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# Heterogeneous Nucleation of a Semicrystalline Polymer on Fiber Surfaces

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## Abstract

Nucleation phenomenon as affected by the surface conditions of six identical wood/non-wood fibers with three levels of fiber treatments were investigated by a combination of complementary techniques. This study was based on results of a preliminary study on the influence of surface characteristics of thermo-mechanical pulp (TMP) fibers on the transcrystalline layer (TCL) growth and its correlation with interfacial strength properties. Surface morphology of fiber material and heterogeneous nucleation phenomenon on the fiber material was carried out using scanning electronic microscopy and polarizer light microscopy. The nucleation efficiency was examined in a

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polymer matrix to determine unity factors ( $\phi$ ), which directly explains Gibbs free energy in a correlation of homogeneous and heterogeneous nucleation. The factor was generated from the crystalline deposit angle measurement on the fiber surface during isothermal crystallization temperature at  $140^\circ \pm 0.1^\circ\text{C}$ . Both measurements indicate that surface properties of extracted and surface washed fibers influence surface induced heterogeneous nucleation of polypropylene. Morphological changes on the fiber surface were reported due to an elimination of relatively small particles from each level of surface treatment and fewer particles on the fiber surface indicated decreased nucleation ability on the surface.

## Introduction

The occurrence of an extended source of nuclei confined on the wood fiber surface is called crystallization. The term transcrystallization is used when nucleation density is considerably high. A vast amount of research has been conducted on various aspects of transcrystallinity in fiber-reinforced semi-crystalline polymer composites. The studies have focused on mechanical properties, which are affected by transcrystallinity more than crystal growth in the bulk (Sharples 1966, Mullin 1993, Quillin 1993, Lin 1999,

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Ebengou 1997, Hsiao 1990, Chang 1977). However, a detail nucleation mechanism on the wood fiber surface remains uncertain and insufficient to explain material functionality on the interfacial phenomenon of matrix materials.

Previous researchers have proposed concepts to increase the nucleation ability by modifying or controlling the polymer matrix and surface characteristics such as copolymer, additives, chemical composition, surface roughness, and surface free energy (Gray 1974, Liu 1994, Wang 1996, Lee 2002). However, an increased surface free energy was an unlikely influence on nucleation ability to induce transcrystallization on the fiber surface because a transcrystalline layer (TCL) was generated on the fiber surface regardless of whether the surface free energy was changed by surface treatments (Westerlind 1988, Hsiao 1990, Mahlberg 1998). Wang (1996) found that a thicker TCL formed at higher temperatures, and larger residual stresses at the interface indicate an important role of the mechanical strength of the composites compared to crystallization at a lower temperature. Yin (1999) found that the nucleation density with addition of MAPP (maleic anhydride polypropylene) from 1 to 10 percent was significantly increased, and a sufficient amount of nuclei on a single wood fiber induced transcrystallization around the wood fiber. The nucleation ability is also related to chemical containment and topography of the fiber surface during the nucleation process of thermoplastic polymers (Wang 1994). However, a clean natural cellulose surface of cotton and purified wood fibers easily induced transcrystallization when the surface was exposed (Gray 1974).

In the acid-base theory, hydrogen bonding is the main form of bonding at a polymer interface with hydroxyl group rich surfaces. The theory is based upon interaction energies that are dependent on the acidity of the hydrogen donor and the hydrogen acceptor. Acid-base interactions cover any interaction that involves the sharing of an electron pair, particularly hydrogen bonding. In the case of cellulose, the acid-base interactions can be described as predominantly hydrogen bonding with a surface dominated by hydroxyl groups. Interfacial energy and internal bond (IB) measurements indicate a strong correlation between the hydroxyl-rich (acid-base) interface and good adhesive properties (Jensen 1978, Pizzi 1994). An important application of interfacial acid-base bonding is the predictable enhancement of interfacial bonding accomplished by surface conditions of

materials to enhance the interfacial acid-base interactions (Fowkes 1987).

