Influence of Surface Morphology of the Kraft Pulp Fibers on the Growth of the Transcrystalline Layer of Polypropylene

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ABSTRACT: The objective of this study was to evaluate the influence of the wood fiber surface on the crystallization behavior of thermoplastic polymers. Unbleached and bleached kraft pulp fibers were used for this study with 100% polypropylene (PP), 95% PP/5% maleic anhydride polypropylene (MAPP), and 100% MAPP at 150°C. Nuclei were induced at the ends of the fibers and on damaged surfaces while poor crystallization behavior was observed on the fiber surfaces using 100% PP. Enhanced MAPP induced transcrystallization on the wood fiber surfaces; the nucleation density also increased with the addition of MAPP. Oxygen/carbon (O/C) ratios of smooth surfaces, damaged surfaces, and the ends of wood fibers also indicated that the oxidation process of both wood fiber and thermoplastic polymer affected the crystallization process without MAPP addition. It was observed that the MAPP played a role in increasing numbers of nuclei on the linear fiber surface to induce transcrystallization. Dynamic mechanical properties increased 52% with 100% MAPP compared to the use of 100% PP. Therefore, the increased thickness of transcrystalline layer and nucleation density on the surface of wood fiber positively correlated with the dynamic mechanical properties of wood fiber-plastic composites. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1958–1966, 2010

Key words: crystallization; nucleation; poly(propylene); surface

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INTRODUCTION

Polymer composition (chain mobility), temperature, pressure (stress), molecular weight, solvents, and orientation in polymer structure are well-defined conditions for crystallization of semicrystalline polyolefins.[1] Under crystallization conditions, nuclei can be induced easily on material surfaces and the bulk area. The occurrence of an extended source of nuclei is called transcrystallization where nucleation is homogeneous and nucleation density is high enough to induce nuclei on the fiber surface (Fig. 1).

Many fundamental studies have focused on the mechanical properties of wood fiber-plastic composites (WPC), which are affected by transcrystallinity more than crystal growth in the thermoplastic matrix. These studies have identified the need for a better understanding of the major causes for the high nucleation density. Crystallization and high nuclei density of semicrystalline polyolefins on the natural fiber surface can be explained by wettability, surface energy, surface topography, and the chemical composition of the substrates.[2,3] Increased surface lignin and hemicellulose content on the fiber surface can slow the rate of transcrystalline growth.[4] Thicker transcrystalline layer (TCL) formed at higher temperatures, near the melting temperature, and larger residual stress which occurred at the fiber surface and the molten matrix interface. The TCL plays an important role in the mechanical strength of composites compared to crystallization at lower temperatures. TCL thickness effects on adhesive fracture energy are also inconsequential in polytetrafluorothylene (PTFE) fiber/polypropylene (PP) composites with no significant increase in nucleation density.[5] However, the TCL improved the shear transfer between fibers depending on the thickness of TCL created by interrupting the isothermal crystallization.[6] Thermal conditions can be sufficient to obtain satisfactory interfacial properties.

Dispersion aids and coupling agents have been applied to increase transcrystallinity of polymers on the wood fiber surface. Maleic anhydride polypropylene (MAPP) is one of the well-known coupling agents used for WPC.[7,8] The MAPP behaved as a

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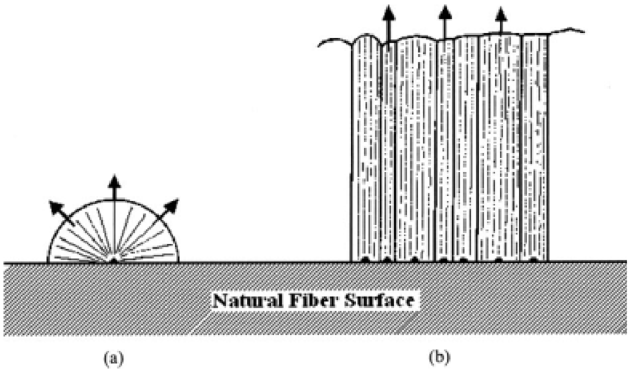


Figure 1 Single and trans-crystal growth initiated from nuclei on the surface of wood fibers.[1] (a) Single crystallization and (b) Transcrystallization.

true coupling agent and property enhancements resulted from a chemical linkage between hydroxyl groups on lignocellulosic fiber surfaces and the thermoplastic polymer.[9] The proof of a chemical reaction of MAPP with bleached Kraft pulp fiber was confirmed by an infrared absorption band near 1730 cm^{-1} which varies with carbonyl content.[10] Nucleation densities were significantly increased with the addition of MAPP from 1 to 10% and induced TCL around the wood fiber with the sufficient amount of nuclei.[11] The nucleation ability was also increased with silane (SiH_4) treatment on the wood surface and a uniform spherulitic structure on wood fibers was observed.[12]

The nucleation ability, fiber/matrix adhesion, and the transcrystallization of thermoplastic polymers is also related to chemical contamination and topography of the fiber surface.[13] While a poor crystallization behavior of PP was observed with regenerated cellulosic fibers, cotton and purified wood fibers easily induced transcrystallization when the surfaces were exposed.[2]

