Plasma Enhanced Modification of TMP Fiber and its Effect on Tensile Strength of Wood Fiber/PP Composite

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Abstract

Plasma-assisted surface treatment on thermomechanical pulp (TMP) fiber and polypropylene (PP) film was investigated to obtain interfacial adhesion at the wood fiber and PP interface. A metal plate between electrodes prevented thermal damage to the TMP fiber handsheets and PP film. Oxygen-plasma treatment provided better surface activation on the TMP fiber and PP film than argon-plasma treatment. When the surfaces of both TMP fiber handsheets and PP film were treated with the oxygen-based plasma, the tensile strength substantially increased. The optimum exposure period for TMP fiber to plasma with ionized oxygen gas was 30-90 sec. and resulted in 43-80% increased tensile strength over the untreated samples. AFM topographies showed that oxygen plasma treatment changed the surface tomography and surface roughness of the wood fiber and PP. Nodular structures were found on the flat areas of the wood fiber and PP after undergoing oxygen plasma treatment. The size of the nodules increased as treatment time increased. The surface roughness decreased with O_2 plasma treatment as also did the thermal characteristics of the glass transition point (T_g) and crystallinity (X_C) from DSC. The RMS roughness and thermal quantities were reduced with 30 seconds of plasma treatment but slightly recovered after 60 seconds of treatment. The treatment also resulted in relative uniform surfaces with reduced RMS of TMP fiber and PP film.

Introduction

Lignocellulosic materials are widely utilized in wood fiber and thermoplastic composites (WPC) because of their low weight, relatively high strength and stiffness and machinability (Maldas and Kokta 1991, Rievld and Simon 1992, Kolosik et al. 1992, Wolcott et al. 2000, Xue and Tao1 2005**)**. Surface activation by plasma treatment is a means to increase interfacial strength at the hydrophilic and hydrophobic interface. Considerable effort has been placed chemical and physical methods to improve the interfacial adhesion between the wood fibers and the polymer matrix (Karlsson et al. 1996,

Espert and Karlsson 2004). Chemical modification on both wood fiber and the thermoplastic matrix was well characterized with coupling agents such as maleic anhydride (Maldas and Kokta 1990, Raj et al. 1990, Mohanakrishnan et al. 1993, Collier et al. 1996, Mahlberg et al. 2001, Hristov et al. 2004) and silane (Beshay 1989, Kokta et al. 1990). Another method is the plasma associated ion implantation by introducing a magnetic field and ionized gas using electronic discharges. The plasma associated ion implantation on wood fiber materials is still not fully understood.

Plasma treatment of polymer surfaces can promote wettability, printability, and adhesion (Chaoting et al. 1993, Mahlberg et al. 1998, Lee et al. 1999, Denes et al. 1999, Rehn and Viöl 2003). In most applications, dielectrics are used to make stable operation without material deformation. This application requires discharge power of about 100 to 400W. Useful frequency range was 10–30 kHz (Draou et al. 1999, Kazayawoko et al. 1999, Jang and Yang 2000). The technique can lead an effective surface modification and uniform surface coatings. The treatment of surfaces at low temperature and pressure is an important factor for large-scale WPC production (Badey et al. 1996, Poncin-Epaillard et al. 1997). However, the process is essentially a simple surface modification of wood and wood fibers using ionization of oxygen or silane with nitrogen or argon gas as a carrier (Brown and Mathys 1997, Montes-Morán et al. 2001). Plasma enhanced ion implantation treatment with gas ionization is a simple and advanced technology for surface modification. The ion implantation has been applied to both wood and non-wood materials to obtain an activation layer on the material surface (Porta et al. 1990, Posadowski and Radzimaki 1993, Denes et al. 1999, Ihara et al. 2001).

Heat generated between electrodes is less beneficial to modifying wood surface due to the thermal degradation of wood fiber (cellulose, hemicellulose, and lignin). The temperature is generally over glass transition temperatures of the wood materials as well as the melting point of thermoplastics (Maldas and Kokta 1991). Therefore, some researchers have conducted cold-plasma system to obtain an optimum treatment effect as well as alter surface layers (Chaoting et al. 1993, Young et al. 1995, Poncin-Epaillard et al. 1997, Rehn and Viöl 2003, Bente et al. 2004). The cold plasma is generated when an electromagnetic field and gas flow at low pressure and near-ambient temperature from the power sources of DC, radio, and microwave frequency (Mahlberg et al. 1998, Lennon et al. 2000, Ihara et al. 2001). A great variety of surface effects can be generated by controlling plasma variables, notably the chemistry of the gas used to sustain the plasma, gas flow rate and pressure, applied power and exposure time (NPPS 1995). Both the surface chemistry and morphology of the treated wood fibers and plastics may be modified to electron donor rich and oxygen activated surface (Young et al. 1996, Poncin-Epaillard et al. 1997).

