The Seventh International Conference on Woodfiber-Plastic Composites
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Impact Toughness of Cellulose-Fiber Reinforced Polypropylene: Influence of Microstructure in Laminates and Injection Molded Composites

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Abstract

Unlike their glass reinforced counterparts, microstructure and dynamic fracture behavior of natural fiber-reinforced thermoplastics have hardly been investigated. Here, we characterize the microstructure of cellulose fiber-reinforced polypropylene and determined its effect on impact toughness.

Fiber lengths were reduced by one-half when compounded in a high-intensity thermokinetic mixer and then injection molded. At low fiber contents, injection molded specimens showed little fiber orientation; at high fiber contents, a layered structure arose exhibiting differing fiber orientations through the specimen thickness. To better control composite microstructure and understand its influence on impact toughness, model laminates containing aligned fibers were produced and tested.

Instrumented Charpy impact tests were performed and analyzed using linear elastic fracture mechanics. Dynamic critical energy release rates and dynamic critical stress intensity factors increased with cellulose content and with orientation of fibers perpendicular to the crack plane. Preliminary evaluation of a simple model relating the microstructure to the dynamic fracture toughness for both injection molded composites and laminates showed promise.

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Introduction

Recently, natural fibers have been used as fillers and reinforcements in low-melting-point thermoplastics. When added to thermoplastics, natural fibers represent low-cost, renewable reinforcements that enhance mechanical properties such as stiffness, strength, and heat deflection under load. Having low densities compared with conventional inorganic fillers and reinforcements, these fibers are often used in applications such as interior automotive paneling where the relatively low density of the natural fibers is an advantage.

The limited fracture toughness of natural fiber-reinforced thermoplastics at high strain rates

can preclude their use in some applications. To understand and ultimately improve the fracture performance of these composites, one must thoroughly understand the composite microstructure and how it affects fracture toughness. Because of methodological difficulties, little work has been performed on characterizing the microstructural parameters such as fiber length and fiber orientation distribution in natural fiber-reinforced thermoplastics. Even less has been done relating microstructure to composite performance such as impact toughness. We undertook a research program to investigate the dynamic fracture toughness of cellulose fiber-reinforced polypropylene (1). Here we explore the effect of microstructure.

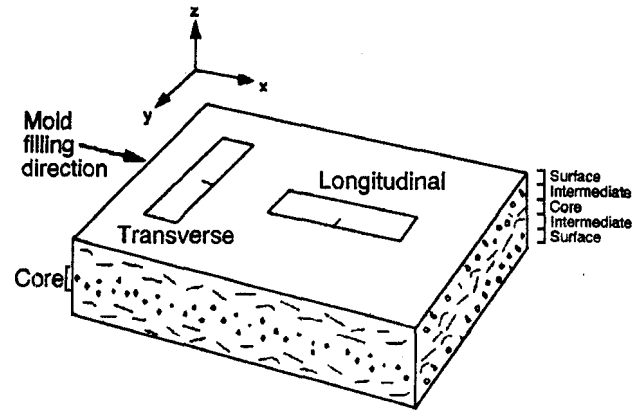

Figure 1. ~ *Fiber alignment with respect to melt flow direction for injection molded composites. containing high fiber content.*

Experimental

Materials

The polypropylene (PP) was a 12 g/10 min. melt flow index (MFI) homopolymer (Fortilene HB 1602, BP Amoco Chemical Company). Polypropylene is a low cost, low melting point matrix of industrial interest in injection molding applications. The specific PP was chosen for consistency with past research (2,3) and because we needed a high MFI polymer to offset the high viscosity due to fiber addition. The cellulose fibers were a bleached chemical kraft pulp fiber supplied as pressed and dried pulp sheets (Ultranier-J, Rayonier, Inc.). The cellulose fibers were selected as the reinforcement due to their high aspect ratio, high purity, and good thermal stability and for consistency with past research (2,4).

