Crystallinity in the Polypropylene/Cellulose System. I. Nucleation and Crystalline Morphology

DANIEL T. QUILLIN,[1,†] DANIEL F. CAULFIELD,[2,*] and JAMES A. KOUTSKY[3]

[1] Materials Science Program, University of Wisconsin at Madison, 1410 Johnson Drive, Madison, Wisconsin 53706;
[2] USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53705;
[3] Department of Chemical Engineering, University of Wisconsin at Madison, 1415 Johnson Drive, Madison, Wisconsin 53706

SYNOPSIS

The amount of research on lignocellulosic/thermoplastic composites has increased dramatically. Little attention, however, has been directed towards the subject of crystallinity at the interface (interphase). Optical microscopy and differential scanning calorimetry were used in this work to study crystallinity in the cellulose/polypropylene system. The results verify that cellulose acts as a nucleating agent for polypropylene, producing a transcrystalline region around the fiber. Treatment of the fibers with alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), or stearic acid, inactivates the surface features responsible for transcrystallinity. These treatments also affect the overall degree of crystallinity of the sample. Morphological features, resulting from a transcrystalline or nontranscrystalline interphase, may have a significant effect on mechanical properties. A possible mechanism for the appearance of transcrystallinity involving crystal structure matching is also proposed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

During the processing of a fiber-reinforced thermoplastic composite, interactions between filler and matrix, as well as resultant morphological features, will have a direct effect on the mechanical properties of the composite. Stress transfer from matrix to filler is dependent on the degree of intimate contact between the two phases. The efficiency of this transfer will depend on the structure of the matrix in the vicinity of the fiber. This structure is often referred to as the interphase.

During the cooling of many thermoplastic/fiber systems, the fiber surface acts as a series of nucleating sites for the polymer, resulting in a transcrystalline region around the fiber. This region is characterized by a high density of nucleating crystallites, which, as growth proceeds, impinge upon each other, forcing the crystals to grow perpendicular to the fiber surface with a columnar or disk-like morphology. This phenomenon is also known as row nucleation.

The exact mechanism for transcrystallinity is not fully understood. Explanations proposed include crystal structure similarity,[1] shear stresses due to a mismatch in thermal expansion coefficient,[2] surface energy of the substrate,[3] and absorbed impurities from the bulk.[4] In general, none of these explanations alone is sufficient to account for the appearance of a transcrystalline region.

In polypropylene, several different types of fiber surfaces have been shown to induce transcrystallinity. These include Kevlar,[5,6] nylon,[4–6] poly(ethylene terephthalate),[4,7] carbon,[6] cellulose,[8] and glass[2,9] under certain conditions.

Although numerous articles have been published describing the study of polypropylene/lignocellulosic composites,[10–19] little effort has been devoted to the study of the crystallinity of the interphase in these systems. The purpose of this study is to investigate the effect of various chemical surface treatments on the nucleation ability of cellulose in polypropylene, using optical microscopy and differential scanning calorimetry. The chemicals under investigation are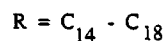 alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), and stearic acid (see Fig. 1). AKD and ASA are both chemical-sizing agents, widely used in the alkaline papermaking process to

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Alkyl Ketene Dimer (AKD)

$$R-CH=C-CH-R$$
$$\underset{|}{}\quad\underset{|}{}$$
$$O-C=O$$

$$R = C_{14} - C_{18}$$

Alkenyl Succinic Anhydride (ASA)

$$
\begin{array}{c}
O \\
\parallel \\
R-HC-C \\
\quad | \qquad\searrow O \\
H_2C-C \nearrow \\
\quad\parallel \\
O
\end{array}
$$

$$R = C_{16} - C_{20} \text{ alkenyl group}$$
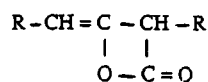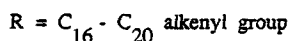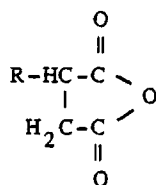
Figure 1 Chemical structures of alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA).

increase the hydrophobic character of the naturally hydrophilic cellulose surface. Both have been shown[20,21] to react with the cellulose surface. Stearic acid is believed to impart its sizing effect without a covalent bond to the cellulose surface.[22]

EXPERIMENTAL

Materials

The polypropylene, used in all tests, was Danaklon SOFT 71 fiber, produced without any surface finishes, obtained from Danaklon A/S (Denmark). This polypropylene typically has a number-average molecular weight of 51,700 and a weight-average molecular weight of 186,000.