Numbers of processes take place in plasma on the surface of bio-based materials such as dissociation by electron impact, ionization, and molecular excitation at the low pressure and ambient temperature (Badey et al. 1996, France and Short 1997, Draou et al. 1999, Lee et al. 1999, Montes-Morán et al. 2001). Gas sources for ionization have been used in plasma treatment on the surface of fibers or plastics, such as Ar, O_2, cyclohexane, NH_3, N_2, MMA (methacrylic acid) (Felix et al. 1994, Young et al. 1996, Poncin-Epaillard et al. 1997, Rehn and Viöl 2003). Oxygen plasma induced the surface activation from the process of such as excited molecules, atomic oxygen, ozone, molecular ions and the relevant atomic ions which may behave as active sources. Ar or O_2 plasma treatment improved 5 to 15

times in interfacial adhesion properties from the peel strength test between polypropylene (PP) film and cellulose filter paper. In contrast, the cyclohexane plasma was less effective in the improvement on the adhesion as well as surface treatment on the regenerated cellulose (Young et al. 1996). Therefore, Ar or O_2 plasma was shown to be very effective in improving interfacial adhesion at the fiber and PP. The incensement was due to formation of an interactive layer on the cellulose surface and resulted in strong acid/base interactions. The NH_3 or N_2 plasma treatment for 15 seconds on cellulose fibers contained 86% cellulose and 13% hemicellulose also yielded lower modulus properties in PS composites (Felix et al. 1994). Oxygen and carbon (O/C) ratio of cellulose fibers at 15 second treatment time reduced significantly but further exposure in the plasma environment cause the O/C value to increase, due to the induced thermal degradation and ablation of the modified surface layers (Felix et al. 1994, Mahlberg et al. 1998, Denes et al. 1999).

Physical adhesions, acid-base interactions and chemical linkages may be all involved in the adhesion between the plasma modified thermomechanical pulp (TMP) fibers and plastics, but their relative contributions to the interfacial adhesion may varies and depends on the nature of ionized gases and plasma treatment procedures. The surface modification can also change mechanical interlocking between wood fibers and thermoplastic matrix without chemical modification and altering the chemical composition of the fiber materials. The interaction of TMP fiber surface and a semicrystalline polymer with Ar and O_2-plasma treated interface has not known clearly. Therefore, improving and investigating the effect of DC-based plasma treatment for the interfacial interaction at the TMP fiber handsheet and PP interphase is the purpose for this study. This study used DC-based Ar and O_2-plasma modification on the surface of TMP fiber handsheet and PP film.

Materials and Methods

Materials

Thermomechanical pulp (TMP) fibers (loblolly pine; *Pinus taeda* L.) were generated from mature wood at 8 bar digester/refining pressure in a continuous, pressurized, single-disc refiner. Average moisture content of the TMP fibers was 8.2 percent respectably. Macerated TMP fibers were prepared in laboratory and filter papers used in this study were Sharkskin lot No. X31 from Schleicher & Schuell inc. Keene, NH. Five grams of fibers soaked in 500 ml water for 24 hours and formed 5.5-inch diameter handsheet.

Film types of polypropylene was used for the evaluation of the Ar and O_2 plasma source effect on tensile strength of the TMP fiber handsheet and PP film laminates. The PP was provided by Plastic Suppliers, Inc. Columbus, OH (CO-EX, biaxial oriented PP film).

Plasma treatment

Fig. 1 shows the modified ion sputter (Ladd sputter Coater, Ladd Research Industries, Inc. Williston, VT) that was used for Ar and O_2 plasma treatment on the TMP fiber handsheets and PP films. This plasma system has parallel electrodes and a DC-based power source. The distance between two electrodes is 2 inches, and a plasma barrier plate is located 1 inch from the top and bottom electrodes. The Ar and O_2 plasma treatment was performed with a 20 sccm gas flow rate and exposure times of 30, 60, 300, and 600 seconds.