Composite Preparation

The PP and cellulose fiber were compounded in a 1-L, high-intensity thermokinetic mixer (K Mixer, Synergistics, Inc.). The thermokinetic mixer is a high shear compounder that adequately dispersed the cellulose fibers in PP. Cellulose fiber content was easily and precisely controlled in the batch mixer and metering and feeding problems due the low bulk density cellulose fibers were avoided. The material was discharged at a set temperature and granulated. Batches of 150 g were processed at a rotor speed of 5,000 rpm (rotor tip speed of 32.9 m/s) with discharge temperatures ranging from 180° to 210°C depending upon the cellulose fiber loading. Resulting batch times ranged from 30 to 60 seconds. The processing conditions were varied to ensure adequate dispersion and proper discharge. After compounding, injection molded specimens or laminates were produced.

To produce injection molded composites, the compounded material was cooled in a cold press, granulated, and then dried at 105°C for at least 4 hours before molding. A 33-ton reciprocating screw injection molding machine (Vista Sentry VSX-33, Cincinnati Milacron) was used to mold plaques measuring 76 by 127 by 6.4 mm (3 by 5 by 1/4 in.). Barrel temperatures did not exceed 200°C, and the mold temperature was 40°C. Injection speeds and pressures necessarily varied with the different formulations and material viscosities. Longitudinal and transverse specimens measuring 63.5 by 12.7 by 6.4 mm (2.5 by 1/2 by 1/4 in.) were cut from the injection-molded composite plaques **(Fig. 1).**

To produce laminates, the molten material discharged from the thermokinetic mixer was immediately pressed between two metal cauls at 190°C to 1.4 mm and cooled to 100°C in about 5 minutes to form thin, flat discs. Fibers aligned radially and so were nearly parallel at the disc's edges. Rectangular plies, 64 by 70 mm (2.5 by 2.75 in.), were cut from these discs and preheated at 160°C for 5 minutes. Plies were then stacked, pressed at 180°C for 1 minute, and cooled to 100°C. To investigate fiber orientation, specimens measuring 63.5 by 12.7 by 6.3 mm (2.5 by 1/2 by 1/4 in.) were cut from the laminates with fiber alignment angles (angle between fiber and radial direction) between 0 and 90°.

Dynamic Fracture Tests

The injection molded specimens or laminates were notched with a fly cutter (V notch, 45° angle)

to the desired depth, and the resulting crack was then sharpened with a razor blade. Specimens were tested at a speed of 1 m/s on an instrumented impact tester (gravity driven) with related software (Dynatup GRC 8250, Instron Corporation). A Charpy jig with a 51-mm (2-in.) span was used.

Linear elastic fracture analysis (7) was used to evaluate dynamic fracture toughness of whole specimens before sectioning. For evaluation of dynamic critical stress intensity factors K_c, we used:

$$s\,Y = K_c\,(a)^{-1/2} \qquad [5]$$

where:

s = maximum gross bending stress,
Y = a calibration factor, and
a = crack length (7).

Inertial energy effects were previously found to be negligible for our experimental setup (8). Specimens with various crack depths were tested, and fracture toughness parameters were determined from the slopes of s Y plotted against $(a)^{-1/2}$ At least 10 specimens were used for each K_c determination. Values for Y have been determined elsewhere (9).

Fracture surfaces were sputtered with gold and analyzed on a scanning electron microscope (SEM) (JSM-840, JEOL) at a working distance of approximately 25 mm and a voltage of 15 kV.

Fiber Orientation Determination

For fiber length and orientation determinations, specimens were divided into five equally thick layers: two surface, two intermediate, and one core.

Surface, intermediate, and core layers of each composite were extracted in xylenes for 8 hours. The extraction did not disturb the arrangement of fibers in the layer. The resulting cellulose fiber mats were analyzed using an X-ray diffractometer with related software (HI-STARR detector with GADDS 3.310 software, Siemens Energy and Automation). Each extracted sample was irradiated with Cu K_a X-rays for 60 seconds at 40kV and 20 mA using a 0.8-mm collimator. The resulting intensities from the [200] plane of the cellulose crystal structure at 2q = 22.9° were used to determine orientation parameters (f_p). The following equations were used (9) that are based originally on the work of Hermans (10):

$$f_p = 2\ \langle\cos^2\ c\rangle - 1 \qquad [1]$$

$$\langle\cos^2\chi\rangle = \frac{\sum N(\chi_i)\cos^2\chi_i}{\sum N(\chi_i)} \qquad [2]$$

where:

c = azimuthal angle and
N(c) = intensity at a given c.

