Exploratory Microscopic Investigation of Impacted Paper Fiber-Reinforced Polypropylene Composites

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Introduction

Natural fibers offer an attractive reinforcement for low-melt-temperature thermoplastics. Natural fibers represent low-cost, renewable reinforcement that provides improvements in mechanical properties such as stiffness, strength, and heat deflection properties when added to thermoplastics. In addition, natural fibers are less dense, less abrasive, and often cheaper than conventional inorganic fillers and reinforcements.

The technology for the use of natural fibers as reinforcing fillers has fallen significantly behind that of more conventional fibers such as glass and carbon fibers. Scientists at the Forest Products Laboratory have been working to change this situation. In order to optimize the mechanical performance of these composites, it is necessary to understand microstructure-property relationships. Considerable work at the lab currently centers around the impact performance of these composites. In order to better understand the mechanisms of fracture of these composites under impact loading (fiber pullout, debonding, fiber fracture, etc.), fracture surfaces were studied using scanning electron microscopy. These mechanistic details along with simple energy balances were used to explain observed trends in impact data.

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Experimental

The following materials were used in the investigation. Unprinted newsprint was obtained from Madison Newspapers, Inc. (Madison, Wis.) as a stub roll. The newsprint was fiberized during compounding. Dissolving pulp fiber was Ultranier-J supplied by Rayonier (Stamford, Conn.). The polymers used were Fortilene 1602, a 12-melt-flow index polypropylene homopolymer from Solvay Polymers, Inc. (Deer Park, Tex.) and Tenite P6-005, a high-impact polypropylene copolymer from Eastman Chemical Products, Inc. (Kingsport, Tenn.). The coupling agent was G-3002, a maleated polypropylene also supplied by Eastman Chemical Products, Inc. and added in a pellet form to the compounder.

To investigate the effects of several material variables on fracture mechanisms and impact performance, a full factorial experimental design was employed:

Variable	Level
Reinforcing fiber	Newsprint or dissolving pulp
Fiber loading	20% or 40% by weight
Polymer type	Polypropylene homopolymer or polypropylene copolymer
Coupling agent	0 or 1.3% maleated polypropylene

In addition, unfilled polymers were also studied and several blends containing polypropylene homopolymer and 40 percent dissolving pulp were made at an intermediate coupling agent content of 0.7 percent. A formal statistical analysis of the full factorial design was completed. All of the main effects and nearly all of the two-factor interactions were found to be significant at a confidence level of 95 percent for both notched and unnotched impact energies. Rather than focusing further on the significance of these variables, a more qualitative discussion centers on general trends in impact behavior and the mechanistic details that explain these trends.

The raw materials were compounded in a 1-liter, high-intensity thermokinetic mixer (K Mixer; Synergistic, Inc., St. Remi de Napierville, Quebec) for approximately 40 seconds at 5500 rpm. The resulting blends were granulated, dried, injection molded, and then stored in a dessicator for at least 3 days before testing. The injection molder used was a 33-ton reciprocating screw injection molder (Cincinnati Milacron, Batavia, Oh.). Barrel temperatures were kept below 200°C and the mold temperature was maintained at 40°C. Injection speeds and pressures necessarily varied with the different formulations but the overall cycle times and temperatures were kept constant.

Both notched and unnotched Izod impact energies were measured on a Baldwin-Southwark Izod Impact tester according to ASTM D 256-90b (1). Fractured specimens were then mounted and analyzed on a Jeol JSM-840 scanning microscope.

Results and discussion

Composite microstructure

A number of general comments on the fracture behavior and the microstructure of the composites were found in initial exploration of fracture surfaces of the composites. The specimens had Up to three distinct regions with differing morphology 1) the region opposite the notch; 2) the edge region; and 3) the center region (Fig. 1). The majority of each fracture surface showed apparent brittle behavior of the polymer. Little evidence of yielding of the polymer component is seen. Even the unfilled homopolymer showed brittle behavior (unfilled copolymer did not fracture) (Fig. 2). Near the edge opposite the notch, however, a region was found with more ductile flow of the matrix material (Figs. 3 and 4). This behavior is consistent throughout most of the notched Izod specimens. Considering that many of the specimens had a tendency to hinge when impacted, this region of more ductile behavior is not surprising. Since the ability of a polymer to yield is rate-dependent, the region of microductility would suggest a slower fracture as the specimen is bent over during the final portion of the impact event.