Bleached softwood kraft α-cellulose fiber (Acetanier-P), obtained from ITT Rayonier, was used for hot-stage microscopy. Natural ramie fiber (decorticated, degummed, and bleached) and 5.5 denier rayon fiber (North American Rayon Co.) were also used in the investigation. Avicel PH101 microcrystalline cellulose (FMC Corp.) was used for all DSC samples, due to its greater surface area. Avicel has

a specific surface area of approximately 1.84 m^2/g and a crystallinity index of 84.5.[23]

The alkyl ketene dimer used was Aquapel 364 (Hercules) AKD wax, which is produced from a mixture of 55% stearic acid and 45% palmitic acid.[24] Commercial grade ACCOSIZE 18 synthetic ASA size (American Cyanamid) was also used. Impurity content for the ASA is low and consists mainly of residual olefin or maleic anhydride.[25] The stearic acid used (99+%) was obtained from Aldrich. All chemicals were used in reagent-grade toluene solutions to treat the cellulose.

Treatment Method

Approximately 30 mg of cellulose fiber was treated at room temperature with 30 mg of AKD, ASA, or stearic acid, dissolved in 25 mL of toluene. Treatment time was 10 min. After decanting the solution, the fibers were allowed to air-dry in a laboratory hood for 10 min. This was followed by an additional 20 min in a 105°C circulating oven for drying and/ or curing. This resulted in a weight gain of approximately 0.1%. If an orientation perpendicular to the surface is assumed for all of the molecules, surface coverage is approximately 23–29% of a planar oriented monolayer (POML).

Avicel microcrystalline fiber was treated in an identical manner, although treatment levels were of a comparable or slightly higher level to ensure complete surface coverage.

Optical Microscopy

Crystallization behavior was investigated using a Reichart–Jung heating stage under a Leitz optical microscope fitted with polarizers. A video camera, ADR PM-1 photo module, and Polaroid camera were fitted to the microscope for taking micrographs. A small piece of polypropylene film (previously pressed between two microscope slides on a hot plate), along with treated and/or untreated cellulose fibers, were placed on the heating stage and were heated to 200°C. A cover slip was placed on top of the sample and was pressed firmly to help ensure the fibers were completely enveloped in the molten polymer. This was then maintained at 200°C for at least 3 min to produce a blank melt. The sample was then allowed to cool at a rate of approximately 5–10°C/min.

Differential Scanning Calorimetry

DSC samples were made by placing 1.5–5.2 mg of treated or untreated Avicel in the bottom of an alu-

minum sample pan. On top of this, 1.2–3.3 mg of polypropylene fiber were placed. No premixing of the materials was done in this study in order to avoid the loss of cellulose surface treatment before measurement. A later article will discuss the effects of sample mixing.

DSC measurements were carried out under nitrogen using a Perkin–Elmer DSC 7 system. The heating and cooling rate was 10°C/minute. All samples were cycled from 30°C to 200°C, were held at that temperature for 2 min, and then were cooled to 50°C. This cycle was repeated 3 times for each sample to facilitate mixing.

Reported data is the average of the third cycle data for three samples.

RESULTS AND DISCUSSION

Optical micrographs in Figure 2 show the appearance of a transcrystalline region around an untreated cellulose fiber in polypropylene [(a) molten, (b) fully crystallized]. This is identical to results obtained by Gray.[8] When a surface-treated fiber is introduced into the melt, no transcrystallinity is produced, as can be seen in Figure 3 [(a) AKD, (b) ASA, (c) stearic acid]. This contradicts other results[26] obtained with ASA-treated cellulose in polypropylene, where nucleation on the fiber surface was seen. This is most likely due to the lower treatment level employed in that study.

To prove these results were not caused by uneven sample cooling or other artifacts, an untreated and a treated fiber were placed together in the same melt. Figure 4 shows the results upon cooling. As can be seen, the untreated fiber nucleates polypropylene and produces a transcrystalline region, while the treated fiber does not, showing greatly reduced nucleation. Identical nucleation results are seen when Avicel microcrystalline cellulose is placed in the melt.