Because there is a distribution of crystalline cellulose orientation around the fiber axis, values of $|f_p|$ were artificially low. Instead of attempting to quantitatively deconvolute the fiber orientation and cellulose crystal distributions, an approximate method was used. The orientation parameter f_p was normalized using an average orientation parameter of solid loblolly pine (*Pinus taeda*), which was used to represent a perfectly aligned composite.

Fiber Length Determination

Approximately 0.4 mg of residual fibers from the extracted samples were dispersed in 1 L of deionized water. Fiber lengths were then measured by an automated optical method (Kajaani FS-100 measurement apparatus, Kajaani GmbH Automation). In this method the cellulose fibers are forced through a capillary pipette located between a light source and a photocell. The shadow falling on the diodes in the detector was used to calculate fiber length. At least 2,000 fibers were measured for each sample. Average fiber lengths were calculated using

$$L_n = \frac{\sum n_i L_i}{\sum n_i} \qquad [3]$$

$$L_w = \frac{\sum n_i l_i^2}{\sum n_i l_i} \qquad [4]$$

where:

L_n and L_w = the number and weight average fiber lengths, respectively, and
n = the number of fibers of length l in the ith range.

An average fiber diameter D of 20 µm was determined by examining many SEMs and was used in determining aspect ratios.

Results and Discussion

Composite Microstructure

For injection molded composites, scanning electron microscopy (SEM) of the high cellulose fiber content composites revealed a layered

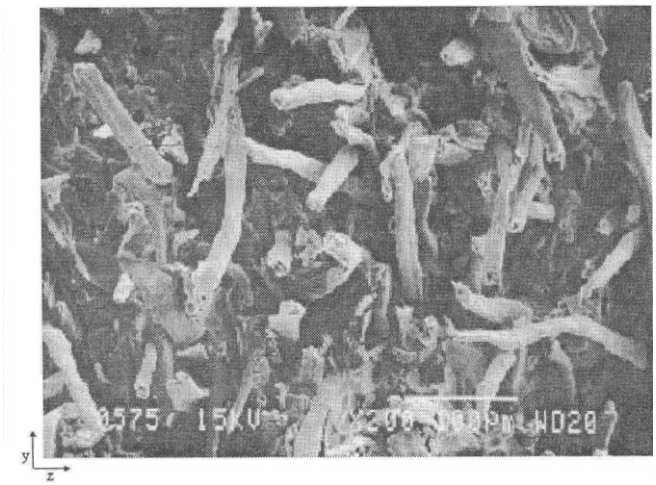

Figure 2. ~ *Fracture surface of injection molded composite containing 40% cellulose fiber. Near outer surface of a longitudinal specimen. Fiber orientation out of y-z plane in Figure 1.*

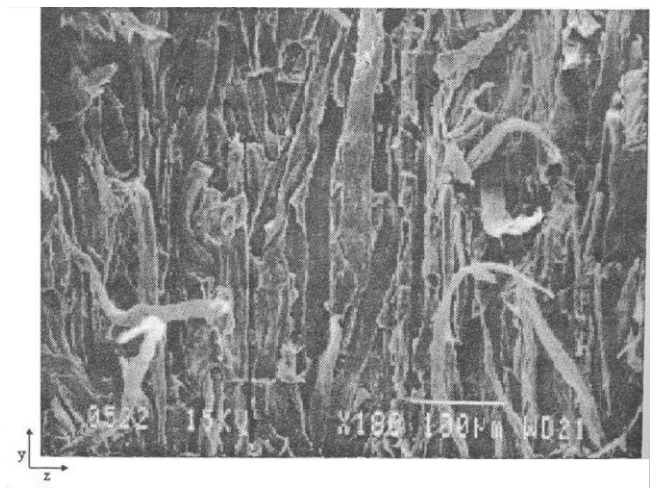

Figure 3. ~ *Fracture surface of injection molded composite containing 40% cellulose fiber (core of a longitudinal specimen). Fiber orientation in the y direction of the y-z plane in Figure 1.*

structure (illustrated in **Fig. 1**) resembling that of injection molded glass fiber-reinforced thermoplastics (5). As the melt enters the mold, the sudden increase in channel dimensions causes deceleration along the flow direction, and hence a compressive force. This compression aligns the fibers transversely to the melt flow direction. Fibers near the plaques's surfaces orient parallel to the filling through elongational flow at the flow front. Rose calls this the "fountain effect" (6). Due to rapid injection, flow in the core region approaches plug flow, and the transverse fiber alignment created at the gate is maintained. This morphology was most obvious in the composite samples with high fiber contents. **Figures 2 and 3** show different regions of a fracture surface of a longitudinal specimen exhibiting this layered structure. Identifying precise transitions between core and surface morphologies was difficult so each sample was divided into five equally thick layers (one core, two surface, and two intermediate) for further microstructural analyses.