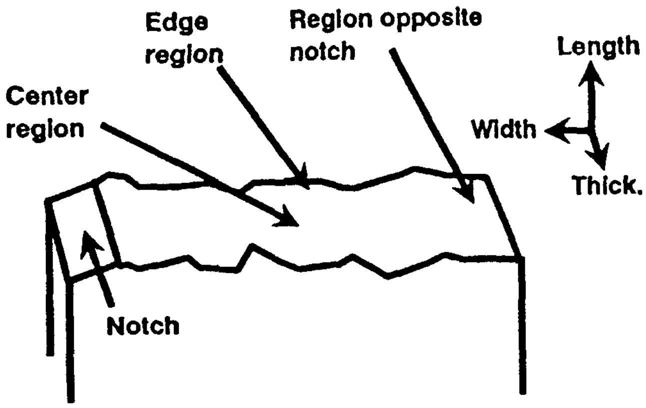

FIGURE 1.— *Microstructural regions of fracture surface.*

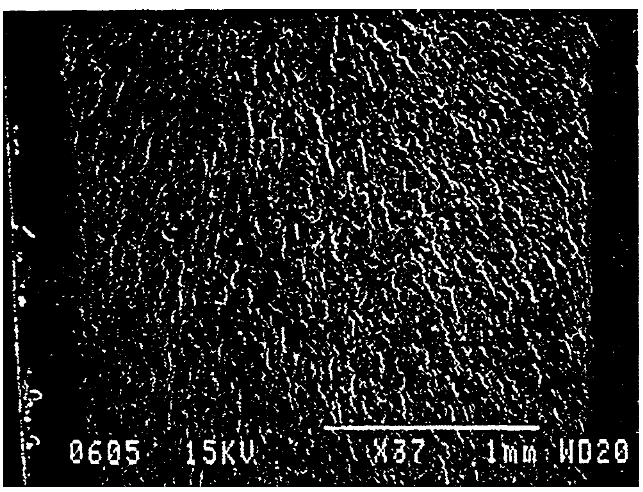

FIGURE 2.— *Overall view of fracture surface of unfilled polypropylene homopolymer.*

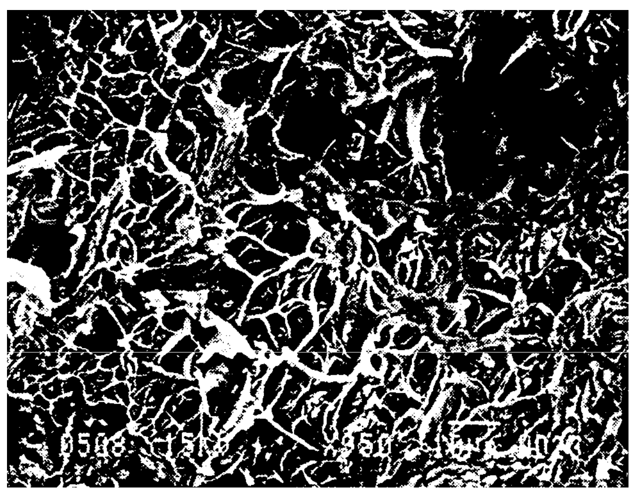

FIGURE 3.— *High magnification micrograph of fracture surface of polypropylene homopolymer with 40 percent newsprint and no coupling agent. Region opposite notch.*

A number of the samples containing 40 percent dissolving pulp began to exhibit a layered structure similar to that of injection-molded inorganic fiber reinforced thermoplastics described by other authors (2,3). The fibers near the outer surfaces of the specimen (edge region) are oriented in the direction of filling because of the shearing across the thickness of the specimen during molding. In the center region of the specimen the fibers tend to be oriented perpendicular to the flow direction. This effect is demonstrated by the scanning electron microscopy photographs in Figures 5 to 7. This morphology, however, is only seen in the dissolving pulp samples with 40 percent fiber content. Figures 8 and 9 demonstrate this effect of fiber content on composite morphology of the composites containing dissolving pulp. As the fiber content is decreased from 40 to 20 percent (by weight), the layered morphology disappears.