Oxygen/carbon (O/C) ratios of softwood fibers with different percentages of the C_1 (C—H), C_2 (C—O), C_3 (O—C—O, and C=O), and C_4 (—COOH) are shown in Table I. All pulps have O/C ratios lower than pure cellulose (0.83) but higher than that of pure lignin (0.33). The high carbon content indicates the presence of increased lignin and extractive concentrations on the fiber surface. The kraft pulping process may contribute to the partial elimination of extractives, fatty acids and their ester, sterols, and terpenes, and phenolic materials such as lignans and lignin. All of these compounds have higher carbon contents than polysaccharides and their removal makes the holocellulose more accessible on the fiber surface. On the basis of the above considerations, the increase of O/C ratio upon the post-treatment of the pulp appears to be a logical consequence of the increased hydroxyl groups on the wood fiber surface. The improvement of mechanical properties of handsheets made from kraft pulp fibers is also suggestive of a higher exposure of holocellulose on the fiber surface.[14,15] As the chemical composition of the fibers can be important for transcrystallization growth,[16] the O/C ratio was monitored to better understand the effect of surface chemistry on composite performance and transcrystalline development.

The two most common methods to measure the O/C ratio is through energy dispersive X-ray analysis (EDXA) and X-ray photoelectron spectroscopy (XPS). In general, the surface sensitivity of the EDXA in energy levels of a kα X-ray source is about 1–2 μm depending on the surface conditions of natural fibers, voltage setting, detector angle, detector type, and optimum collection time.[17] Conversely, XPS, also known as electron spectroscopy for chemical analysis, is a surface analysis technique used to obtain oxygen/carbon (O/C) ratios on fiber surfaces with 3–10 nm in surface sensitivity.[18–21] The XPS is often considered superior to EDXA when nano scale resolutions are desired, but can be disadvantageous when mean O/C ratios at the micrometer scale are

TABLE I
The Oxygen/Carbon (O/C) Atomic Ratios and the Relative Amounts of Different Carbons (C_1s) of Model Compounds and Components in Softwood Fibers[15]

Model compound	O/C	C_1	C_2	C_3	C_4
Cellulose (theoretical)	0.83	–	83	17	–
Bleached kraft pulp	0.80	6	75	18	1
Arabinoglucuronoxylan (theoretical)	0.81	–	78	19	3
Xylan (from pulp)	0.83	5	67	24	4
Lignin (theoretical)	0.33	49	49	2	–
Kraft lignin (from pulp)	0.32	52	38	7	3
Oleic acid (theoretical)	0.11	94	–	–	6
Extractives (from pulp)	0.12	93	5	–	2

C_1, % of carbon bound to hydrogen or carbon atoms only (C—H); C_2, % of carbon with one bond to oxygen (C—O); C_3, % of carbon with a double bond to oxygen or with single bonds to two oxygen atoms (O—C—O and C=O); C_4, % of carbon in carboxyl groups (—COOH).

needed. Additionally, the quantitative analysis was easy to access with a scanning electron microscope (SEM), and the technique is common in plant and animal cell analysis.[22,23]

The goal of this study was to better understand the relationship between dynamic mechanical properties and the growth of TCL using unbleached and bleached kraft pulp fibers. The effects of the crystallization process on strength properties of WPC were studied using PP as a semicrystalline polymer. Previous findings have focused on clarifying certain influences of the PP crystallization on the nonwood fiber surface and illustrate limited aspects of crystallization behavior in WPC. Therefore, this study focused not only on the effect of a coupling agent but also on morphology of the pulp fiber surface.

MATERIALS AND METHODS

Materials

Unbleached and bleached kraft pulp fibers were obtained from Potlatch Co. in Lewiston, Idaho. The wood species was Western hemlock (*Tsuga heterophylla*). Dried wood fibers were milled using thomas-wiley laboratory mill (Model 4) to pass through a 20-mesh screen.

The commercial PP and MAPP were EXXON PP-7292W (Exxon Mobil Company, Baytown, TX) and Epolene G-3003 (Eastman Chemical Company, Longview, TX,), respectively. Three formulation types of the matrix polymers were 100% PP, 100% MAPP, and 95% PP/5% MAPP which was precompounded using a miniature injection molder in the laboratory.

Instruments

For analyzing oxygen/carbon (O/C) ratios, a scanning electron microscope with energy dispersive X-ray analysis (SEM-EDXA) was used. The characterization of surface morphology of the kraft pulp fibers was investigated using a JEOL scanning electron microscope (SEM: AMRAY 1830). Smooth surface, damaged surface, and ends of 20 wood fibers in each location were used for surface properties and chemical composition analysis. The EDXA was used for the quantitative analysis of chemical elements on the surfaces of different fiber types. Quantitative chemical elements (Fig. 2) and O/C ratios of kraft fibers were carried out with an EDXA detector equipped with a dual ultrathin beryllium window. This analysis was intended to clarify the element composition of the aggregates between 10 and 30 μm. For the surface morphology and chemical element analysis, mounted fibers were coated with an approximately 15-nm 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 10 kV with magnifications from 1000 to 5000×. For SEM-EDXA analysis, an accelerating voltage of 10 kV and a working distance of 22 mm were used. Both specimen tilt and detector angle were 40.5° to optimize the signal for X-ray microanalysis. The analysis represented a quantitative result expressed in O/C ratio and in photomicrographic images to describe the surface roughness.