These results were verified by the DSC results. Figure 5 shows cooling curves for neat polypropylene, polypropylene/untreated cellulose, and polypropylene/treated cellulose. Again, untreated cellulose nucleates polypropylene, producing a high-temperature shoulder on the crystallization curve. Treated cellulose, on the other hand, does not nucleate, and hence no shoulder is observed.

The effect of cellulose on the degree of crystallinity of polypropylene can also be determined using DSC measurements. Table I lists the peak melting temperatures for each sample, the observed melting
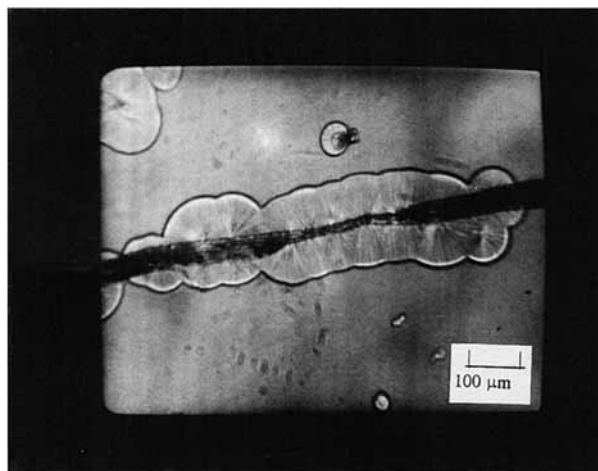
(a)
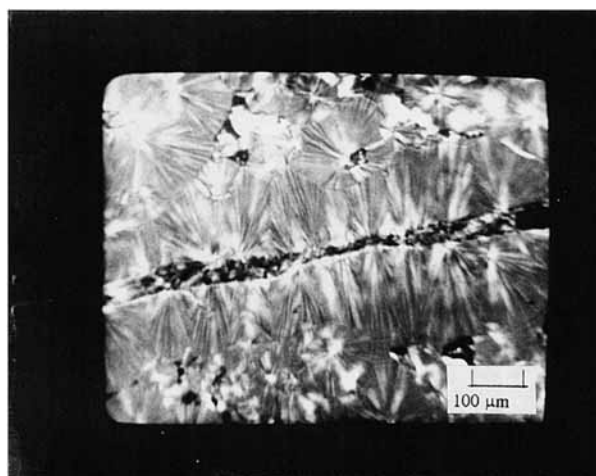
(b)

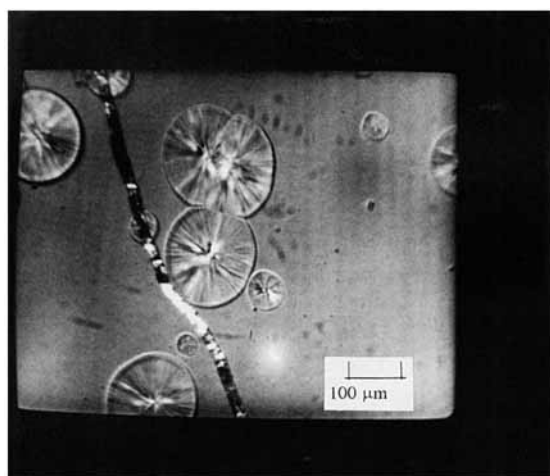**Figure 2** Untreated cellulose fiber in polypropylene. (a) molten, (b) fully crystallized.