Figure 4 summarized the orientation parameters f_p from the X-ray analysis. The f_p function yields a positive value for orientation in the flow direction, a negative value for orientation across the flow direction, and zero for random orientation. The trends shown in **Figure 4** confirm observations from the SEM work. The preferred fiber orientation is perpendicular to the flow direction in the core layer and parallel to the flow direction in the surface layer. This layered structure decreases

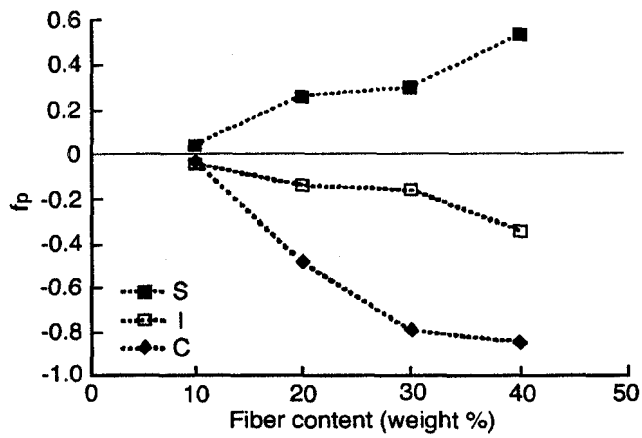

Figure 4. ~ *Fiber orientation parameters for injection molded composites. (S, surface; I, intermediate; C, core.)*

with decreasing cellulose fiber content, and nearly random orientation is found at low cellulose fiber contents.

Number average aspect ratios L_n/D and L_n/L_w ratios are summarized in Table 1. Average aspect ratios were cut in half during compounding and injection molding. Surprisingly, the fiber lengths nearly matched for composites of differing fiber content, despite differences in viscosities and processing conditions during compounding and molding.

Table 1. - *Microstructure determination.*

CF[a] (wt.%)	Source	L_w/D	L_f/L_w	f_p
100	Fiber[b]	50	0.53	NA
20	Ply	24	0.43	0.33[c]
20	Laminate	24	0.44	0.31
20	Injection molded	26	0.50	−0.05[d]

[a] Cellulose fiber.
[b] Fibers before processing.
[c] Fiber orientation parameter for 0" fiber orientation angle.
[d] Overall fiber orientation parameter for longitudinal specimen.

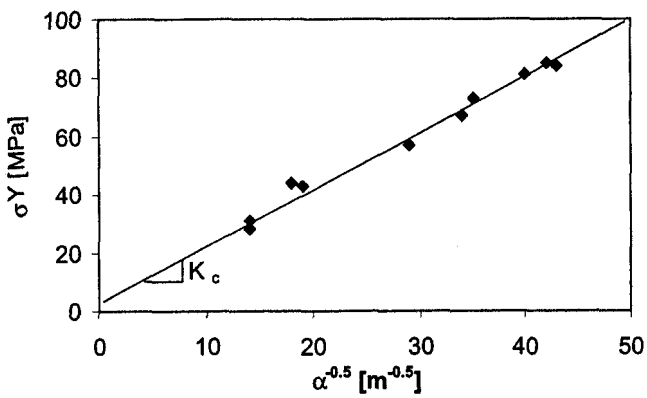

Figure 5. ~ *Determination of dynamic critical stress intensity factor from Charpy impact tests for PP with 20% cellulose fiber by weight. Transverse specimens.*

Microstructural control during injection molding is limited. Despite vaned microstructures in surface, intermediate, and core layers in our injection molded composites, overall fiber alignment was small. To better control composite microstructure, laminates of aligned plies were produced and tested. **Table 1** compares the fiber lengths before processing with those in the laminates and injection-molded composites. Both compression molding and injection molding yielded composites with similar fiber lengths.