The chamber was evacuated below 30 mtorr and argon gas was purged twice at a chamber pressure of 100 mtorr to clean the chamber and the sample. Argon-based plasma was performed at the chamber pressure of 100 mtorr, 2.5 kV, and 34 mA. Oxygen-based plasma was carried out at 100 and 200 mtorr chamber pressure, 1.5 kV, and 40 mA. After the plasma treatment, the chamber was re-evacuated to 30 mtorr and slowly purged with air.

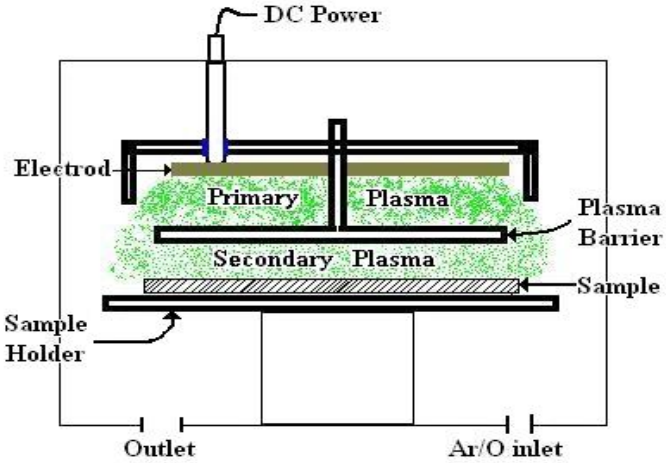


Fig. 1. Parallel plate DC-based dielectric barrier discharge with a plasma barrier plate to generate secondary plasma on the substrate.

Surface tomography and morphology

Atomic force microscopy (AFM) was applied to characterize surface topography of substrates as well as observe adhesion and mechanical properties on scales from hundreds of microns to nanometers. This study used a Nanoscope IIIa AFM (Digital Instruments) mounted on a pneumatic isolation table with an acoustic hood. The scanning area was 1 (360 samples) and 6.25 um^2 (120 samples). All AFM micrographs were taken at a resolution of 512×512 pixels in tapping mode. The images evaluated and statistically analyzed using the quantify RMS surface roughness.

The morphology of the TMP fiber handsheet and PP films was investigated using scanning electron microscopy (SEM: Hitachi S-3600N). Mounted fibers were coated with an approximately 15-nanometer thin gold layer using an ion sputter (Technics Hummer V). The morphological characteristics were analyzed from photomicrographic images to identify the fiber surface conditions. Images were generated at 15 kV and 1,000× mag.

Laminates fabrication and property enhancement

A weight fraction of TMP fiber handsheet and PP film was 50/50. Two handsheets and 12 PP films were cut into 2×4 - inch sizes to perform the plasma treatment. Treated samples were laminated and pressed at 100 psi pressure with a pressing temperature of 400°F for two and half minutes using a 6×6-inch laboratory press.

One hundred eighty dog-bone tensile samples were cut in nominal dimensions of 2×0.6×0.027 - inch with a neck width of 0.18 inch. Tensile strength properties were tested using an Instron 4465 mechanical testing machine at a crosshead speed of 0.05 $in{\cdot}min.^{-1}$

according to ASTM D638-03 (ASTM 2003). At least 6 specimens were tested for each set of samples and the mean values as well as the standard deviations were calculated.

Thermal characteristics

Thermal characteristics were evaluated with differential scanning calorimetery **(**DSC; Perkin-Elmer DSC 7**)** under nitrogen atmosphere. 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 were applied for DSC samples. Finally, thermal characteristics of glass transition (T_g), onset (T_{om} and T_{oc}), and peak temperature (T_m and T_c) were determined by endothermic and exothermic curves during the polymer relaxation and crystallization process based on ASTM E793-01 and E794-01 (ASTM 2001a, b). For calculation of the percents of crystallinity (X_C) of the plasma treated samples from the area of under the cooling curve, the following equation was used:

$$X_C = \left[\frac{\Delta H_f}{w \Delta H_f^0} \right] \times 100 \qquad (1)$$

Where ΔH_f and ΔH_{f_0} are heat of fusion (J g^{-1}) from the area under the crystallization curve and heat of fusion from 100% crystalline polypropylene (207.14 J g^{-1}). The w is the mass fraction of PP in the TMP fiber/PP samples.