enthalpy, and the calculated degree of crystallinity. In order to obtain consistent peak areas between samples, endpoints for each peak baseline were chosen by examining the derivative-curve for each peak. Endpoints were then chosen as the points where the derivative became equal to zero, marking the start and the finish of the melting process. The degree of crystallinity was calculated by comparing the measured melting enthalpy per gram of polypropylene
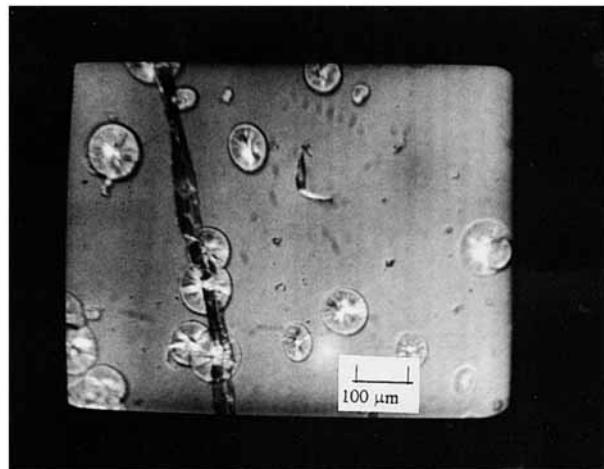
(a)
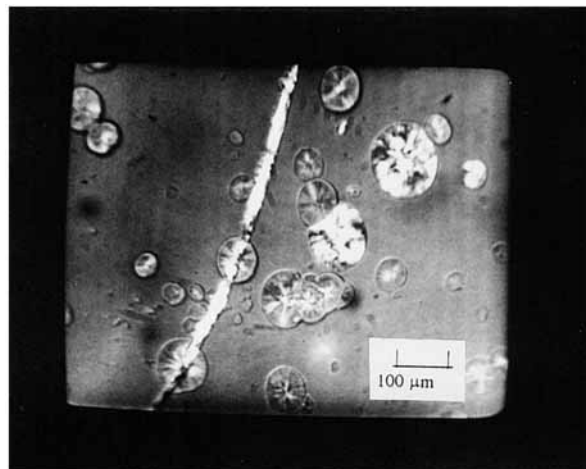
(b)

(c)

Figure 3 Surface-treated cellulose fibers in molten polypropylene. (a) AKD, (b) ASA, (c) stearic acid.

to a literature value[27] for a completely crystalline sample. It is interesting to note that, for the samples that produce transcrystallinity (polypropylene with untreated cellulose), the percent crystallinity is slightly greater than that of neat polypropylene. For polypropylene with surface-treated cellulose, the percent crystallinity is slightly lower than for neat polypropylene. In addition, filled samples showed a slightly higher melting point (1–1.5°C) than neat

polypropylene. This may not be a real effect, but merely a result of the difference in heat capacity between filled and unfilled samples, resulting in an apparent temperature lag in the measurement. Examination of melting exotherms shows identical curve shapes, with filled samples shifted up slightly in temperature.

An exact mechanism for the occurrence of a transcrystalline region in the polypropylene/cellu-
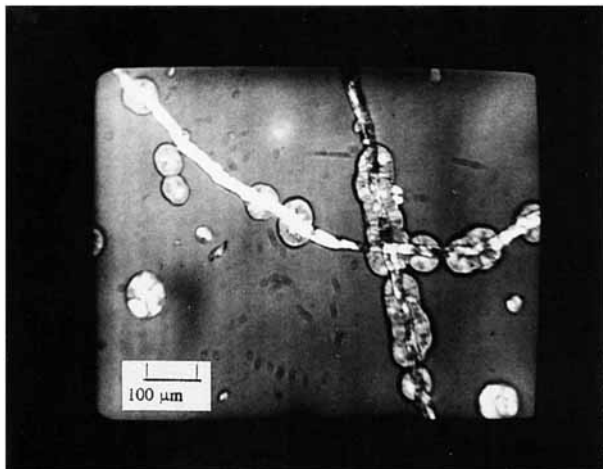
Figure 4 Cellulose fibers in molten polypropylene. Vertical = untreated, and horizontal = treated.

Table I Results of DSC Measurements

Sample (PP/Cellulose)	T_m[a] (°C)	ΔH_{obs} (cal/g)	Crystallinity[b] (%)
PP	158.9	24.0	48.0
PP/untreated	161.3	25.7	51.5
PP/AKD treated	160.1	23.4	46.9
PP/ASA treated	160.3	23.6	47.3
PP/stearic acid	160.5	23.1	46.3

[a] Average peak temperature of three samples.
[b] Calculated using a value of 50.0 cal/g for 100% crystalline material.