Attractive forces exist between any molecules when their distance of separation is closer than 9Å (Chung 1991). The attractive forces are usually insufficient for strong bonding when the molecules are small, but the attractive forces become strong when the molecules are large. A classical theory of polymer nucleation is based on changes of the overall excess free energy ( $\Delta G$ ) between small particles as a foreign body and semicrystalline matrix. Gibbs free energy is also influenced by intimate molecular contact, volume of the matrix, and size of the nucleus. However, most of the nucleation is heterogeneous induced by foreign particles or the surface of materials rather than a spontaneously induced nucleation known as homogeneous nucleation (Mullin 1993).

$$\Delta G = \Delta G_S + \Delta G_V = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_V \quad [1]$$

$\Delta G$  (Equation [1]) is generally combined with two quantities of positive (surface free energy;  $\Delta G_S$ ) and negative (volume free energy;  $\Delta G_V$ ). The Gibbs free energy at the  $\gamma_c$  is called a critical free energy ( $\Delta G_{Crit}$ ). However, the heterogeneous nucleation on the foreign surface differs from the homogeneous nucleation because of differences in nucleus sizes ( $\gamma_c$ ). The differences are also associated with the critical free energy ( $\Delta G_{Crit}$ ). Therefore, heterogeneous nucleation has less unity than homogeneous nucleation and the unity factor can be expressed with a correlation between two different nucleations.

$$\Delta G'_{Crit} = \phi \Delta G_{Crit} \quad [2]$$

The factor highly correlates with interfacial tensions at the boundaries of crystalline deposit, amorphous region, and foreign surface. The contact angle ( $\theta$ ) between a crystalline deposit and a wood fiber surface can be generated to calculate the unity factor. The factor equation is:

$$\phi = \frac{\Delta G'_{Crit}}{\Delta G_{Crit}} = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \quad (0 < \theta < 180) \quad [3]$$

## Objectives

The objectives of this study were to:

1. determine interaction mechanisms at nucleation sites caused by fiber surfaces,

- investigate the effectiveness of increased hydrophobicity of the fiber surface on the polypropylene (PP) matrix, and
- provide factors from the quantitative measurements of crystalline deposit angles and h/E ratios of the crystal deposit system on the fiber surface.

## Materials and Methods

### Materials and surface conditioning

A total of six fiber types (8 bar thermomechanical pulp [TMP], refined mechanical pulp [RMP], commercial TMP, bleached Kraft, unbleached Kraft, and carbon fibers) were used to evaluate the influence of surface morphology and hydrophobicity on the surface induced heterogeneous nucleation phenomenon. Three different fiber conditions (control, extracted, and water soaked) were used. Extraction was performed with dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) on 8 bar TMP fibers, which were produced from juvenile portions in a continuous, pressurized, single-disc refiner (80  $\mu\text{m}$  refiner plate gaps). The Soxhlet extraction was performed in accordance with TAPPI standard T 204 om-88 (Tappi 2004). All of the fiber materials were washed out with distilled water at room temperature after 24 hours of water soaking. The fibers were examined for microscopic morphological changes on the fiber surfaces due to the removal of extractives and extraneous materials. The carbon and Kraft fibers are examples of extreme surface characteristics of hydrophobicity and hydrophilicity as well as changes in the surface chemical compositions.

Polypropylene (Escorene PD7292N E7, Exxon Mobil Chemical Co.) was used for the evaluation of heterogeneous nucleation phenomenon at the interface of the fiber surface and the semicrystalline polymer with an isothermal temperature of  $140^\circ \pm 0.1^\circ\text{C}$ .

### Instruments for monitoring the interfacial phenomena

A polarizing light microscope (PLM) (Leica DM LB 30TL implemented with HCS302-STC200 cold/heating stage) was used to determine the number of nuclei, h/E ratios, and crystalline deposit angles during the crystallization process when each polymer blend was placed with the TMP fibers. The isothermal PLM observation characterized each crystallization process relative to the different surface characteristics of the wood/non-wood fibers with PP. The PLM photomicrographic images were provided h/E ratios and crystalline deposit angles to calculate unity factors ( $\phi$ ) on the linear fiber surface (Fig. 1). A Spot RT digital camera (Diagnostic Instruments Inc., Model #3,1,0 with 1600 by 1200 resolution) was used for developing images as a function of observation time. Image-Pro<sup>®</sup> Plus software was used to conduct the image analysis and collect quantitative measurements of h/E ratios and crystalline deposit angles.