Results and Discussion

Effects of the plasma barrier on the tensile strength properties

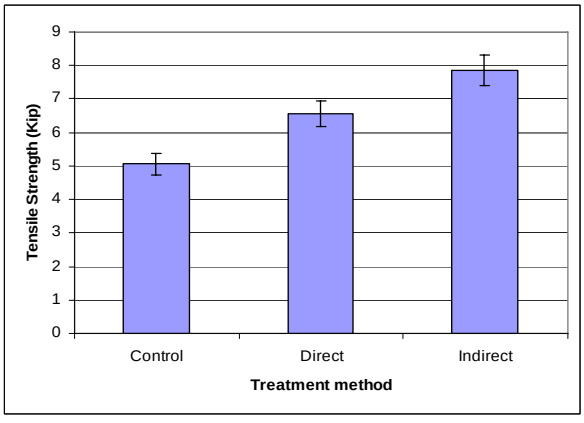


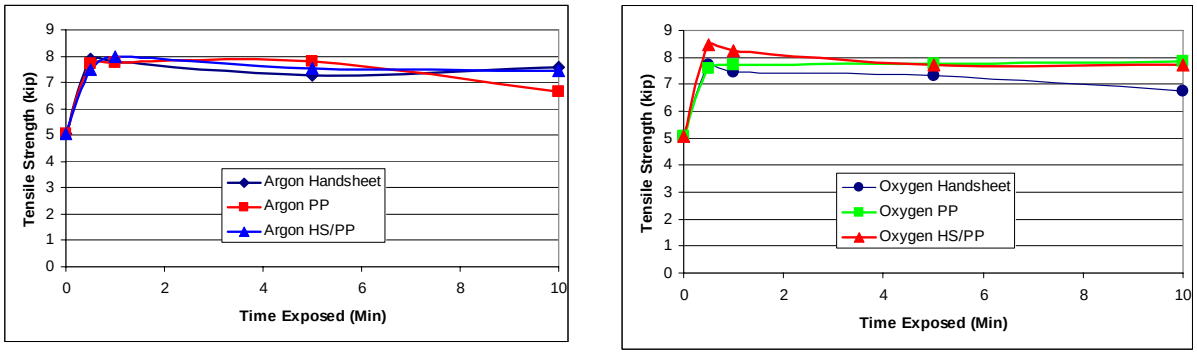
Fig.2. Effects of O_2 plasma treatment methods on the tensile strength properties of TMP fiber handsheet and PP laminates (The error bars represent one standard deviation)

Fig. 2 shows the secondary O_2 plasma field effect on the tensile strength properties of TMP fiber handsheet and PP laminates. The plasma barrier provided O_2 plasma overflow

from the primary to the secondary region on the surface of the samples. The barrier minimized thermal damages on the surface of the TMP fiber handsheet and PP film. The barrier also provided 55% increased tensile strength over control samples and also resulted in a 20% increase compared to samples treated without the plasma barrier plate. The TMP fiber handsheets and PP films could not be treated for 5 minutes due to the extreme thermal damages. Therefore, the plasma barrier plate was used to prevent thermal transfer from the electrode to the surface of TMP fiber handsheets and PP films.

Effects of the plasma sources on the tensile strength properties

Fig. 3 shows the effect of Ar- and O_2-plasma sources on tensile strength of TMP fiber handsheet and PP film laminates as a function of surface exposal time. The tensile strength properties of treated laminates increased 60 to 85% with O_2-plasma and 50 to 78% for Ar-plasma treatment. The optimum plasma effect was obtained in 30 to 60 seconds of a treatment time range. The plasma enhanced process showed a couple of limitations of material conditions of a complex geometry as wood-based lignocellulosic materials. The limitation mainly related to low vacuum and thermal damages. Moreover, the strong interaction between the two substrates and experiment provided an increased tensile strength gain of laminates from short surface treatment on an ion rich environment.



(a) (b)

Fig. 3. Effect of (a) Ar- and (b) O_2 -plasma sources on tensile strength as a function of surface exposal time to plasma under 100 mtorr pressure condition.