lose system is not apparent. A difference in thermal expansion between fiber and melt does not seem to be responsible for the occurrence, since treated and untreated fibers behave differently in the same melt (Fig. 4), even though they should have identical thermal properties. The migration of contaminants from the melt also seems to be unlikely because of the same evidence. Matching of crystal structure is not a ready explanation for the phenomenon, since the two structures are appreciably different (PP: (a) 6.65, (b) 20.96, (c) 6.50; cellulose: (a) 8.2, (b) 10.3, (c) 7.9). Surface energy, or more specifically, surface character, is also an unlikely driving force. In this case, affinity between hydrophilic untreated cellulose and hydrophobic polypropylene is low. Treatment
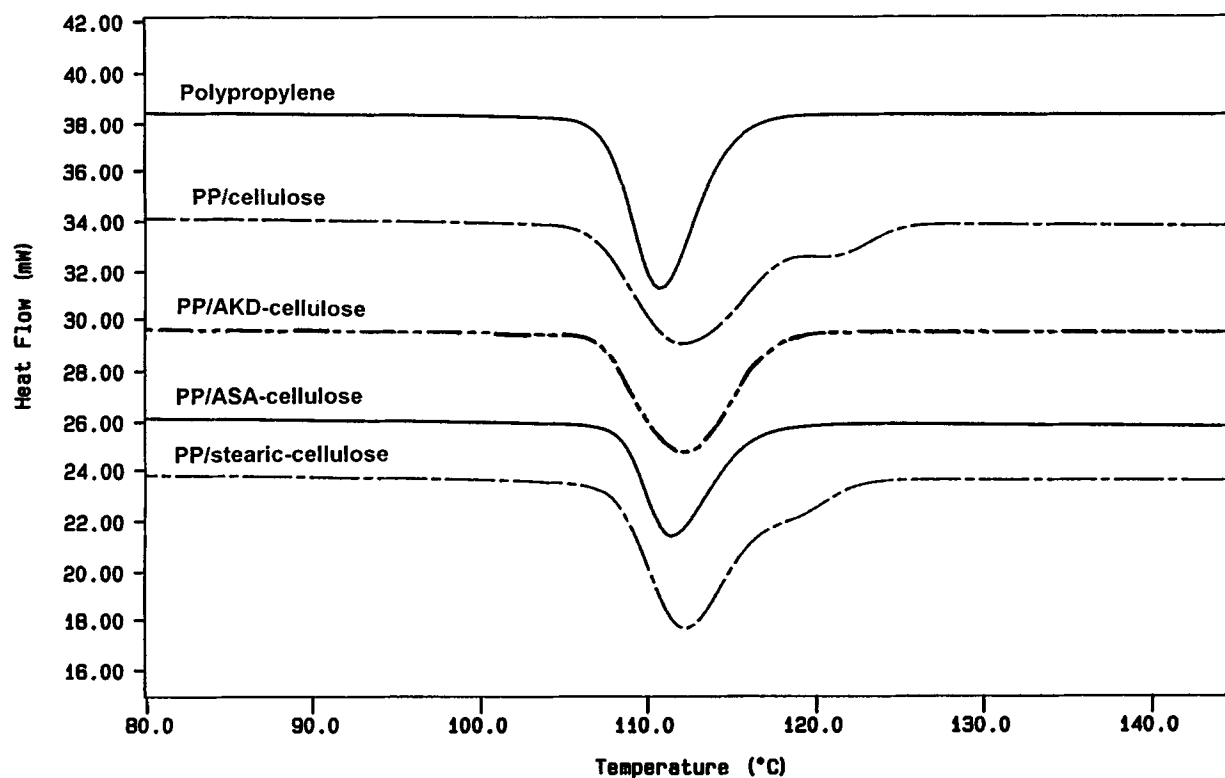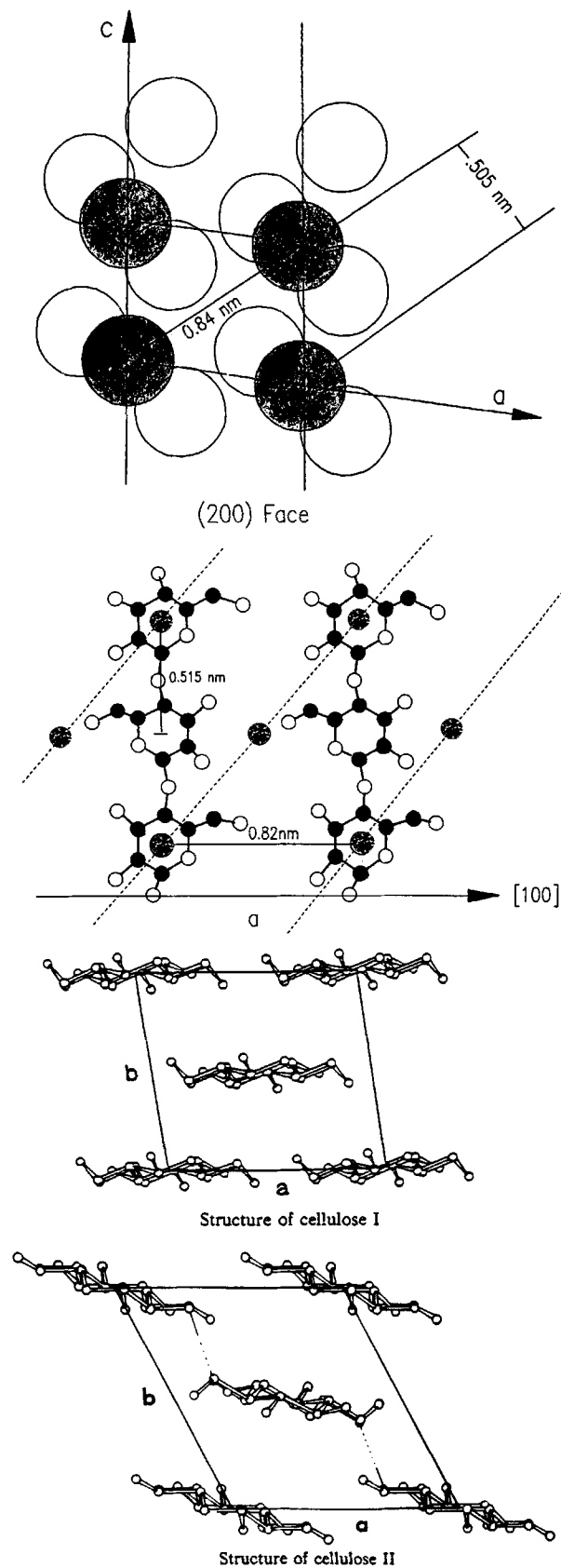