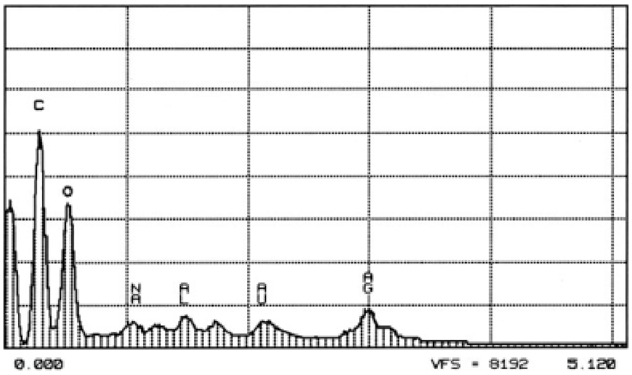


Figure 2 Chemical elements collected from scanning electron microscope with energy dispersive X-ray analysis (SEM-EDXA) with a dual ultrathin beryllium window for the light element analysis on fiber surfaces of the bleached kraft pulp.

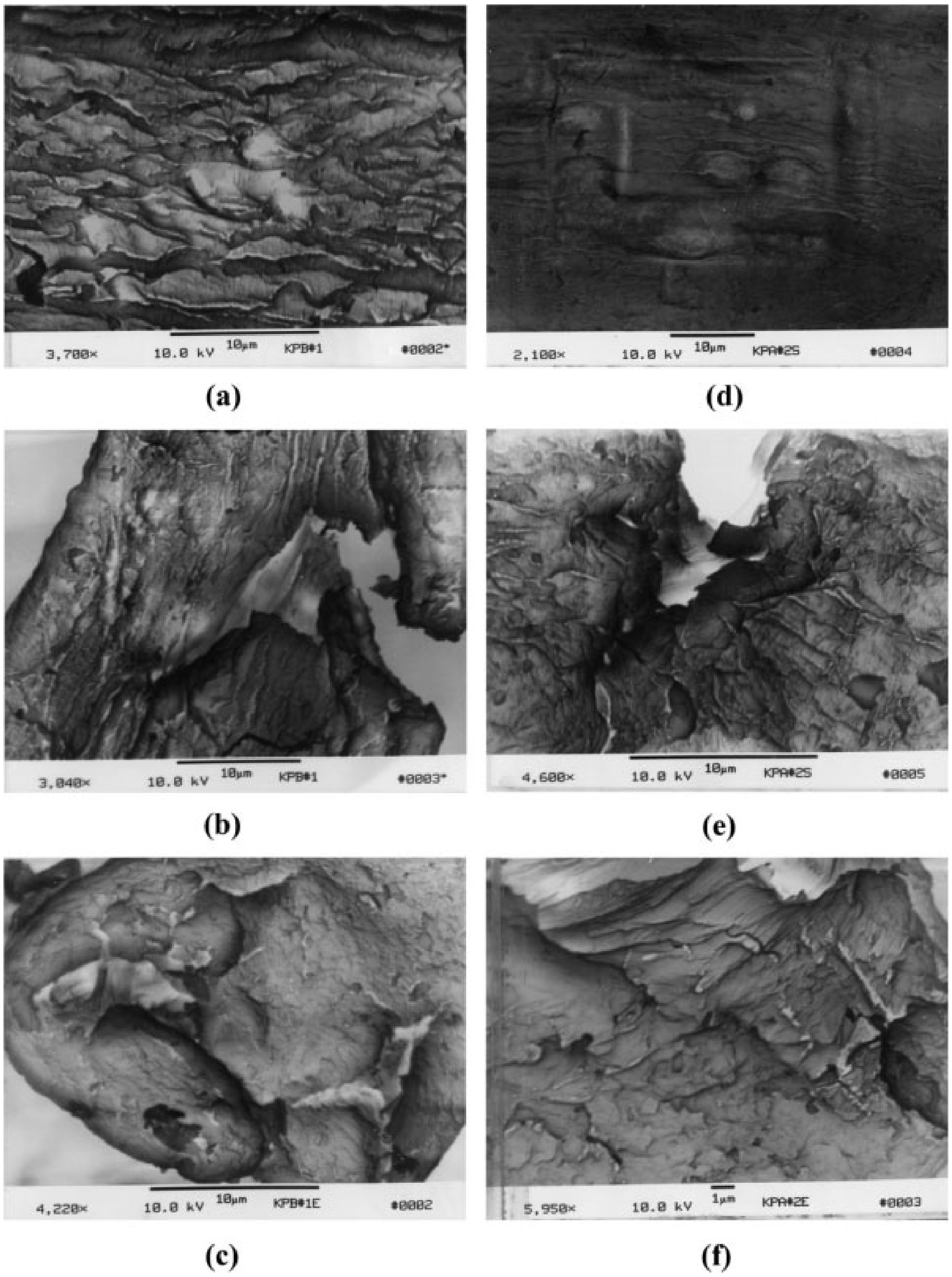
TABLE II
Dynamic Mechanical Analysis (DMA) Set Up for the Evaluation of the Mechanical Properties of Laminated Handsheets with Different Thermoplastic Combinations