Morphological characteristics of the wood and non-wood fibers were investigated using a scanning electron microscope (SEM) (Hitachi S-3600N). Fibers, which were coated with a thin layer (approx. 15 nanometers) of gold, were observed in the SEM. The morphological characteristics and surface conditions were analyzed from photomicrographic images with image generation conditions of 20 Kv and 1,500x.

Particle size analysis (PSA) was achieved using a particle size analyzer (Ro-Tap) and micrographic image analysis to obtain quantitative particle distributions on the fiber surfaces. The quantitative measurement addressed possible PP nucleation caused by relatively small particles on the fiber surface. Accusizer<sup>™</sup> 770A SIS-Syringe Injection Sampler with a wide dynamic range sensor (LE400-0.5; covers 0.5 to 400  $\mu\text{m}$  of particle radius) was used to analyze parti-

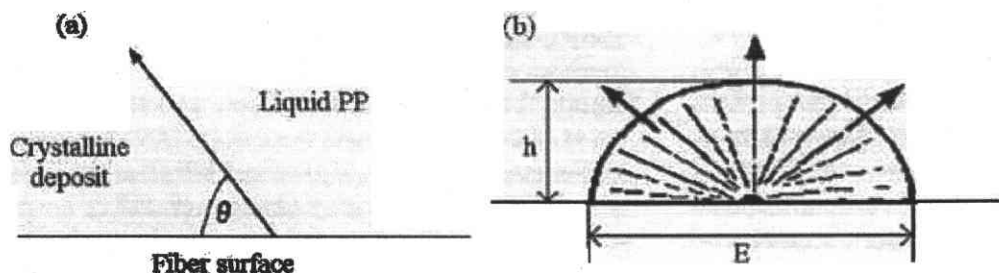


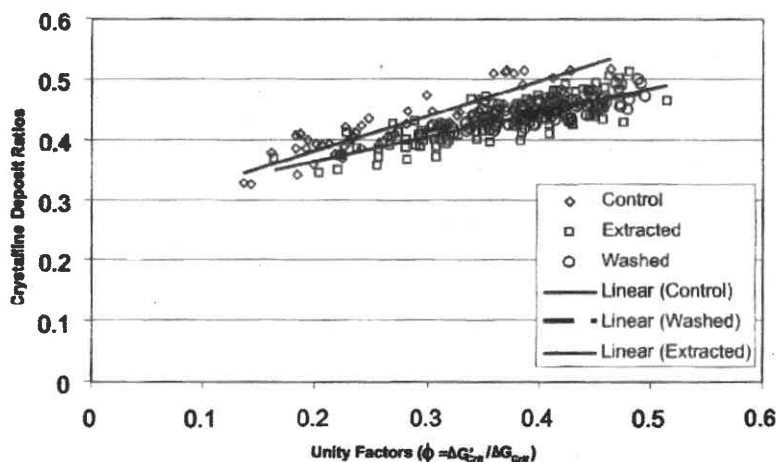
Figure 1. — (a) Measurements for crystalline deposit angles and ratios of lamella deposit between the fiber surface and the bulk area; and (b) h/E ratios.

**Table 1.** — General characteristics of the sample fibers.

Pulping process	Thermomechanical		Kraft		Mechanical	HT Batch
Fiber	8 barJ	Cm_TMP	UKP	BKP	RMP	
Species	Loblolly pine ( <i>Pinus taeda</i> )	Ponderosa pine ( <i>Pinus ponderosa</i> ) Western hemlock ( <i>Tsuga heterophylla</i> ) Western white pine ( <i>Pinus monticola</i> )	Western hemlock ( <i>Tsuga heterophylla</i> )		na	
Producer	BCCUW	Plum Creek MDF, Inc.	Potlatch Co. Lewiston, ID		Inland Empire Paper Co.	Zoltek Companies, Inc.
Properties	175°C preheating	163°C preheating	5% to 7% lignin	99.5% cellulose	na	>99.5% carbon
Moisture content	5.6%	10.5%	5.6%	5.2%	11.8%	0.03%
Extractives	3.2%	3.9%	0.78%	0.36%	1.2%	

8 barJ is 8 bar juvenile (TMP); Cm\_TMP is commercial TMP fibers; UKP is unbleached kraft pulp; BKP is bleached kraft pulp; RMP is refined mechanical pulp; and BCCUW is Bio Composites Center, University of Wales.