Table 1 also summarizes the fiber orientation parameters (f_p) determined by X-ray diffraction for the plies and laminates. Complete fiber alignment was desired (f_p = 1). Though not fully aligned, the fiber alignment in the plies exceeded the overall fiber alignment in the injection-molded composites. Because the laminating pressure and time was short and the temperature (180°C) was not much above the melting point, most of the fiber alignment was maintained during pressing of the plies into laminates.

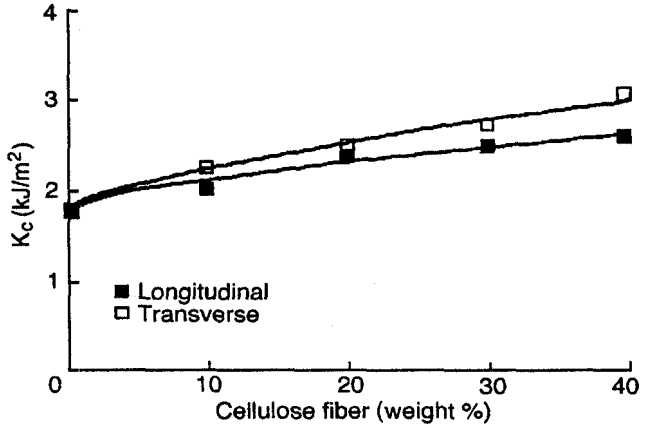

Figure 6. ~ *Effect offiber content on dynamic critical stress intensity factors (K_c) of injection molded composites. Longitudinal and tangential specimens.*

Fracture Toughness Tests

At an impactor speed of 1 m/s, most composite samples exhibited brittle, linear elastic behavior with almost all of the energy used in crack initiation rather than propagation. Similarly, the plots of s Y versus $(a)^{-1/2}$ were linear **(Fig. 5)** except for some slight curvature at a filler content of 40 percent. In unfilled polymers, curvature is usually attributed to polymer yielding, resulting in delocalization of the stress concentration at the crack tip. Delocalization of the stress state in our composites containing 40 wt.% fiber, suggests that some energy is absorbed by mechanisms such as polymer yielding or fiber debonding ahead of the crack tip and prior to crack movement.

Figure 6 summarizes the critical stress intensity results for the injection-molded composites. The increase in fracture toughness with fiber content is consistent with reports of other reinforcing fibers in PP (5). A slight difference in fracture toughness was seen between transverse and longitudinal specimens. This slight difference can be attributed to the greater overall fiber alignment across the crack path in the transverse specimens **(Figs. 1 and 4).**

The effect of fiber orientation angle on the dynamic critical stress intensity factor (K_c) in laminates containing 20 percent fiber was also investigated **(Fig. 7).** Fracture toughness decreased as fewer fibers align perpendicular to the crack

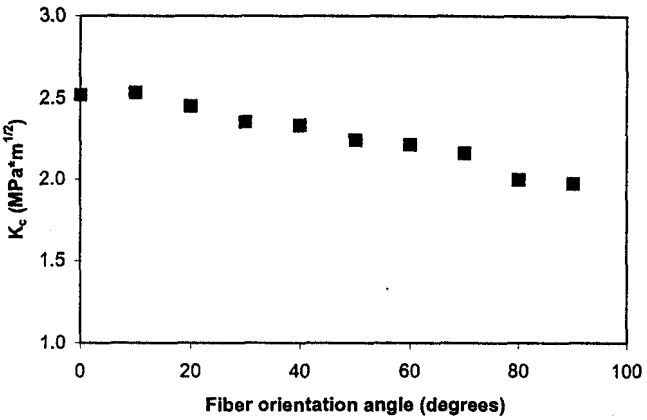

Figure 7. ~ *Effect of fiber orientation on the dynamic fracture toughness, K_c, of PP laminates containing 20 wt. % cellulose fiber. Error bars indicate 1 standard deviation.*

plane. This is consistent with the findings for the injection molded composites.

To quantitatively relate fiber orientation and other microstructural parameters for both laminates and injection-molded composites, we used Friedrich's microstructural efficiency concept. To relate the microstructure to the fracture performance of various short-fiber composites, Friedrich used an empirical relationship (5,11,12):

$$\frac{K_{c,C}}{K_{c,M}} = a^* + nR \qquad [6]$$

where:

$K_{c,C}$ = fracture toughness of the composite and

$K_{c,M}$ = matrix toughness.