Results of impact tests

The results of the impact tests are summarized in Figures 10 to 15. If a specimen did not fracture during the test, it was assigned with a value of 800

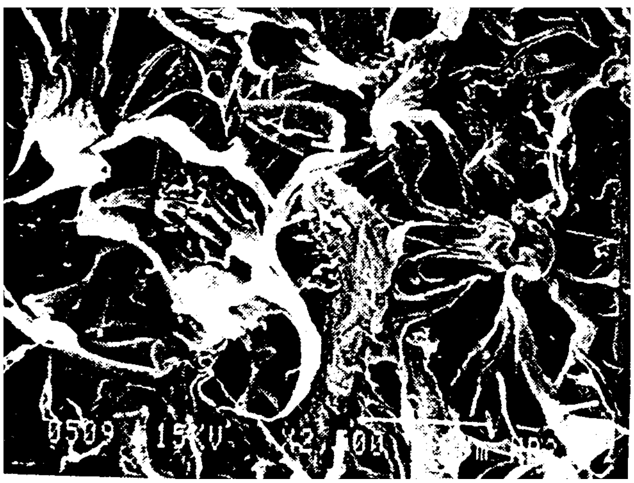

FIGURE 4.— *High magnification micrograph of fracture surface of polypropylene homopolymer with 40 percent newsprint and no coupling agent. Region opposite notch.*

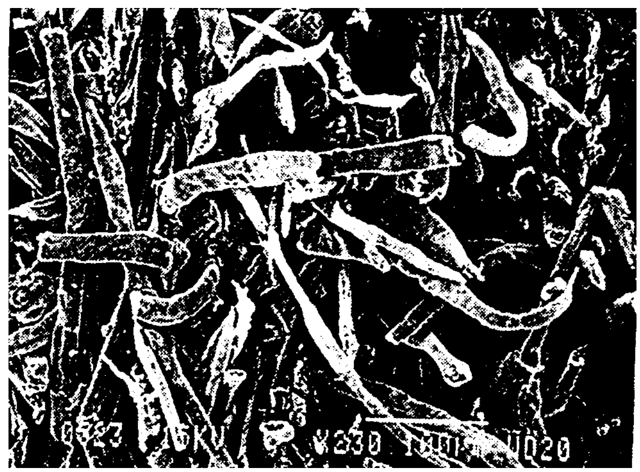

FIGURE 6.— *High magnification micrograph of fracture surface of polypropylene copolymer with* 40 *percent dissolving pulp fiber and no coupling agent. Edge region.*

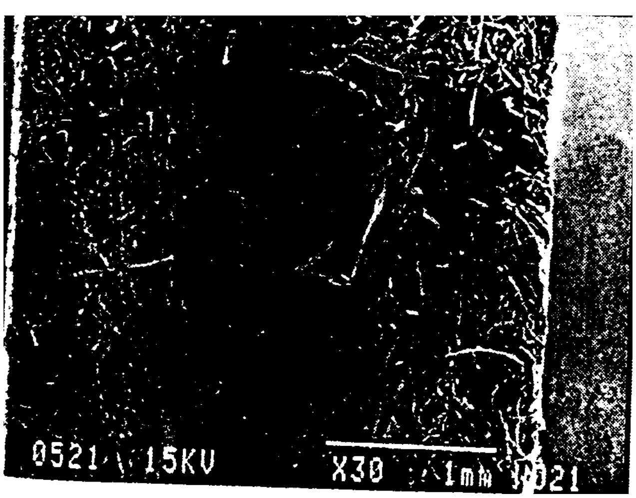

FIGURE 5. — *Overdall view of fracture surface of polypropylene copolymer with 40 percent dissolving pulp fiber and no coupling agent.*

FIGURE 7.— *High magnification micrograph of fracture surface of polypropylene copolymer with 40 percent dissolving pulp fiber and no coupling agent. Center region.*

J/m (800 J/m is the maximum energy applied by the pendulum). Although a more quantitative prediction of impact behavior would require a far more in-depth investigation, many of the trends shown in Figures 10 to 15 can be qualitatively explained by identifying the mechanisms occurring during fracture using scanning electron microscopy. Ignoring the effects of notch root radii, a first order approximation of the total work of fracture can be determined by adding the different energy-dissipating mechanisms.