Figure 5 Differential scanning calorimetry results for polypropylene with various cellulose fibers.

(200) Face

Structure of cellulose I

Structure of cellulose II

with AKD, ASA, or stearic acid produces a more hydrophobic surface[28] and would result in greater compatibility between the two phases. Yet, only untreated cellulose produces transcrystallinity.

A closer examination of the crystal structures of the two components yields a possible explanation for the appearance of transcrystallinity. As noted by Wittman and Lotz,[29] structural features, other than the interchain distance, may be the overriding feature in crystal structure matching. For isotactic polypropylene, this feature is the rows of methyl groups that form planes parallel to the ⟨101⟩ directions of the monoclinic crystalline form of polypropylene. For what is denoted the "B" (010) face of isotactic polypropylene,[30] methyl groups are spaced 0.84 nm apart in planes that are 0.505 nm apart, as shown in Figure 6(a). These distances correspond almost identically to the distance between cellulose chains on the (100) face of natural cellulose I (0.82 nm) and the distance between the centers of adjacent glucose units along the chain (0.515 nm), as shown in Figure 6(b). In Figure 6, shaded spheres represent the methyl groups of the polypropylene chain described above, while the dotted line represents the chain axis of polypropylene. Hence, those (100) planes of cellulose that are positioned parallel to crystal surfaces may provide sufficiently similar spacings of pyranose rings to polypropylene methyl groups to initiate epitaxial polypropylene growth.

While these chain distances are identical for cellulose II, cellulose II does not transcrystallize polypropylene, while cellulose I does.[8] A possible explanation is that the pyranose rings on this face of cellulose II are not aligned in a "flat" manner, as shown in Figure 6(c), and do not provide the same configuration for the polypropylene chains to crystallize on.

When a surface treatment is applied to cellulose, the ordered surface is covered up and no transcrystallinity is produced. The hydrocarbon chains of the AKD, ASA, and stearic acid treatments appear to be unable to cocrystallize with the polypropylene and they actually produce a region of reduced crystallinity around the fiber.