Test parameters	Set up
Mode	Dual cantilever fixture
Temperature	From 200 to 100°C
Strain amplitude	5×10^{-4}
Frequency	1 Hz
Initial load	40 g

Polarizing light microscopy (PLM: Zeiss Universal microscope) with a Leitz 350 heating stage was applied to observe transcrystallization behaviors of different PP/MAPP combinations on the wood fibers. Nucleation densities as functions of surface conditions and polymer types were collected from the early stage of melt-crystallization process. The number of nuclei was counted from micrographs and standardized by a unit area of fiber surface. Crystal and transcrystal growth rates of polymer combinations were examined on the wood fiber surface. An equation to calculate a modified growth rate is:

$$G = \frac{R_{n+1} - R_0}{T_{n+1} - T_n} (n = 0, 1, 2, 3, 4, \ldots) \tag{1}$$

where G = growth rate of crystal and transcrystal; R = radius changes of crystal and transcrystal;



(a) (d) (b) (e) (c) (f)

Figure 3 The observational positions of smooth (a, d), damaged (b, e), and fiber end (c, f) for the unbleached (a–c) and bleached (d–f) kraft pulp fibers for the scanning electron microscope with energy dispersive X-ray analysis (SEM-EDXA).

T = time difference in the photographing; n = number of the photographing.

The PLM used a Nikon F2 camera for photographing the transcrystallization process with magnifications of 265× and 320×. The evaluation of the correlations from the surface transcrystalline layer to strength properties of the WPC was based on the measurements of a dynamic mechanical analysis (DMA: Rhometrics solid analyzer RSA II) in dual cantilever mode. The dual cantilever fixture held a solid rectangular sample composite in horizontal position to prevent sample shrinkage as temperature changes from 200 to 100°C. Storage modulus (E'), the phase angle (tan θ), and first time derivative (dE'/dt) were measured by DMA, which provided solidification details of the thermoplastic polymer with temperature changes.

Sample preparation and procedures

The pulp fibers (about 20–50 μm in diameter, 150 μm–2.4 mm in length) were placed on the top of molten plastic film at 200 °C ± 1 °C. After the sample was covered by a cover glass, slight pressure (0.2 MPa) was applied to minimize the sample thickness (∼ 30 μm) and the final sample was moved to the

TABLE III
Ratios of the Chemical Elements on the Three Different Positions of the Wood Fiber Surface

Fiber type	Overall O/C ratios[a]	Surface type	Ratios[b] O/C	Na/C	Ca/C
Unbleached kraft pulp	0.74 (0.18)[c]	Smooth	0.6	0.069	0.005
		Damaged	0.45[d] (1.12[e])	0.074	0
		Fiber end	0.53[d] (1.09[e])	0.131	0.012
Bleached kraft pulp	0.81 (0.14)[c]	Smooth	0.87	0.008	0.003
		Damaged	0.67[d] (1.15[e])	0.002	0.003
		Fiber end	0.57[d] (0.89[e])	0.002	0.005

[a] Average of 60 samples.
[b] Average of 20 samples.
[c] Standard deviation.
[d] Lower range of the data collection (average of 10 samples).
[e] Higher range of the data collection (average of 10 samples).

microscope heating stage. The temperature of the heating stage for the microscopic observation was 150 °C ± 1 °C and remained constant for 25 h. An image was captured every 3 h during the 25-h period.

For the DMA samples, pulp handsheets were made (specific gravity of 1.0 g cm^{-3}) after wood fibers were broken down to a 20-mesh size. Sample composites were made using two handsheets (0.35–0.57 mm in thickness per sheet) with a PP film (0.2 mm in thickness) between them using a laboratory hot plate for lamination (Eumetric programmable oven, Micromet Instruments, Inc.) at 200°C for 10 min under slight pressure and another 5 min after it was turned over. The average dimension was 50 mm × 6.07 mm × 0.94 mm. Table II shows instrument settings for the DMA measurement.

RESULTS AND DISCUSSION

Surface analysis using SEM

Figure 3 shows SEM micrographs with three EDXA scan positions on the surface of bleached and unbleached kraft pulp fibers. The EDXA monitored chemical element compositions on the fiber surfaces. Table III shows the results of O/C ratios from the scan positions of fiber surfaces. The O/C ratios from the damaged surfaces and the ends of wood fibers had a higher oxygen content compared to that from the smoother surfaces of the bleached and unbleached kraft pulp fibers. Oxidation process and redeposited materials on the exposed fiber surfaces provided polymer nucleation sites with extended surface areas. Therefore, the crystallization process or single crystal appearances on the fiber surfaces depended on both a surface oxidation of raw materials and redeposited materials on the surfaces. It should be also noticed that the overall O/C ratios obtained from EDXA was 0.81, which closed to published ratio shown in Table I. The inorganic elements may influence the reduction of O/C ratios at the damaged and end regions. Conclusively, the influence of O/C ratios at the ends and on damaged surfaces of fibers reflected on the nucleation and single crystal growth of semicrystalline polymer combinations (Fig. 4).