$$w \approx w_f + w_m + \sum w_{fm} \qquad [1]$$

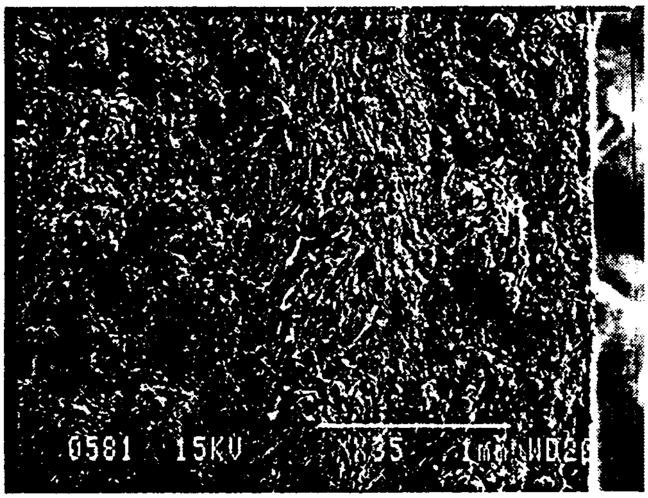

FIGURE 8.— *Overall view of fracture surface of polypropylene copolymer with 40 percent dissolving pulp fiber and 1.3 percent maleated polypropylene coupling agent.*

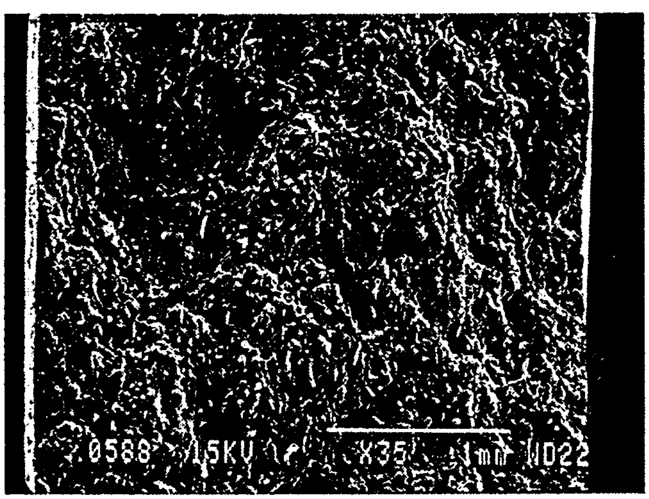

FIGURE 9.— *Overall view of fracture surface of polypropylene copolymer with 20 percent dissolving pulp fiber and 1.3 percent maleated polypropylene coupling agent.*

where:

w_f = work of fracture of fibers and is a function of the number of fibers fractured and their strength

w_m = work of fracture of matrix and is a function of the amount of matrix fracture surface created and the matrix properties

w_{fm} = work due to fiber-matrix interactions (sliding, debonding, fiber pullout, etc.)

These fiber-matrix interactions can be extremely complex and are greatly affected by the relative properties of the matrix and fibers and the compatibility of the two components.

Unnotched Izod impact energies are not only a measure of crack propagation but also of crack initiation. Equation [1] can be modified to include a crack initiation term:

$$w \approx w_i + w_f + w_m + \sum w_{fm} \qquad [2]$$

where:

w_f = crack initiation energy

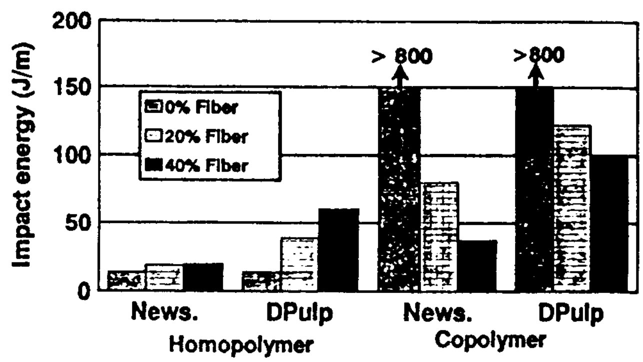

FIGURE 10.— *Notched Izod impact performance of paper-reinforced polypropylene composites without coupling agent.*

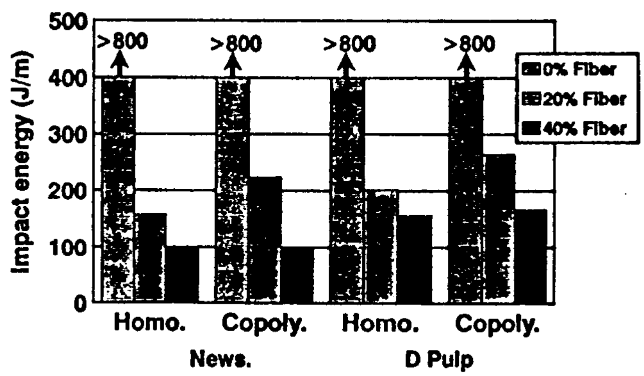

FIGURE 11.— *Unnotched Izod impact performance of paper-reinforced polypropylene composites without coupling agent.*