The a^* is the matrix toughness correction factor, which reflects changes in the fracture toughness of the matrix material as a result of the fiber presence (for example, transcrystallinity at fiber-matrix interfaces). The n is the energy absorption ratio and reflects the increase in toughness directly attributed to the fibers (fiber debonding, pull-out, or fracture). R is the dimensionless reinforcement effectiveness factor:

$$R = \sum_i T_{rel,i} V_{f,i} F_{L,i} F_{O,i} \qquad [7]$$

where:

$T_{rel,i}$ = thickness of the ith layer divided by the overall thickness,

$V_{f,i}$ = volume fraction of the ith layer, and

$F_{L,i}$ and $F_{O,i}$ = fiber length and orientation efficiency factors, respectively.

In this study, the microstructural parameters are summed over the surface, intermediate, and core layers.

Although the thickness and volume fraction are easily represented, efficiency factors for the length and orientation distributions, $F_{L,i}$ and $F_{O,i}$, are more difficult. As a first-order approximation of the aspect ratio distribution, Karger-Kocsis and Friedrich (10) proposed using the product of maximum aspect ratio and a representation of the width of the distribution curve:

$$F_O = \frac{(L/D)_{max}(L/D)_n}{(L/D)_w} \qquad [8]$$

where:

$(L/D)_{max}$ = peak aspect ratio and

$(L/D)_n$ and $(L/D)_w$ = number average and weighted average aspect ratios, respectively.

The effective orientation parameter, $f_{p,eff,i}$, is

$$F_{p,eff} = a\,[1 + \tanh(b\, f_p)] \qquad [9]$$

where:

f_p = orientation factor determined by Equations [1] and [2],

a = 0.5, and

$1 < b < 5$ for $0 \le |f_p| \le 1$ (10).

The reinforcing effectiveness factors were determined for each composite according to Equation [7] and were plotted against normalized critical stress intensity **(Fig. 8).** An approximately linear correlation was found, with little scatter despite the dynamic nature of the test. Values of 1.12 and 0.27 were found for a^* and n, respectively. When a^* exceeds 1 there is an improvement of the matrix toughness with fiber addition. The positive value of n indicates an improvement in composite fracture toughness with increasing cellulose fiber content.

Conclusion

Number average aspect ratios L_n/D were reduced by one-half when compounded in a high intensity thermokinetic mixer and then injection-molded or made into laminates. In injection molded composites, there was little fiber orientation at low fiber contents; at high fiber contents, a layered structure arose. When producing laminates, plies contained higher overall fiber align-

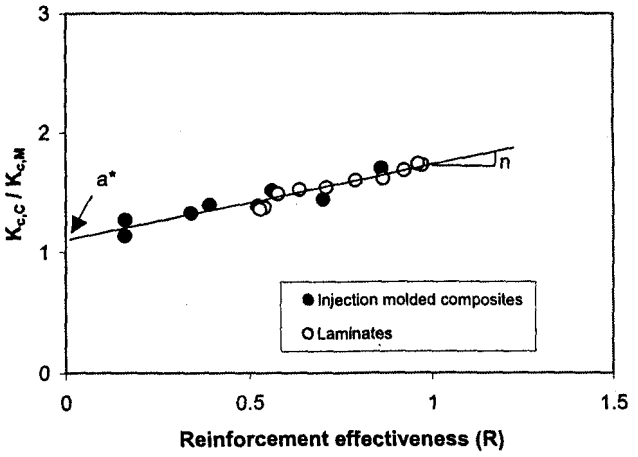

Figure 8. ~ *Effect of microstructure on dynamic fracture toughness. $K_{c,C}/K_{c,M}$ is the ratio of fracture toughness of the composite to that of the matrix.*

ment than in injection-molded composites and little alignment was lost during pressing into laminates.

Dynamic fracture toughness decreases with fiber alignment angle. Linear elastic fracture mechanics analysis appears to work well for composites with up to about 40 percent cellulose fiber content by weight. Dynamic fracture toughness increased with cellulose content and with orientation of fibers perpendicular to the crack direction. A preliminary evaluation of Friedrich's microstructural efficiency model relating microstructure to dynamic fracture toughness showed promise.

Acknowledgment

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