**Figure 2.** — Correlation between the crystalline deposit ratios ( $h/E$ ) and unity factor ( $\phi$ ) changes of crystalline deposit angle measurements with the three levels of fiber treatment.



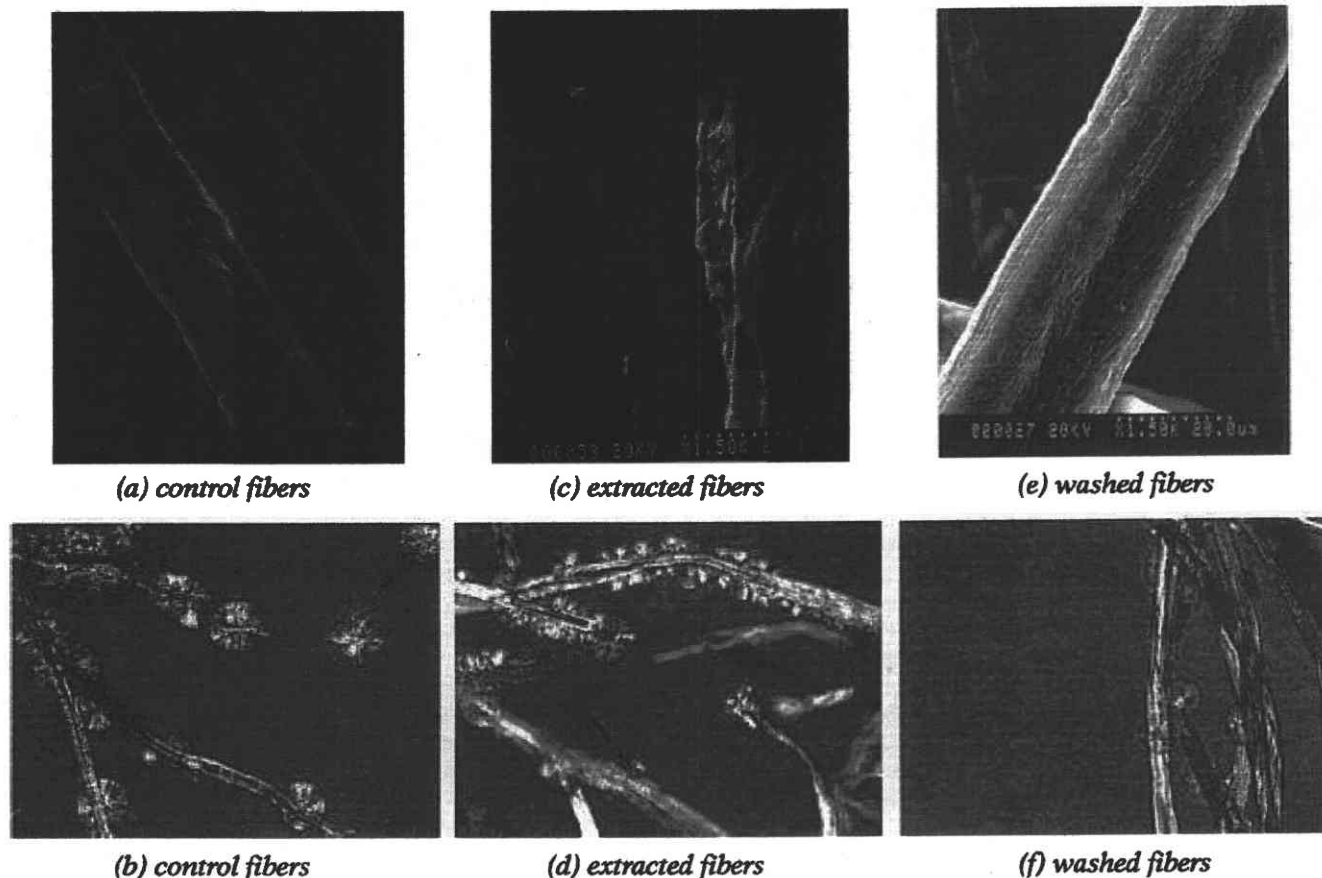
cle sizes on the fiber surfaces. Number of nuclei, particle size, and distribution were generated from PLM and SEM images. Quantitative evaluation of polymer nucleation on the fiber surface from 200x micrographs as a function of unit surface area were determined with a mounted digital camera equipped with Image-Pro Plus software.