O_2-plasma treatment on three different fiber surfaces

Fig. 4 shows the effect of the O_2-plasma treatment on tensile strength properties of three levels of lignin content. The fibers were controlled with different lignin contents in the chemical composition of each fiber type. TMP fibers consisted of 25.4% lignin, and the lignin content decreased under 6.8% with macerated TMP fibers and lignin-free filter paper (contains less than 0.02% lignin content). Cellulose contents in TMP fibers provide more than a two time increase in the tensile strength property from TMP fiber to filter paper fiber handsheet and PP film laminates. However, TMP fiber handsheet and PP film laminates were the most effective O_2-plasma treatment for tensile strength. Thirty second treatment on the TMP fiber handsheet increased the strength properties by 80% while other fiber types increased 17 to 18%. It should be noted that 30 second O_2-plasma treatment on the

TMP fiber handsheets, contained 25.4% lignin, obtained a better property enhancement over the treatment types of PP film only and both handsheets and film surfaces.

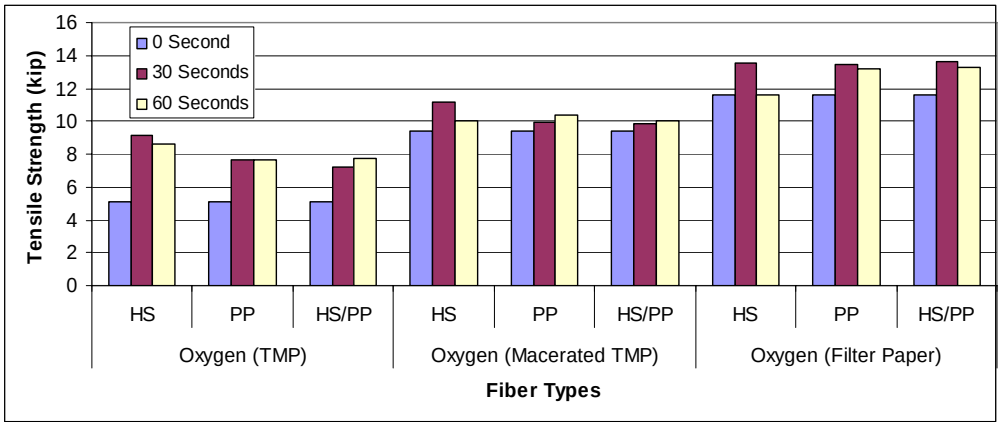


Fig. 4. Effects of O_2 plasma sources on tensile strengths as function of three different fiber conditions.

Thermodynamic characteristics

Table 1. Thermodynamic quantities of O_2 based DC-plasma treated wood fiber handsheet and PP laminates.

