

# Dicumyl Peroxide-Modified Cellulose/ LLDPE Composites

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## Synopsis

The present study reports results on the processing and mechanical properties of composites modified by the addition of dicumyl peroxide (DCP). The addition of minute amounts of peroxide to the cellulose/polymer system during processing has been shown to significantly improve the physical properties of composites. SEM micrographs of fracture surfaces of the peroxide modified composites reveal direct grafting of polyethylene onto cellulose fibers. The existence of a critical peroxide concentration indicates that the grafting reactions terminate when cellulose surfaces are no longer accessible. Possible mechanisms involved are discussed.

## INTRODUCTION

There are environmental and economical advantages to producing composite materials based on natural polymers and their fibers. The use of cellulose fibers in thermoplastic composites has recently attracted significant attention.<sup>1-12</sup> However, due to the inherently poor compatibility between the hydrophilic cellulose fibers and typical hydrophobic commodity thermoplastics a pretreatment of the fiber surfaces<sup>4-9</sup> or the incorporation of surface modifiers<sup>2,10,11</sup> is generally required. It has been reported that under certain conditions the untreated cellulose fibers can be grafted directly to the polymer matrix during processing.<sup>12,13</sup> Gaylord<sup>12</sup> found that processing of cellulose fiber and molten polyethylene in the presence of maleic anhydride and dicumyl peroxide (DCP) gives a compatibilized mixture wherein the maleic anhydride acts as a bonding agent, bridging segments of the polymer with sites on cellulose fibers. More recently, Flink et al.<sup>13</sup> reported on the bonding of untreated cellulose fibers to natural rubber during curing, without any specific bonding system.

Peroxides alone may modify properties of polyolefins: examples range from crosslinking at high levels of addition to the controlled degradation during reactive extrusion known as viscobreacking.<sup>14,15</sup> However, very little is known about the chemistry and kinetics of these reactions and since they occur in the melt their study is further complicated.

Due to the potential practical importance of peroxide-induced adhesion in cellulose-containing composites this one-step approach to processing has been pursued in our laboratory.<sup>16,17</sup> It has been shown previously that the addition of a small quantity of benzoyl peroxide to cellulose/LLDPE composites during processing improves markedly their tensile properties.<sup>17</sup> In this work, the pro-

cessing and mechanical properties of composites modified by the addition of dicumyl peroxide (DCP) has been investigated.

### EXPERIMENTAL

A commercial linear low-density polyethylene (LLDPE) supplied by Esso Co. Canada (Escorene LL-3010) was used as polymer matrix. The LLDPE has a density of  $0.918 \text{ g/cm}^3$ , a melt flow index of 0.8 and a melt point of  $122^\circ\text{C}$ . The reinforcing fibers were highly bleached hardwood pulps from Sigma Chemical Co. (weight-average length of  $240 \mu\text{m}$ ). Dicumyl peroxide (Lucidol, obtained from Penwalt), was used as a modifier. For comparison, some composites were prepared using benzoyl peroxide (BPO).

Composites containing up to 50% by weight of fibers were prepared on a Brabender mill at  $160^\circ\text{C}$ , and at a mixing screw speed of 60 rpm. The cellulose fibers were predried in the mixing head for 2 min, then the polyethylene powder premixed with peroxide (up to 0.5% by weight of matrix) was added to the mixing head. About 12 min of mixing time was required for complete dispersion of cellulose fiber. The torque was continuously recorded during this period.

The composites were compression-molded at  $160^\circ\text{C}$ , then rapidly quenched in cold water. Typical lengths, widths, and thicknesses of test samples were 15 mm, 3.2 mm, and 0.9 mm respectively. The tensile stress-strain behavior was investigated at room temperature using an Instron model 4201 at constant elongation speed ( $20 \text{ mm/min}$ ). The results presented here are average values of 5 tests.

### RESULTS AND DISCUSSION

The effect of the benzoyl and dicumyl peroxides on the yield strength of composites is shown in Figure 1. It is seen that the yield stress increases sharply

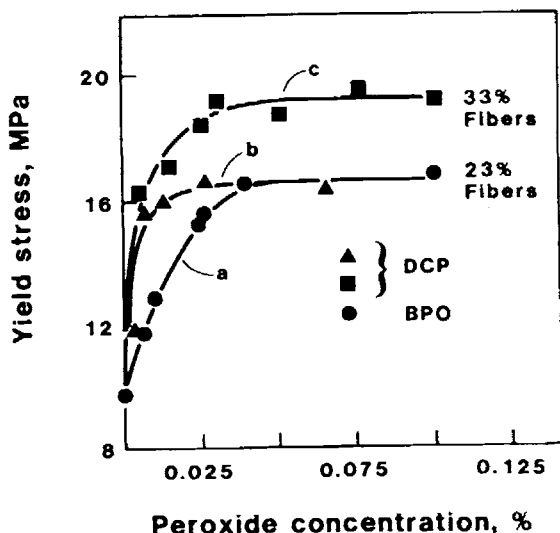


Fig. 1. Yield stress as a function of peroxide and fiber content.