This initiation term is a function of the properties of the matrix, the volume, shape, and size of fillers/reinforcements which can act as stress concentrators, and the adhesion of the fiber and matrix. As can be seen by comparing Figures 10 and 11, unnotched Izod impact energies are considerably larger than notched Izod impact energies. This leads to the conclusion that the crack initiation term is quite large and would tend to dominate Equation [2].

Uncompatibilized composite systems

The differences in microstructure between composites containing the two different fiber types are quite dramatic. Figures 16 and 17 show the different fracture surfaces of newsprint-filled and dissolving pulp-filled copolymer, respectively. The newsprint fibers were fractured because of the intensity of mixing during compounding. Many broken fibers and fiber fragments are seen embedded in the matrix material. Relatively little fiber pullout is seen and considerable fiber fracture is evident. On the other hand, the dissolving pulp maintained a greater fiber length (Fig. 17). Many long fibers which have been pulled out of the polymer matrix are apparent. The fiber pullout mechanism requires a significant amount of energy (large w_{fm} term) and helps to distribute the applied energy to a greater volume of material resulting in greater notched impact energies (Fig. 10). The dissolving pulp consistently outperforms newsprint fiber as a reinforcement. The fiber-matrix interactions in composites containing dissolving pulp dissipate more energy than the fiber-matrix interactions and/or the fiber fracture in composites containing newspaper fiber.

Figure 10 shows opposite trends for fiber addition when the homopolymer and copolymer are compared. Since the homopolymer matrix has a low impact energy (i.e., w_m), addition of fibrous material can result in increased impact performance. Although the matrix fracture energy is decreased because of a reduction in matrix fracture surface area as fiber is added, it is more than compensated for by the additional energy dissipated by fiber breakage (w_f) and fiber-matrix interaction mechanisms (w_{fm}, fiber pullout, etc.). This is particularly the case with the stronger and longer dissolving pulp fiber. The

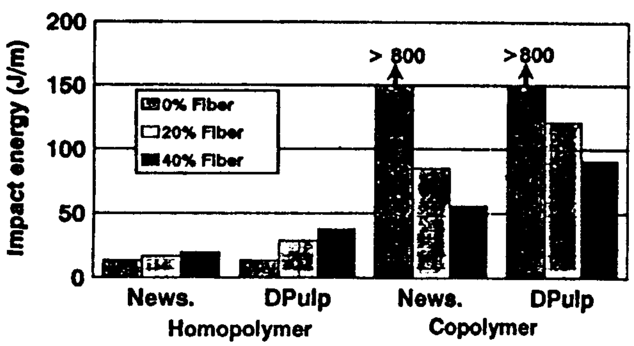

FIGURE 12.— *Notched Izod impact performance of paper-reinforced polypropylene composites with 1.3 percent maleated polypropylene coupling agent.*

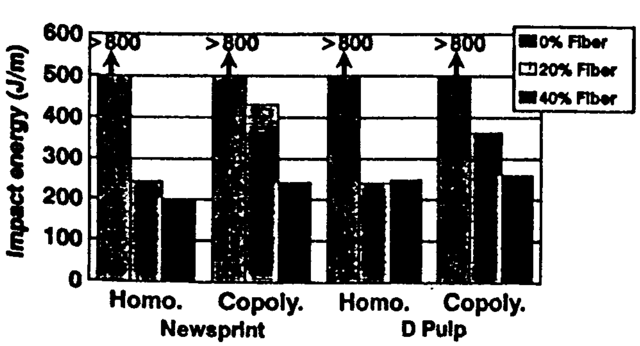

FIGURE 13.— *Unnotched Izod impact performance of paper-reinforced polypropylene composites with 1.3 percent maleated polypropylene coupling agent.*