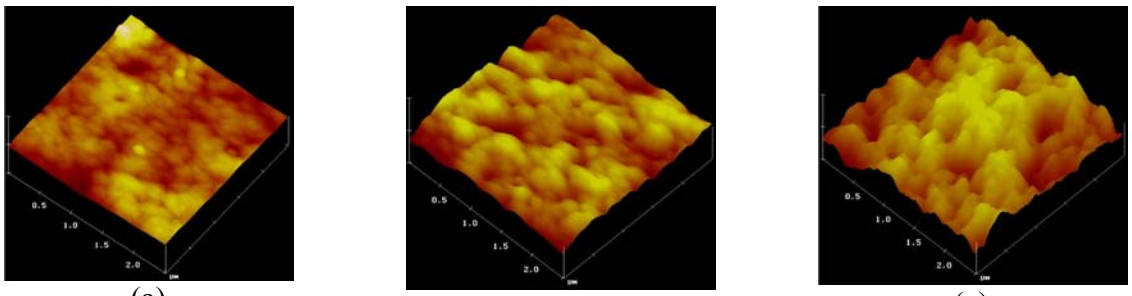
Processing Conditions and Time		Density (g cm^{-3})	Endothermic Curve				Exothermic Curve			
			T_g (°C)	T_O (°C)	T_m (°C)	ΔH (J/g)	T_O (°C)	T_C (°C)	ΔH (J/g)	X_C (%)
PP film		---	-21.1	156.9	161.7	69.6	121.4	117.3	95.0	46
TMP	0	1.05	-12.5	152.7	163.1	56.1	120.9	116.2	82.2	40
Handsheet	30	1.13	-14.0	149.8	162.9	48.2	121.1	116.9	74.2	36
	60	1.17	-14.0	150.4	162.8	38.8	121.1	116.4	63.2	31
PP	30	1.06	-22.6	153.0	162.9	41.9	121.0	116.3	71.2	34
	60	1.08	-18.2	151.8	162.8	51.6	121.2	116.7	77.8	38
Both	30	1.06	-22.4	151.5	163.0	46.4	121.2	116.8	75.2	36
	60	1.06	-21.8	149.9	162.3	43.0	121.3	116.6	68.2	33
Macerated TMP	0	1.18	-20.9	149.9	162.7	40.1	121.2	116.9	64.5	31
Handsheet	30	1.17	-22.7	149.7	162.8	41.1	121.3	117.1	68.5	33
	60	1.15	-22.3	150.0	162.5	41.7	121.5	117.3	66.7	32
PP	30	1.16	-21.6	154.4	163.4	41.6	121.2	116.7	64.5	31
	60	1.17	-21.5	155.1	162.3	34.1	121.2	116.8	60.9	29
Both	30	1.22	-22.9	150.2	162.4	37.1	121.0	116.8	63.9	31
	60	1.09	-22.7	149.4	162.6	44.8	121.4	117.3	71.8	35
Filter Paper	0	1.10	-20.7	149.7	160.9	38.7	126.0	120.4	68.4	33
Handsheet	30	1.17	-22.8	150.9	160.0	39.7	126.4	120.5	65.0	31
	60	1.15	-22.7	150.4	160.1	44.5	126.3	122.7	70.0	34
PP	30	1.11	-22.3	149.9	160.6	39.9	126.3	120.1	68.3	33
	60	1.07	-22.3	150.6	161.4	47.3	125.8	120.3	80.5	39
Both	30	1.12	-22.6	150.4	159.6	37.7	126.0	122.6	62.9	30
	60	1.13	-22.1	150.6	160.2	38.9	125.8	122.0	71.5	35

Note: PP=Polypropylene, TMP=Thermomechanical pulp fiber.

Table 1 shows thermal characteristics of wood fiber handsheet and PP laminates fabricated with O_2 based DC-plasma treated handsheets and PP films. In general, the thermal quantities reduced due to the 30 second treatment and then slightly increased with 60 seconds of treatment as determined from both the endothermic and exothermic curves. PP crystallinity (X_C) decreased to 30's and glass transition temperatures (T_g) increased with the TMP fibers. The crystallinities are lower than 100% PP film scan. The decreased melting point (T_m) with TMP fibers may be influenced by introducing an ion implanted surface which may reduce crystallinity (Bai et al. 1999, Ali et al. 2005). Addition of the wood fibers as filler and ion implantation may reduce the T_m and X_C. This result indicates that thermal behaviors PP with O_2-plasma treatment were influenced and resulted in the interfacial strength enhancement.

Surface topography and roughness

Polypropylene film surfaces that had been treated with oxygen plasma using different exposure times and applying DC power are shown in Fig. 5. Three dimensional AFM images of 24 plasma treated handsheet and PP film samples were generated. The AFM images increased treatment time on the film surface and was filled with small spherical nodules structure. The AFM images appeared to have rough surfaces without Z scales due to the plasma treatment was preceded. However, a closer look at the nanometer scale reveals a distinct difference among the three surfaces. It should be recognized that the smoothening that occurred as the treatment time increased is valid only beneath 2.5 μm × 2.5 μm areas (Mahlberg et al. 1998). The untreated surface consisting of small irregular structure appeared while the treated surface appears with nodule structures forming a layer on the PP film surface. The PP film surface is nearly smooth and completely covered with small spherical nodules and resulted in a reduction in surface roughness. The PP surface treated with plasma for 60 seconds is covered with nodules which are about twice in size of those on samples exposed for 30 seconds.