TABLE I  
Critical Concentration of Peroxide in Composites

Fiber content (%)	BPO (%)	DCP (%)
23	0.029	0.010
33	—	0.021

at low peroxide concentration, then above certain critical concentrations  $C_{crit}$  remains relatively constant.  $C_{crit}$  is defined here as a peroxide concentration at which the yield stress reaches 95% of its maximum value for given fiber content. Table I shows that  $C_{crit}$  depends on the type of peroxide used; it is 0.029 and 0.010 for BPO and DCP respectively for composites containing 23% fibers. For a given peroxide,  $C_{crit}$  varies with the fiber content, for example, it varies from 0.010 to 0.021 for composites containing 23 and 33% cellulose.

Comparison of curves *a* and *b* in Figure 1 indicates that DCP is more effective than BPO at low levels of peroxide addition. This may result from the relative rates of peroxide decomposition; DCP has a lower decomposition rate, which ensures better dispersion in the polymeric matrix, and therefore more efficient utilization of the peroxide. In turn, this affects the mechanical properties. A similar effect of peroxides was observed for the stress at rupture.

Figure 2 shows Young's elastic modulus as a function of fiber content. The elastic modulus increases strongly in both untreated and peroxide modified composites, indicating that at small strains (up to 0.1%) the polymer is reinforced even by the untreated fibers. Such behavior has been observed in other cellulose-reinforced composites.<sup>11,18</sup> At high strains, however, due to poor adhesion with the polymer matrix, the untreated cellulose fibers have little or no

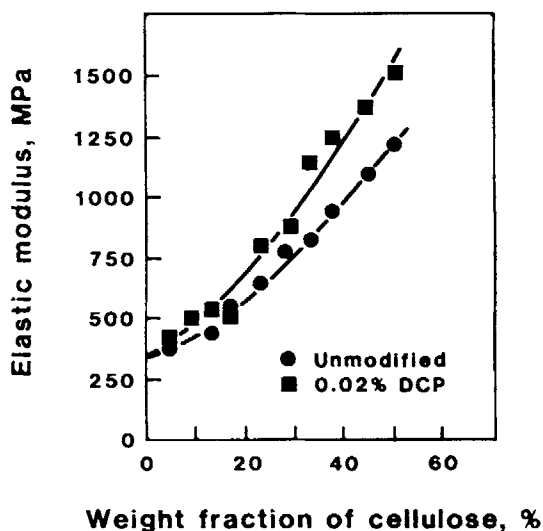


Fig. 2. Elastic modulus of unmodified and modified composites as a function of cellulose content.

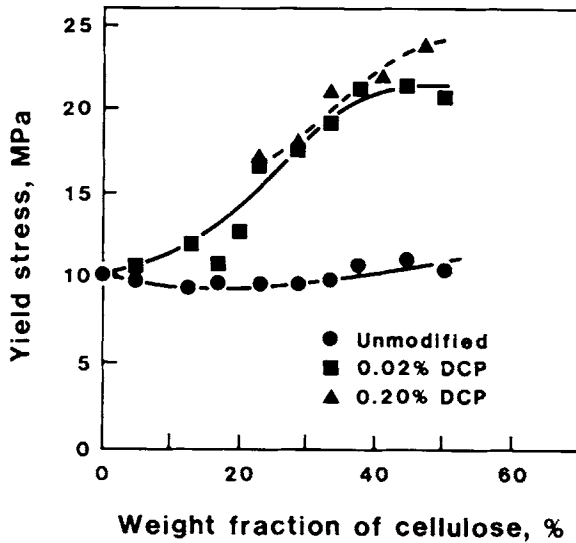


Fig. 3. Yield stress of unmodified and modified composites as a function of cellulose content.

reinforcing effect. As Figure 3 shows, the yield stress of the unmodified composite is practically independent of the fiber concentration. However, the addition of a small quantity of peroxide during processing leads to a significant increase in the yield stress. Typically, for 0.02% dicumyl peroxide added, the yield stress increases from 10 mPa to 22 mPa for composites containing 50% fibers.