### Results and Discussion

It is expected that the fibers would possess similar surface chemical properties due to the removal of extractives and extractable materials from the surfaces (Table 1). The carbon and Kraft fibers also provide extreme surface characteristics of hydrophobicity and hydrophilicity with less extractive. The RMP (fibers produced under the lignin glass transition point of 140°C) had lower extractable materials compared to the TMP fibers. Therefore, there was no lignin rede-

posit after the defibrillation process with the RMP fiber. A higher surface roughness after the process was also noted.

Unity factor ( $\phi$ ) changes from different crystalline angles and crystalline deposit ratios based on PLM observations are shown in Figure 2. The surface morphology and chemistry influenced crystal impurities of fibers and provided a better nucleation site to the PP matrix, and the  $\Delta G'_{crit}$  differences of the fiber surface contribute the nucleation ability of PP. The SEM and PLM results correlated to the unity factor using a method of tabular and numerical comparisons among the fibers. The result also shows what kind of wood fiber surface properties are effective for inducing heterogeneous nucleation and how surface properties influence the purity changes of  $\Delta G'_{crit}$  on the wood/non-wood surface compared to the bulk area. Some degree of material hydrophobicity on the fiber



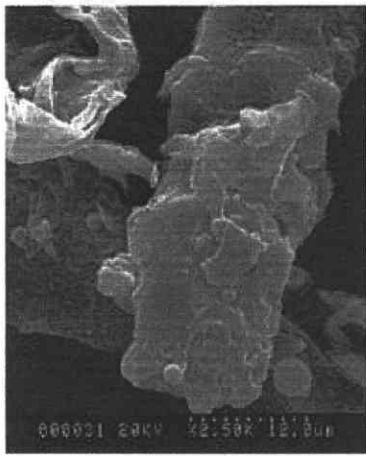
**Figure 3.** - *Heterogeneous nucleation phenomenon associated with the surface morphology due to the fiber treatments.*

surface will be beneficial in the lamella deposit system on a fiber surface and create an intimate contact system between the fiber surface and PP. This mechanism should be addressed in a development of secondary forces (i.e., the role of the van der Waals forces). Surface hydrophobicity of the fiber materials plays a beneficial role on the lamella orientation on the fiber surface.

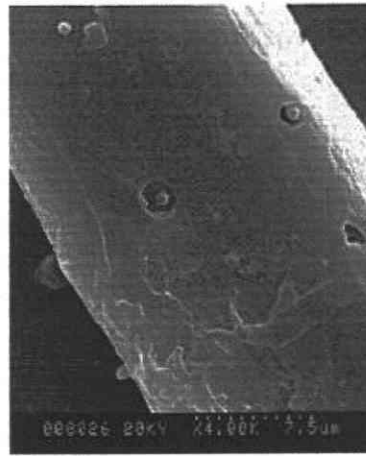
Figure 3 shows heterogeneous nucleation phenomenon associated with surface morphology due to the three levels of fiber conditioning. The micrographs address the morphological changes among the fiber material with each surface treatment. The extraction of the surface did not influence PP nucleation on the extracted fiber surfaces. Surface cracks and particles still remained on the rough surface of extracted fibers. However, the washed surface showed an extreme reduction in the heterogeneous nucleation. The surface showed surface checks but a clean morphology and less particles. Surface roughness could affect the fiber/matrix adhesion and the nucle-

ation ability of semicrystalline polymers (Cai 1997). However, the surface roughness and checks probably did not correspond directly to PP nucleation. Figure 3 also indicates that water isolated materials from the fiber surface plays an important role in the PP nucleation with surface characteristics of chemical compositions and surface free energy.