Polarizing light microscopy observations

The PLM observation on the surface of unbleached and bleached softwood kraft fibers shows an identical process of crystallization and transcrystallization with the thermoplastic types. Figures 4 and 5 show the PP crystallization on the unbleached and bleached kraft pulp fibers for 25 h observation at 150°C. The micrographs showed that morphological characteristics and nucleation density played an important role of the polymer nucleation on the wood fiber with different MAPP combinations. Nucleation occurred where damaged fiber surfaces and fiber ends interacted without using a coupling agent. However, it was hardly observed on the smooth surfaces of the fibers. Hence, the nucleation density was insufficient to form transcrystalline layer along the smooth fiber surface. An increased percentage of a coupling agent in the thermoplastic polymer could increase the transcrystallinity and nucleation density on both fiber types. The figures also clearly presented that the crystal growth initialized at the end of wood fiber and fracture surfaces along the linear surface of the fiber. The different sizes of spherulites were also observed between 95% PP/5% MAPP and 100% MAPP combinations. A smaller diameter of spherulites in the bulk area and on the fiber surface was observed with MAPP. Increased nucleation density with a small radius of spherulites on the fibers possibly induced the transcrystallization

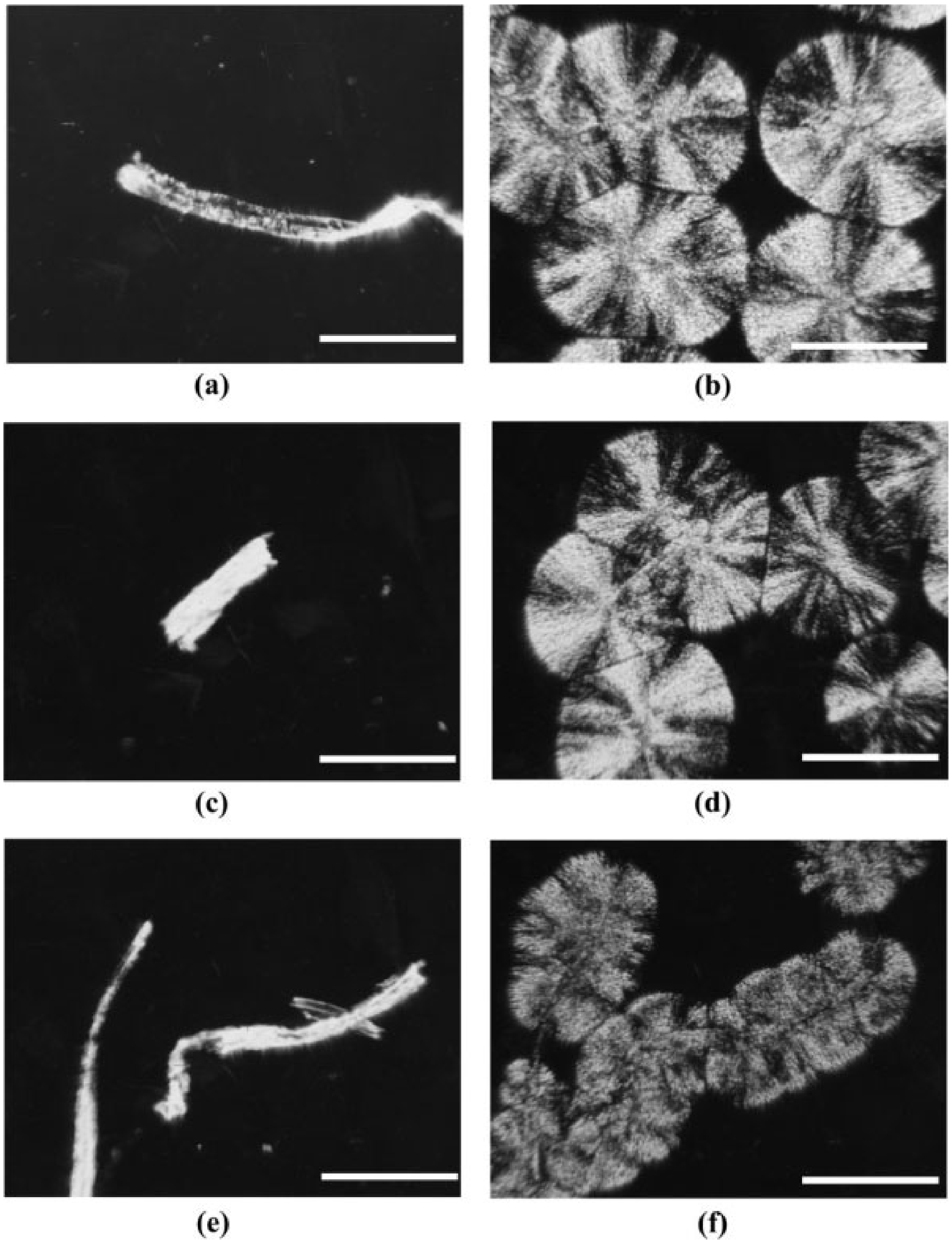


Figure 4 Microscopic observation of crystallization behavior at 150°C. (a) 30 min; 100% PP on the surface of unbleached Kraft pulp fiber, (b) 1200 min; 100% PP on the surface of unbleached Kraft pulp fiber, (c) 30 min; 100% PP on the surface of bleached Kraft pulp fiber, (d) 1200 min; 100% PP on the surface of bleached Kraft pulp fiber, (e) 30 min; 95% PP/5% MAPP on the surface of unbleached Kraft pulp fiber, and (f) 1200 min; 95% PP/5% MAPP on the surface of unbleached Kraft pulp fiber. – Scale bars = 100 μm.

of the semicrystalline polymer. Transcrystallization happens after the spherulites impinge each other. Table IV shows the required nucleation density on the wood fiber surfaces to induce TCL at 150°C.