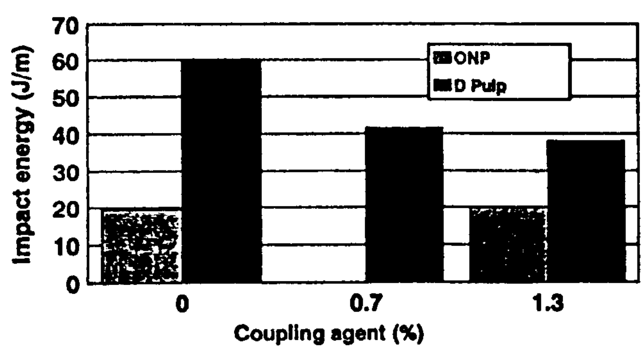

FIGURE 14.— *Notched Izod impact performance of polypropylene homopolymer reinforced with 40 percent paper fiber.*

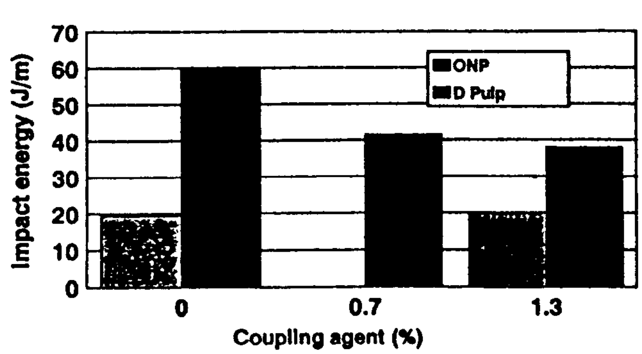

FIGURE 15.— *Unnotched Izod impact performance of polypropylene homopolymer reinforced with 40 percent paper fiber*

copolymer, however, has a much larger matrix fracture energy and the loss in fracture surface results in large decreases in energy which cannot be adequately offset by fiber fracture and fiber-matrix interactions (i.e., w_m dominates Equation [1]). As more fiber is added, the smaller the matrix fracture surface and the lower the impact energy.

Figure 11 shows the unnotched impact behavior for the uncoupled systems. The unnotched Izod impact tests yield much higher values because of the **much** higher energies needed to initiate rather than just propagate a crack. Addition of either type of fiber results in large reductions in unnotched impact energies. The presence of the fibers results in stress concentrations at the fiber ends reducing the energy required for creation of a crack (i.e., dominant w_i term in Equation [2] is decreased with addition of fibers). Although the crack initiation requires the most energy, the other terms in Equation [2] still play a role, albeit a smaller one. At a fiber content of 20 percent, there is still enough continuous matrix to influence the unnotched impact energies. At 40 percent fiber content, the matrix type no longer has an influence and fiber type alone influences the unnotched impact. performance.

FIGURE 16.— *High magnification micrograph of fracture surface of pclypropylene copolymer with 40 percent newsprint and no coupling agent. Edge region.*

Compatibilized composite systems

Interracial effects are complex and depend on many factors. However, scanning electron microscopy can provide insight into the mechanisms occurring during impact testing. The changes in some of the micrographs with addition of the maleated polypropylene coupling agent are dramatic. Figures 18 and 19 give overall views of fracture surfaces of composites containing dissolving pulp without and with the coupling agent. Figures 20 and 21 show the edge regions of similar samples at higher magnification. With the addition of the coupling agent, nearly all the fibers break and very little fiber pullout occurs. This substitution of fiber breakage *(w_f)* for fiber pullout (a component of w_{fm}) results in an overall reduction in notched impact performance for samples containing dissolving pulp (Fig. 14). Compared to dissolving pulp, newsprint fiber-filled composites did not show a reduction in notched impact strength. Most of the newsprint fibers were below their criti-

FIGURE 17.— *High magnification micrograph of fracture surface of polypropylene copolymer with 40 percent dissolving pulp fiber and no coupling agent. Edge region.*

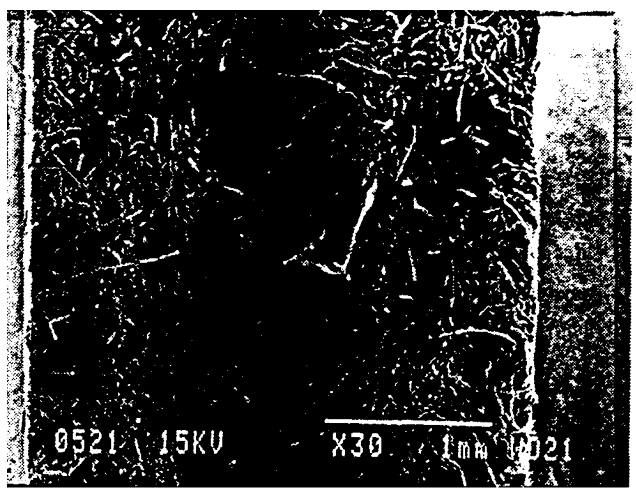

FIGURE 18.— *Overall view of fracture surface of polypropylene copolymer with 40 percent dissolving pulp fiber and no coupling agent.*