Of great importance is the effect that transcrystallinity has on the mechanical properties of the

Figure 6 Crystal structure matching. (a) the "B" (010) face of isotactic polypropylene (after Lotz and Wittman[30]), (b) the (100) face of cellulose I with polypropylene chains superimposed (methyl groups shaded), and (c) differences in cellulose I and II structures[31].

composite. This is a widely debated point, with some arguing that this region is stronger than the bulk material, while others argue that it is weaker than the bulk. Figure 7 shows the effect of transcrystallinity on the distribution of "gaps" or voids between spherulites. Figure 7(a) shows rayon fibers, which do not nucleate polypropylene, in crystallized poly-
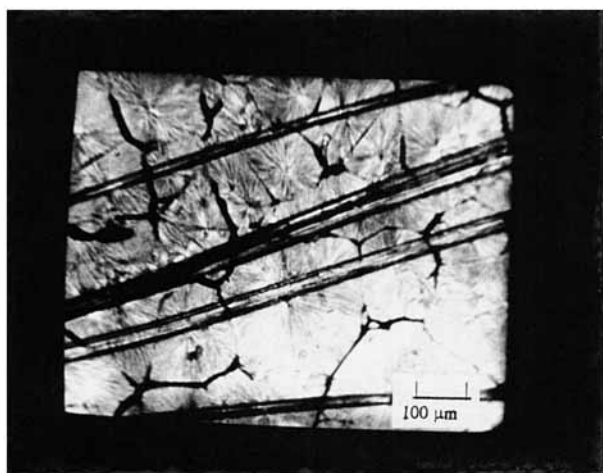
(a)
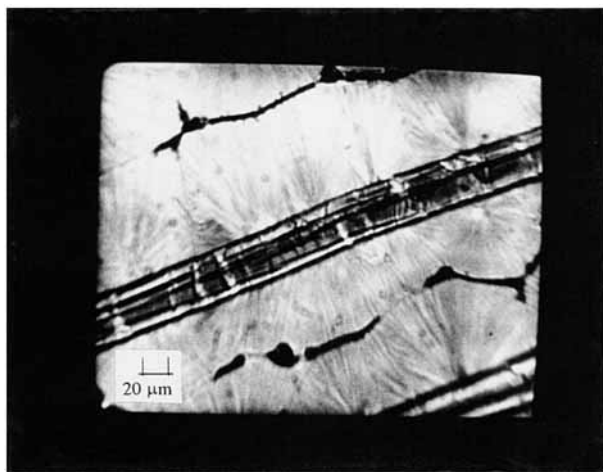
(b)

Figure 7   Distribution of interspherulitic gaps in filled polypropylene. (a) fiber which produces transcrystalline region, (b) fiber without transcrystalline region.

propylene. Figure 7(b) shows natural ramie fibers, which nucleate polypropylene, in crystallized polypropylene. With the rayon fibers, the distribution of interspherulitic gaps is completely random, identical to that of unfilled polypropylene. For the ramie fibers, the gaps are all concentrated between the fibers where the transcrystalline regions have met, but have not grown together. The implications of this are marked. For a unidirectionally reinforced composite with a high volume fraction of fiber, interspherulitic voids between fibers that transcrystallize the matrix material will also run in a direction parallel to the fibers. This can have a dramatic effect on the directional mechanical properties of the composite, especially the shear properties or properties such as toughness that are dependent on fiber pull-out and/or microcracks and voids. If the fibers are nonnucleating, the interspherulitic gaps will be random in three dimensions and will have no overall effect on the mechanical properties of the composite. Hence, although fibers that transcrystallize may be in better contact with the matrix material, the concentration of interspherulitic gaps between the sheathed fibers may lead to poorer properties than if the fibers were non-nucleating.

CONCLUSIONS

The results described above indicate that transcrystallinity is a complex phenomenon and is still not completely understood. Untreated cellulose surfaces act as a nucleating agent for polypropylene, producing a transcrystalline region around the fiber. Surface treatment of the cellulose with AKD, ASA, or stearic acid results in a non-nucleating surface and no transcrystallinity. Because of the lack of a reliable test to measure the strength of the interphase, the debate over its effect on the mechanical properties of lignocellulosic–semicrystalline composites is unresolved. The measurement of the interphase shear strength, by means of a fiber pull-out test or possibly a peel test of fiber mats, could help resolve this question. The nucleating ability of other lignocellulosic surfaces, both modified and unmodified, in various thermoplastics needs to be investigated further in order to help understand the phenomenon of transcrystallinity.

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