No transcrystallization appeared on both pulp fibers with PP. However, the addition of MAPP contributed to extended nucleation ability on both the unbleached and bleached fiber surfaces. The bleached pulp fiber showed more number of nuclei than the unbleached pulp fiber. Fiber types and the MAPP addition affected an increased nucleation ability of semicrystalline polymers and induced the transcrystalline layer around fiber surfaces. The nucleation density of 100% MAPP with both fiber types was higher than other mixing ratios (Fig. 5). Transcrystallization was induced in the early stage of the crystallization process from the PLM observation. Damaged surfaces and ends of wood fibers had higher nucleation ability even with 100% PP. The ends of wood fibers and damaged surfaces exposed reaction groups or rough surfaces to the semicrystalline polymer and thus induced nucleation. The cellulose molecules are changing into disordered or amorphous regions. The length of the crystallites is

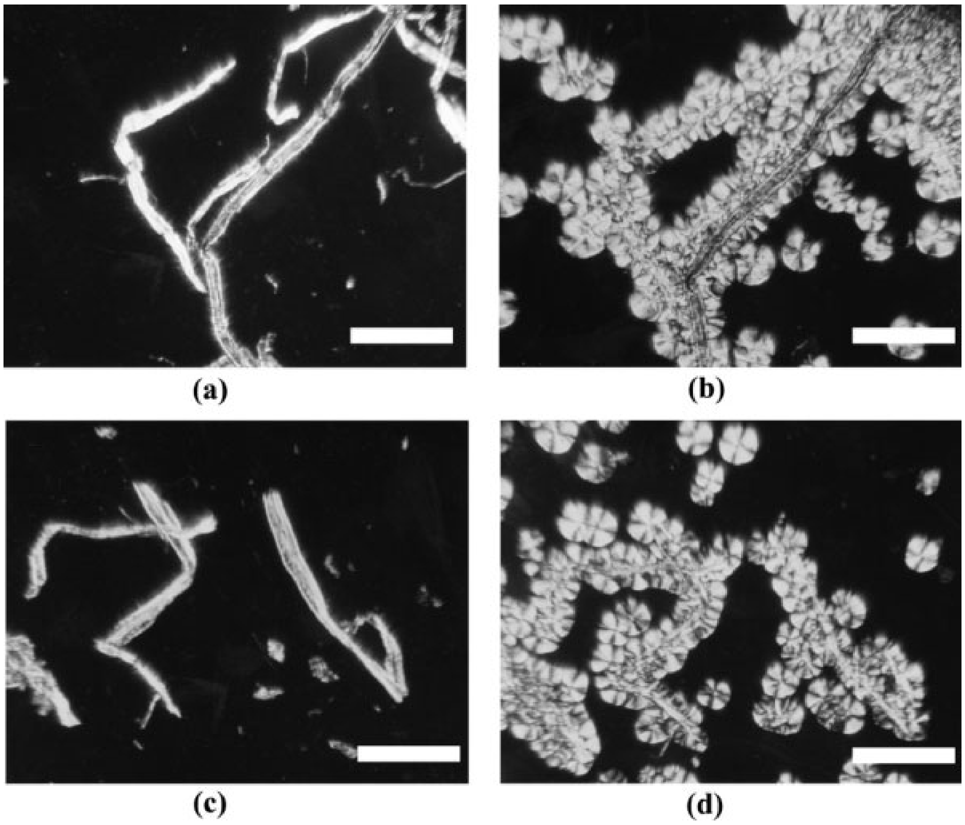

(a) (b) (c) (d)

Figure 5 Microscopic observation of crystallization behavior of 100% MAPP on the surface of Kraft pulp fiber at 150°C. (a) 30 min; unbleached, (b) 420 min; unbleached, (c) 30 min; bleached, and (d) 420 min; bleached. – Scale bars = 200 μm.

100–250 nm in pure cellulose.[15,24] The relatively larger amorphous regions are more highly penetrated and are more susceptible to hydrolysis reactions. Therefore, hydroxyl groups in the amorphous regions can easily react with MAPP which also influenced the nucleation density of polymer matrixes on the surface of wood fibers.