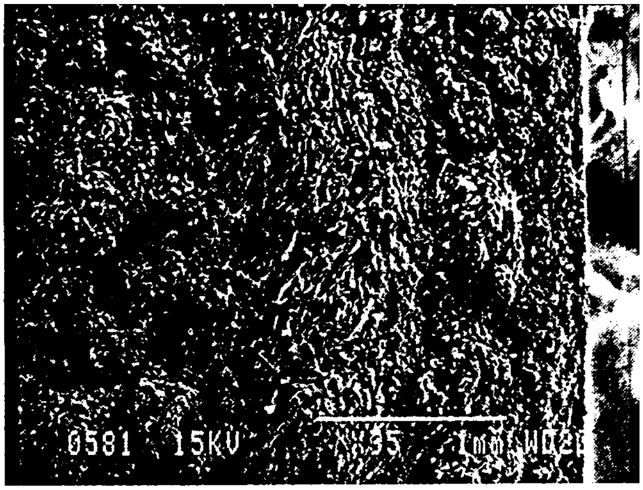

FIGURE 19.— *Overall view of fracture surface of polypropylene copolymer with 40 percent dissolving pulp fiber and 1.3 percent rnaleated polypropylene coupling agent.*

FIGURE 20.— *High magnification micrograph of fracture surface of polypropylene copolymer with 40 percent dissolving pulp fiber and no coupling agent. Edge region.*

cal length and addition of the coupling agent did not significantly affect the type of fracture mechanisms dissipating the applied energy and, therefore, did not affect the notched impact performance (no trade-off between w_f and w_{fm}). With compatibilized blends containing either fiber, the unnotched impact energies are significantly increased. The improved stress transfer between the fibers and matrix allow for

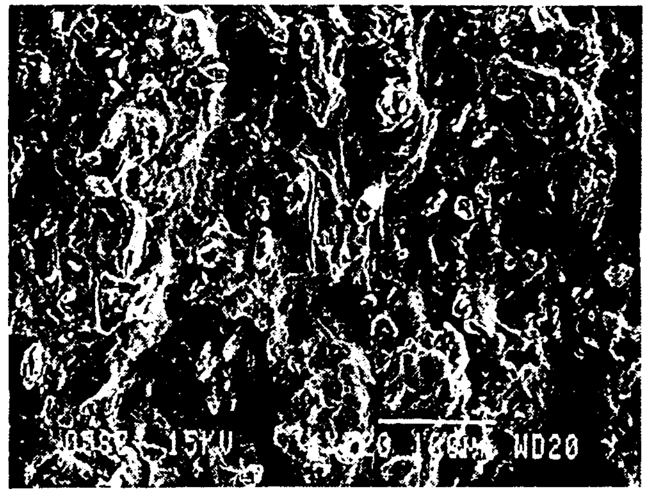

FIGURE 21.— *High magnification micrograph of fracture surface of polypropylene copolymer with 40 percent dissolving pulp fiber and 1.3 percent maleated polypropylene coupling agent. Edge region.*

efficient distribution of applied stresses and inhibits the formation of cracks (dominant w_i term is increased) (Fig. 15).

Summary and conclusions

Various composite components (fibers, polymers, and polymer-filler interactions) can be manipulated in order to affect the Izod impact properties of the composites. Trends in notched and unnotched impact energies are quite different because, to a first order approximation, notched impact energy is a measure of crack propagation and unnotched impact energy is a measure of crack initiation and propagation.

Considerable qualitative information on microstructure and fracture mechanisms was obtained through the use of scanning electron microscopy of fracture surfaces. Fiber fracture (or lack of it), polymer ductility, and fiber polymer bonding all play a role in impact performance. Using these mechanistic observations and simple energy balances, trends in impact behavior can often be qualitatively explained.

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