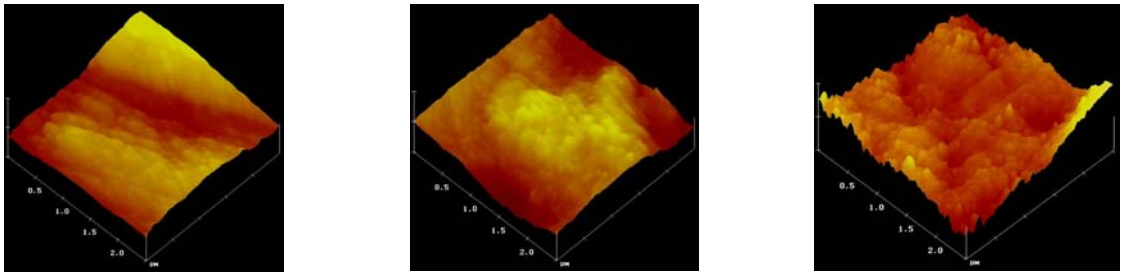


(a) (b) (c)

Fig. 5. O_2 plasma modification on the surface of PP film. (a) Untreated; Z=353.5 nm and 10.9 Hz, (b) 30 seconds; Z=94.6 nm and 1.2 Hz, and (c) 60 seconds surface treatment; Z=35.8 nm and 1.3 Hz.

Three dimensional AFM scan images of O_2-plasma treated TMP fiber handsheet are presented in Fig. 6. The AFM images of a TMP fiber handsheet surface were more difficult to scan than imaging surfaces of the macerated TMP fiber and filter paper surface due to the rough and fracture surface. Plasma treated handsheet surfaces also shows nodule

structures while the special structures were rarely formed on the untreated TMP fiber surface in the scanning size of 6.25 um^2 and 1 um^2. The plasma-treated fiber surface may be covered with ionized oxygen and electromagnetic fields, and could influence surface structure changes. The fiber surface is relatively smooth and the size of the nodule increased when the surface was treated for 60 seconds as seen on PP film surface. The nodule structures were not typical observed with untreated wood fiber surface. The nodular coverage similar to macerated TMP and filter paper fibers was found in flat areas.



(a) (b) (c)

Fig. 6. O_2 plasma modification on the surface of TMP fiber handsheets. (a) Untreated; Z=188.5 nm and 1.3 Hz, (b) 30 seconds; Z=209.5 nm and 0.84 Hz, and (c) 60 seconds surface treatment; Z=67.5 nm and 0.84 Hz.

Table 2. Quantitative RMS from atomic force microscopy.

Sample types	Treat Time	Scan Size 2.5 µm (nm)	PSD Equ.* (nm)	1 µm (nm)
Polypropylene	0 Sec.	14.9	17.9	7.7
	30 Sec.	8.4	9.2	6.4
	60 Sec.	9.99	11.4	7.1
TMP Fiber	0 Sec.	121.5	139.98	37.5
	30 Sec.	65.4	82.9	36.0
	60 Sec.	77.0	91.6	36.3
Macerated TMP Fiber	0 Sec.	52.5	49.0	17.4
	30 Sec.	48.4	54.9	19.5
	60 Sec.	63.5	71.2	30.4
Filter Paper	0 Sec.	44.4	50.7	22.1
	30 Sec.	41.8	46.4	17.4
	60 Sec.	52.7	66.5	17.6

TMP=Thermomechanical pulp fiber
* PSD Equ.= Power spectral density equivalent RMS (Root mean square).

Table 2 shows quantitative RMS measurements from AFM with four material sources, three plasma treatment times, and two scan sizes. The RMS roughness yielded very similar results as thermal characteristics of T_g and X_C from DSC. The RMS roughness of the four material surfaces was reduced with 30 second plasma treatment and slightly recovered with 60 seconds of treatment. It seems likely that the DC-based O_2-plasma is responsible for the change in surface roughness of both fiber and PP film. The modification may generate ionized oxygen and an electron rich donor surface from electromagnetic field

generation. Power Spectral Density (PSD) Equivalent RMS was generated using light intensity and provided the highest surface roughness compared to 2.5 and 1 um scan sizes.

Fracture surface morphology

Fracture surface morphology of tensile failures is shown in Fig. 7. A poor interfacial interaction between TMP fibers and PP was observed with control samples (Fig. 7a). TMP fiber failure rarely occurred and fibers pulled out from the PP matrix without surface damage. Thirty second O_2-plasma treatment showed thermoplastic and TMP fiber failure instead of failure at the wood fiber and thermoplastic interface. Figs 7.6b and d show a distinctive thermoplastic failure. Handsheets exposed for 30 seconds under O_2-plasma showed many stretched PP matrix around TMP fibers. The findings were not observed with 30 second PP treatment. Sixty seconds exposure under the O_2-plasma provided similar results as 30 second handsheet treatment except some of the interfacial failure at the TMP fiber and thermoplastic interface.