Figures 6 and 7 show different growth rates in the bulk area and on the fiber surfaces. The growth rate of spherulites in the bulk area was 20% higher than that on the fiber surface. The slope of growth rate at the higher temperature was very low with PP. In this study, the growth rate for both 100% PP with both fiber types and 95% PP/5% MAPP with unbleached pulp fibers showed slow growth. However, 100% MAPP with both fibers and 95% PP/5% MAPP for bleached pulp fibers had high growth. In the short period at 150°C, the transcrystallinity is significantly increased with the addition of MAPP to the PP matrix. Furthermore, the lack of clustering of low and high O/C ratio groups (before and after bleaching, respectively) in Figures 6 and 7 suggested that the fiber to thermoplastic polymer interface played a larger role on transcrystalline growth than that for the fiber surface chemistry alone. This

TABLE IV
The Minimum Number of Nuclei on the Linear Surface of the Different Wood Fibers to Create Transcrystallization at 150°C

Fiber type	100% PP	95% PP/5% MAPP	100% MAPP
KBB	N/A	20/mm	37.5/mm
KAB	N/A	44.4/mm	57.1/mm

KBB, kraft pulp before bleaching; KAB, kraft pulp after bleaching; PP, polypropylene; MAPP, maleic anhydride polypropylene.

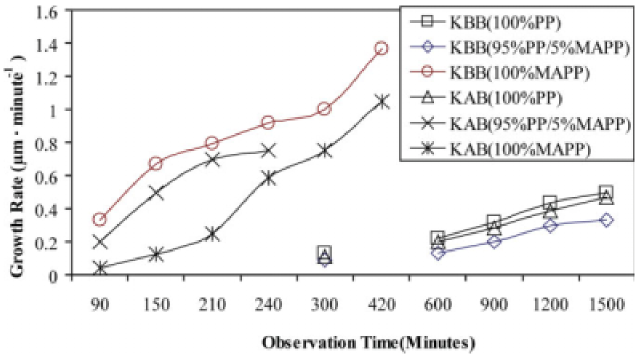


Figure 6 Growth rate of spherules during the crystallization process in the bulk area at 150°C. KBB, kraft pulp before bleaching; KAB, kraft pulp after bleaching; PP, polypropylene; MAPP, maleic anhydride polypropylene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

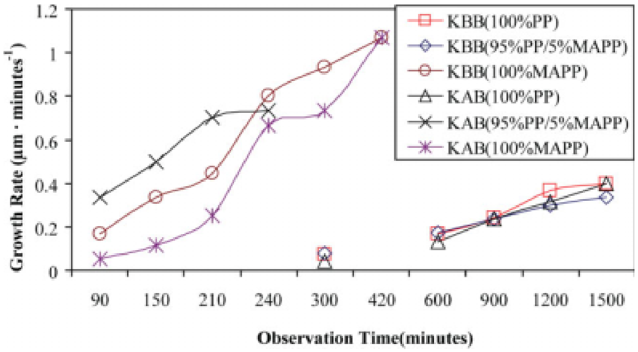


Figure 7 Growth rate of spherules during the crystallization process on the linear fiber surface at 150°C. KBB, kraft pulp before bleaching; KAB, kraft pulp after bleaching; PP, polypropylene; MAPP, maleic anhydride polypropylene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

finding supports that manufacturers of wood plastic composites may better manipulate crystallization behavior by adding MAPP to the PP matrix as opposed to that just do the fiber modification.

Figure 8 shows the growth of TCL on the linear wood fiber as a function of time for fiber types and semicrystalline polymers. After an induced transcrystallization, the TCL thickness changes were insignificant under different conditions until the end of the TCL impinges the other spherulites, which possibly grew in bulk and on the fiber surfaces. However, the inducing points of transcrystallization were slightly different among the sample composites. Higher nucleation ability was obtained for those with 100% MAPP and bleached softwood fiber formed a TCL in an earlier stage.

Effect of transcrystallization on the dynamic mechanical properties

The contents of a coupling agent resulted in the difference enhancement in storage modulus (E') during the solidification process in the wood fiber-plastic composite (Fig. 9). In the growth rate results for TCL, bleached kraft fiber with 95% PP/5% MAPP combination had the highest growth rate on the fiber surface. The DMA results also indicate a possible relationship between growth rate of TCL and increased dynamic mechanical properties. The modulus was 26.7% greater modulus when bleached pulp fibers were used and a 52% difference was shown between 100% PP and 100% MAPP. Consequently, the enlargement in E' was reflected by the thickness of TCL growth and nucleation density on the surface of wood fiber. Different fiber surfaces and chemical composition also contributed to the increased dynamic mechanical properties of WPC. For example, Table I showed that bleached fibers had higher cellulose compositions as conjectured through the higher O/C ratios. The higher O/C ratio content suggested higher cellulose content was present on the surface of the bleached kraft fiber. The higher O/C ratio coupled with addition of MAPP resulted in the highest E'. This suggested that manufacturers could optimize E' by both adding MAPP and using fibers with high O/C ratios.