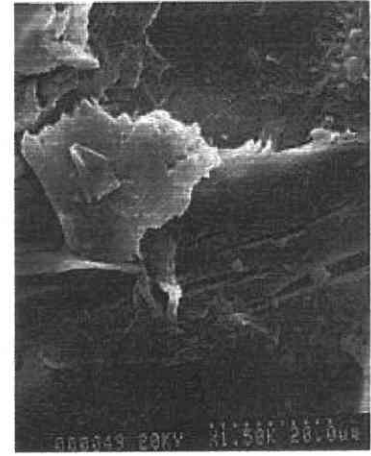
Figure 4 shows particles located on the fiber surface to induce heterogeneous nucleation. Particles of various sizes can be seen on the surface of the wood fibers. Most of the particles are located on surface checks and damaged surfaces. The particles had relatively smooth and round morphology. Based on the nucleation theory, smooth and round surfaces provided lower surface area, which influences Gibbs free energy, as compared to rough surfaces due to the exposed surface area to the molten PP. The function of surface checks and roughness may be a natural holding device for relatively small particles to induce the PP nucleation.



(a) control fibers



(b)



(c)

Figure 4. Particles on the fiber surface to induce nucleation.

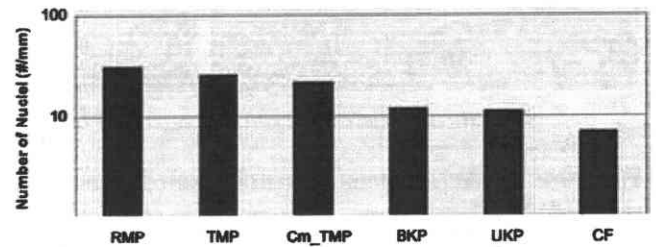
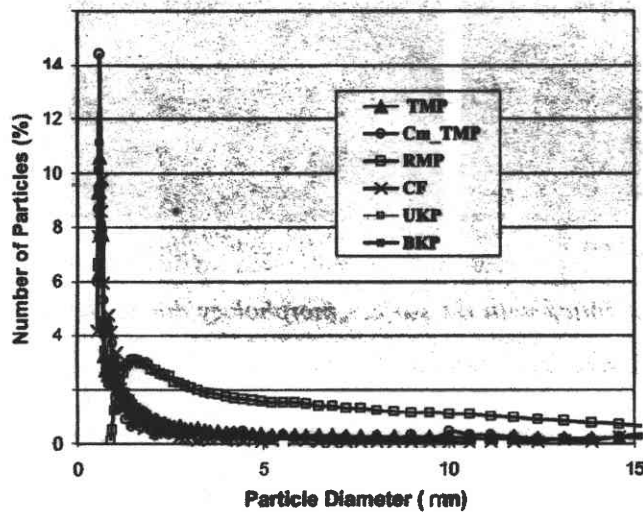


Figure 5. — Particle (left) distribution and (right) number of nuclei on the fiber surface.

Figure 5 shows both particle distribution and number of nuclei on the fiber surface. Wood fibers produced using the mechanical pulping processes also show the highest nucleation ability among the three different pressure conditions. The median from the particle distributions of each fiber types was  $0.64 \mu\text{m}$ , except for RMP ( $2.68 \mu\text{m}$ ). Relatively smaller particles ( $< 0.5 \mu\text{m}$ ) on the fiber surface can be important for the heterogeneous nucleation of PP. However, the instrumental limitation of a wide dynamic range sensor, which covers  $0.5$  to  $400 \mu\text{m}$  of particle radius, indicated further investigation with particle sizes smaller than  $0.5 \mu\text{m}$ . An average radius of nucleus was  $0.64 \mu\text{m}$  and the nuclei radius is much smaller than nucleus.

## Conclusions

The objectives of this study were to determine interaction mechanisms at nucleation sites caused by fiber surfaces, investigate the effectiveness of increased hydrophobicity of the fiber surface on the PP matrix, and provide factors from the quantitative measurements of crystalline deposit angles and  $h/E$  ratios of the crystal deposit system on the fiber surface. Based on the results of this study, the following conclusions can be drawn:

1. rough surfaces serve as a natural particle holding device,
2. smooth and hydrophobic surfaces provide a beneficial role for crystalline deposit,

3. particles and materials extractable from the fiber surface play an important role in heterogeneous nucleation and crystalline deposit, and
4. isolated materials from the fiber surface influence material impurity of the fibers and create polymer nucleation sites.

