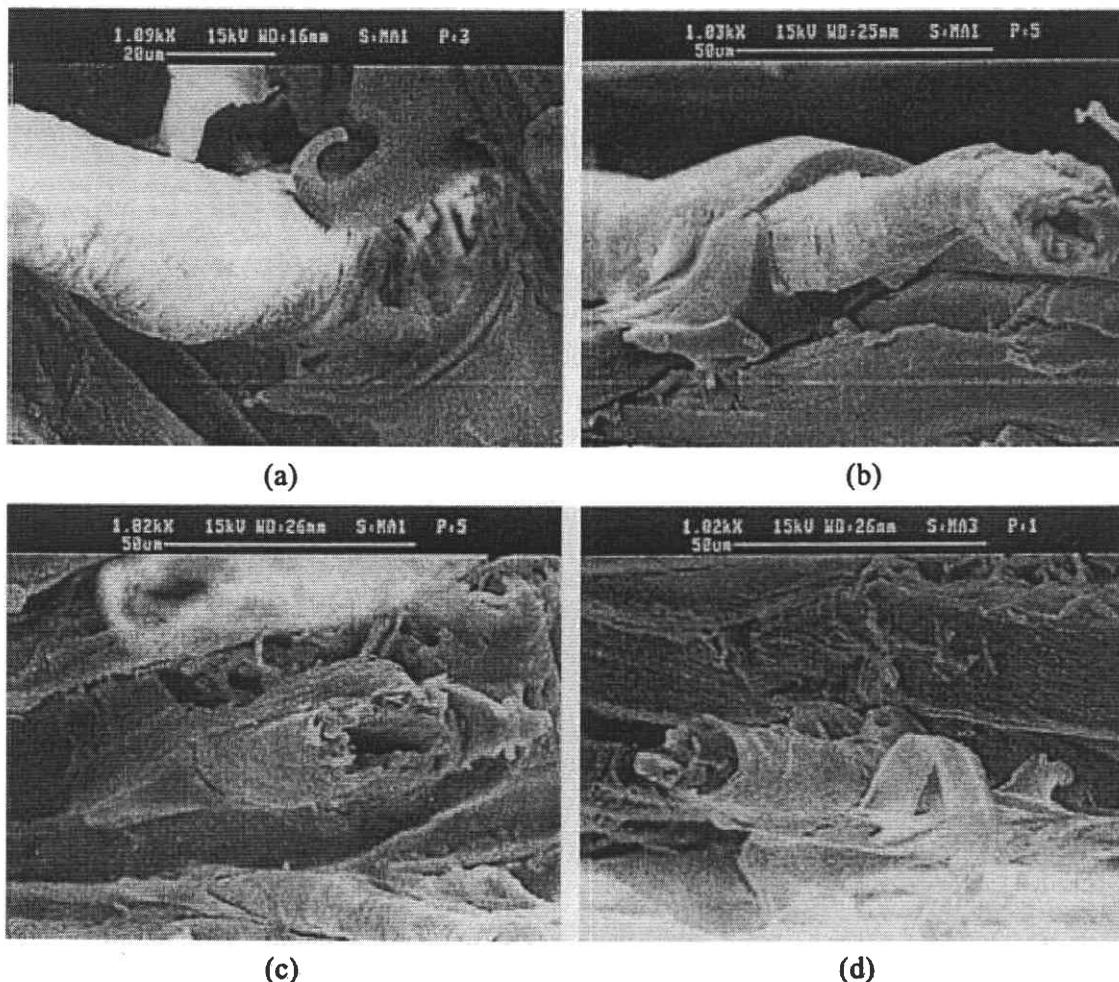


FIG. 6. Scanning electron microscopy micrographs of fracture surfaces of thermomechanical pulp fiber handsheet and polypropylene film laminates; maleic anhydride grafted thermomechanical pulp fiber handsheets. (a) Untreated, (b) MA:BPO = 1:1, (c) MA:BPO = 2:1, and (d) MA:BPO = 4:1.

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