The rate of dE'/dt based on E' changes is shown in Figure 10. Yin et al.[11] found the maximum rate of dE'/dt, used as an index of crystallization rate, corresponded with increased crystallinity. The figure also showed the peak temperatures (T_C) among the three semicrystalline polymer types with two fiber types from the polymer melt using dynamic mechanical analyzer (DMA). When the percentage of MAPP was increased from 5 to 100%, the maximum crystallization temperature decreased. However, the bleached fiber showed a different trend compared to the unbleached fiber with any percentage of MAPP. The recovery of storage modulus (E') from each polymer melt also characterized transcrystallization behaviors

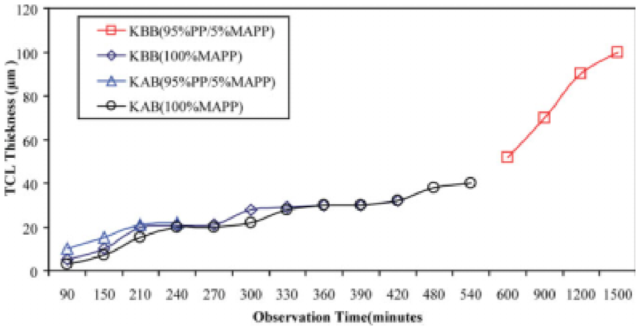


Figure 8 Transcrystalline layer (TCL) thickness changes of the different observation time with two fiber types and three thermoplastic combinations at 150°C. KBB, kraft pulp before bleaching; KAB, kraft pulp after bleaching; PP, polypropylene; MAPP, maleic anhydride polypropylene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

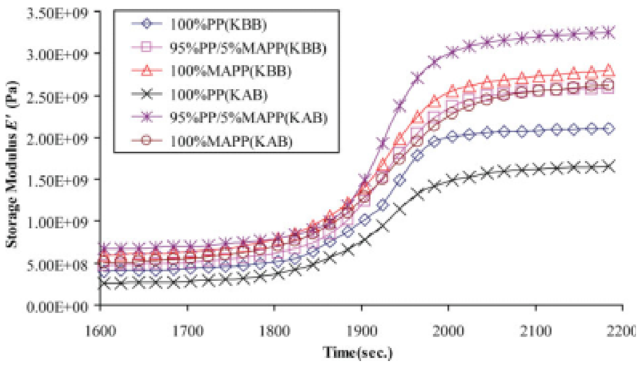


Figure 9 Storage modulus (E') changes of wood fiber-plastic composites due to temperature changes from 200 to 100°C. KBB, kraft pulp before bleaching; KAB, kraft pulp after bleaching; PP, polypropylene; MAPP, maleic anhydride polypropylene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

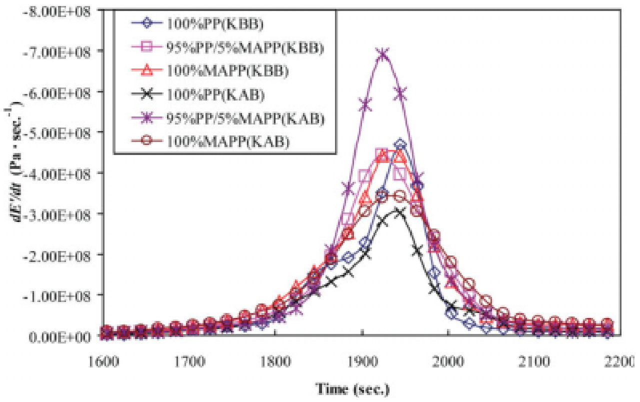


Figure 10 Rate of first time derivative (dE'/dt) based on storage modulus (E') changes of wood fiber-plastic composites due to temperature changes from 200 to 100°C. KBB, kraft pulp before bleaching; KAB, kraft pulp after bleaching; PP, polypropylene; MAPP, maleic anhydride polypropylene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the semicrystalline matrixes such as PP and high-density polyethylene (HDPE).

CONCLUSIONS

The following conclusions can be drawn from this study of the transcrystallization behavior on the fiber surface.

1. Surface morphology of the wood fiber positively affected the induction of transcrystallization of semicrystalline polymer. It was shown that the nuclei were induced at the ends of the pulp fibers and damaged fiber surfaces.
2. Based on the result of EDXA analysis, the crystallization process or single crystal appearances on different wood fiber surfaces depends on the degree of the oxidation process of raw materials and addition of chemical contaminants.
3. Poor crystallization was observed on the surface of unbleached and bleached Kraft pulp fibers with pure PP, and no TCL appeared along the wood fibers. However, bleached wood fibers with broken ends and damaged surfaces might have exposed reactive groups, and developed nucleation sites and higher nucleation density, which induced transcrystallization.
4. Growth rate and size of spherulites were positively affected by the addition of MAPP to the thermoplastic polymer. The thickness of TCL on the fiber surface and the radius of spherulites in the bulk area decreased with the MAPP addition. Furthermore, many smaller crystals were observed both in the bulk area and along the pulp fiber surfaces with 100% MAPP.

It is assumed that the dynamic mechanical properties of WPC can be correlated with the TCL thickness and nucleation density on the surface of pulp fibers. For increasing numbers of nuclei on the linear fiber surface to induce transcrystallization, the coupling agent can play an important role. However, some results from the light microscopy observation and DMA do not support this assumption because the nucleation ability can also be affected by the redeposit materials and surface conditions of the pulp fibers. A comprehensive study of the surface properties and chemical contaminants on pulp fibers will be required to obtain a better understanding of this matter.

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