### Literature Cited

- Cai, Y., J. Petermann, and H. Wittich. 1997. Transcrystallization in fiber-reinforced isotactic polypropylene composites in a temperature gradient. *J. Appl. Polymer Sci.* 65: 71-74.
- Chang, E.P. 1977. Crystallization studies on fire-retardant polypropylene. *J. Appl. Polymer Sci.* 21:937-942.
- Chung, F.H. 1991. Unified theory and guidelines on adhesion. *J. Appl. Polymer Sci.* 42:1319-1331.
- Ebengou, R.H. 1997. Adsorption as a mechanism for nucleating activity: A thermodynamic explanation. *J. Polymer Sci. Part B: Polymer Physics.* 35(9):1333-1338.
- Fowkes, F.M. 1987. Role of acid-base interfacial bonding in adhesion. *J. Adh. Sci. Tech.* 1(1):7-26.
- Gray, D.G. 1974. Polypropylene transcrystallization at the surface of cellulose fibers. *Polymer letters edition.* 12:510-514.
- Hsiao, B.S. and E.J.H. Chen. 1990. Transcrystalline interphases in advanced polymer composites. *Controlled Interphases in Composite Materials*, H. Ishida, Ed. Elsevier pp. 613-622.
- Jensen, W.B. 1978. The Lewis acid-base definitions: A status report. *Chem. Reviews. ACS.* 78(1):778-784.
- Lee, S.Y. 2002. Transcrystallization behavior and interfacial strength of a semicrystalline polymer combined with thermomechanical pulp (TMP) fiber. M.S. Thesis. Univ. of Idaho, Moscow, ID. 72 p.
- Liu, F.P., M.P. Wolcott, D.J. Gardner, and T.G. Rials. 1994. Characterization of the interface between cellulosic fibers and a thermoplastic matrix. *Composite Interfaces.* 2(6):419-432.
- Mahlberg, R., H.E.-M. Niemi, F. Denes, and R.M. Rowell. 1998. Effect of oxygen and hexamethyldisiloxane plasma on morphology, wettability and adhesion properties of polypropylene and lignocellulosics. *Inter. J. Adhe. Adhes.* 18:283-297.
- Mullin, J.W. 1993. *Crystallization*, 3rd ed. Butterworth-Heinemann Ltd. pp. 172-189.
- Pizzi, A. 1994. *Advanced wood adhesives technology*. Marcel Dekker Inc., New York. pp. 2-14.
- Quillin, D.T., D.F. Caulfield, and J.A. Koutsky. 1993. Crystallinity in the polypropylene/cellulose system (I). Nucleation and crystalline morphology. *J. Appl. Polymer Sci.* 50(7): 1187-1194.
- Sharples, A. 1966. *Introduction to polymer crystallization*. Edward Arnold Ltd. London. 21 pp.
- Tappi. 1988. *Tappi test method T204 om-88 Solvent extractives of wood and pulp*. Tappi. Atlanta, GA.
- Wang, G. and I.R. Harrison. 1994. Study of the preferential crystallization of polypropylene on the surface of wood fibers. *In: Proc. of the 52nd Annual Tech. Conf. ANTEC 94. Part 2.* pp. 1474-1475.
- Wang, C. and L.M. Hwang. 1996. Transcrystallization of PTFE Fiber/PP composites (I) crystallization kinetics and morphology. *J. Polymer Sci.: Part B: Polymer Physics.* 34:47-56.
- Wang, C. and L.M. Hwang. 1996. Transcrystallization of PTFE fiber/PP composites (II). Effect of transcrystallinity on the interfacial strength. *J. Polymer Sci. Part B: Polymer Physics.* 34:1435-1442.
- Westerlind, S.B. and J.C. Berg. 1988. Surface energy of untreated and surface-modified cellulose fibers. *J. Appl. Polymer Sci.* 36(3):523-534.
- Yin, S., T.G. Rials, and M.P. Wolcott. 1999. Crystallization behavior of polypropylene and its effect on wood fiber composite properties. *In: Proc. of the 5th International Conf. on Woodfiber-Plastic Composites.* Forest Products Society, Madison, WI. pp. 139-145.

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# **Recent Developments in Wood Composites**

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