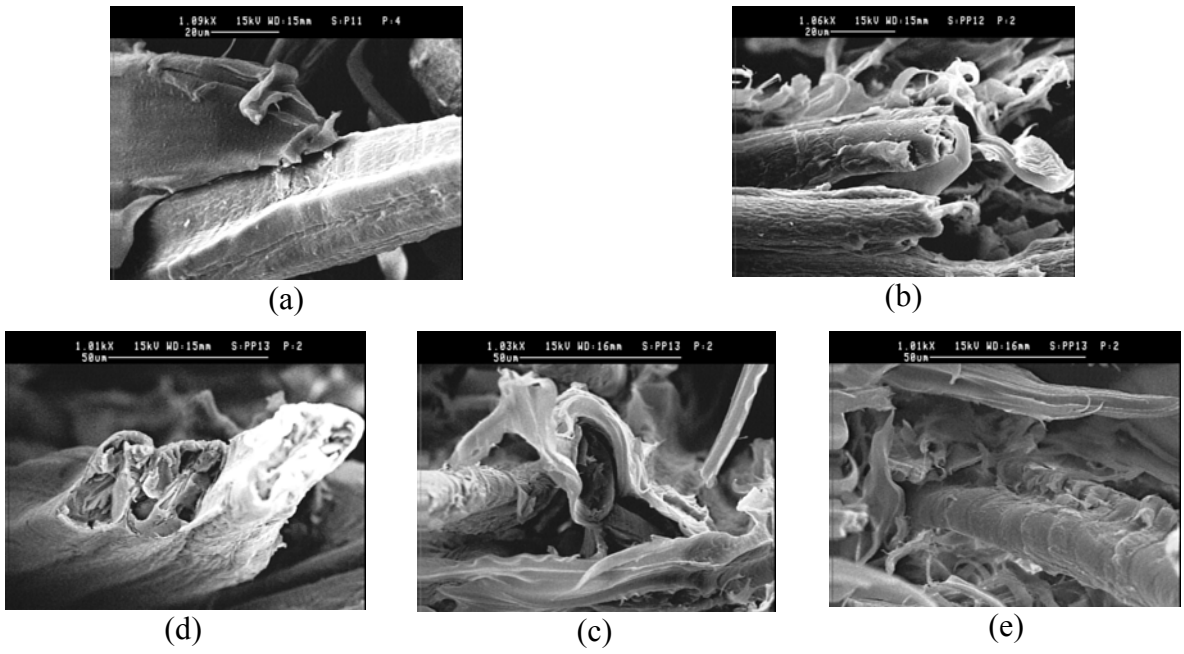


Fig. 7. SEM micrographs of fracture surfaces of TMP fiber handsheets and PP laminates. (a) Untreated, (b) 30 sec. on the handsheet, (c) 60 sec. on the handsheet, (d) 30 sec. on PP film, and (e) 60 sec. on PP film.

Conclusions

Argon and oxygen as inert gases for DC-based plasma treatment of TMP fiber handsheet and PP film surface were used to improve interfacial adhesion and various properties at the TMP fiber and PP interface. The plasma barrier between electrodes prevented thermal damage of the TMP fiber handsheets and PP films during the plasma treatment. The O_2-plasma treatment provided a better surface activation on the TMP fiber and PP film than Ar-plasma treatment. When both surfaces of TMP fiber and PP film were

treated with the O_2-based plasma, the treatment effects on the tensile strength properties were pronounced. Thirty to sixty seconds surface exposure under plasma with ionized oxygen gas was an optimum range for the plasma treatments and resulted in 43 to 80% property enhancement over the non-treated samples. Treatment greater than sixty seconds caused thermal damages on the wood fiber and PP surfaces and led to reduced treatment effects. Oxygen plasma treatment also influenced surface tomography and surface roughness of TMP fiber and PP film. The treatment also changed the topography of the wood fiber and PP to a nodular structure found on flat areas. The size of the nodules increased as the treatment time increased. The RMS roughness yielded very similar results as the thermal characteristics of T_g and X_C from DSC. The RMS roughness and thermal quantities were reduced with 30 second plasma treatment and slightly recovered with 60 seconds treatment. Finally, this study found that the mechanical interlocking with ion implantations on the reinforcement provided further interfacial strength enhancement at the TMP fiber and PP interface.

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