The rupture stress of unmodified composites decreases monotonously with fiber content while that of the modified composites shows a minimum value for composites containing about 20% cellulose fiber (Fig. 4). The existence of

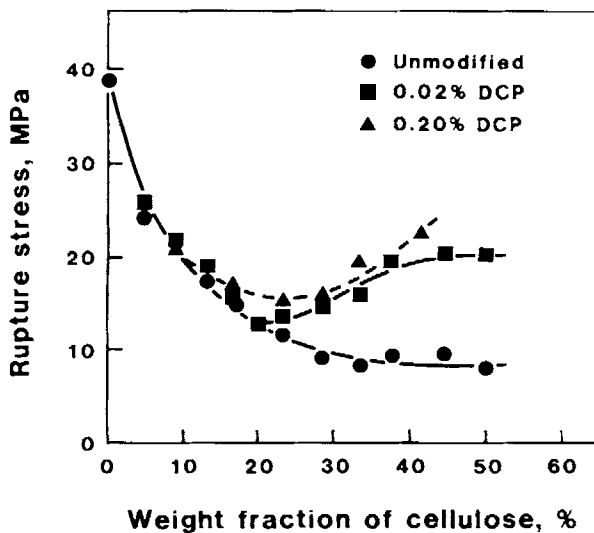
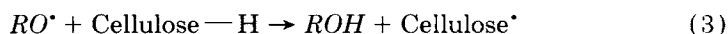
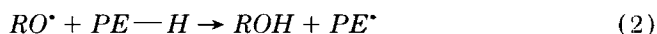


Fig. 4. Rupture stress of composites as a function of cellulose content.

the minimum is typical of many fiber-reinforced composites and its position generally shifts towards lower fiber content when longer fibers are used.<sup>19</sup> The decrease in the rupture stress below 20% fiber content may be due to the partial delamination and debonding of the cellulose fibers. As a result, in this range of fiber content, the fracture behavior of the peroxide modified composites is similar to that of the untreated composites. At high fiber contents, however, cellulose fibers reinforce the polymeric matrix. In this region the rupture stress of the composites is predetermined by the longitudinal and transverse stress properties of the cellulose fibers.

The increase in the yield and rupture stress at high fiber concentrations for peroxide modified composites is undoubtedly related to the peroxide-initiated free radical reactions between the LLDPE matrix and cellulose fibers

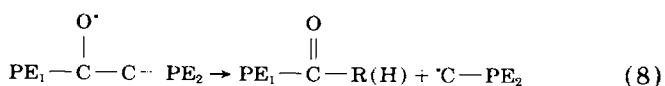
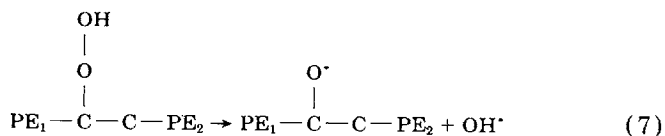
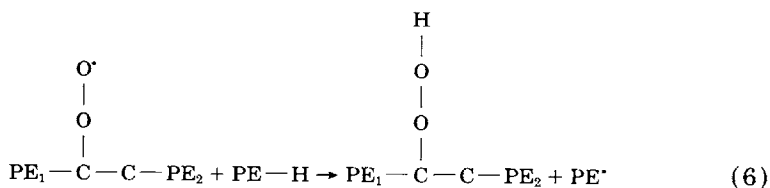
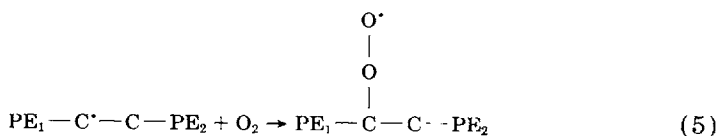


According to the literature,<sup>20,21,22</sup> the hydrogen abstraction in cellulose may occur from  $-OH$ ,  $C-H$  of the cellulose backbone as well as from methylol ( $-CH_2-OH$ ) groups. On the other hand, the LLDPE is a copolymer of alpha-olephins (i.e., butene, hexene, and octene) with ethylene. The hydrogen abstraction may therefore take place at tertiary carbons of the alpha-olephin units. The fact that peroxides are more effective in LLDPE than in HDPE,<sup>17</sup> supports this viewpoint.

The following reactions may take place during the processing of composites: (1) Increase of molecular weight and crosslinking of the polymer matrix by combining macro-radicals of polyethylene



(2) Introduction of polar groups (such as acidic and ketonic) into the nonpolar polyethylene chains by oxidative degradation



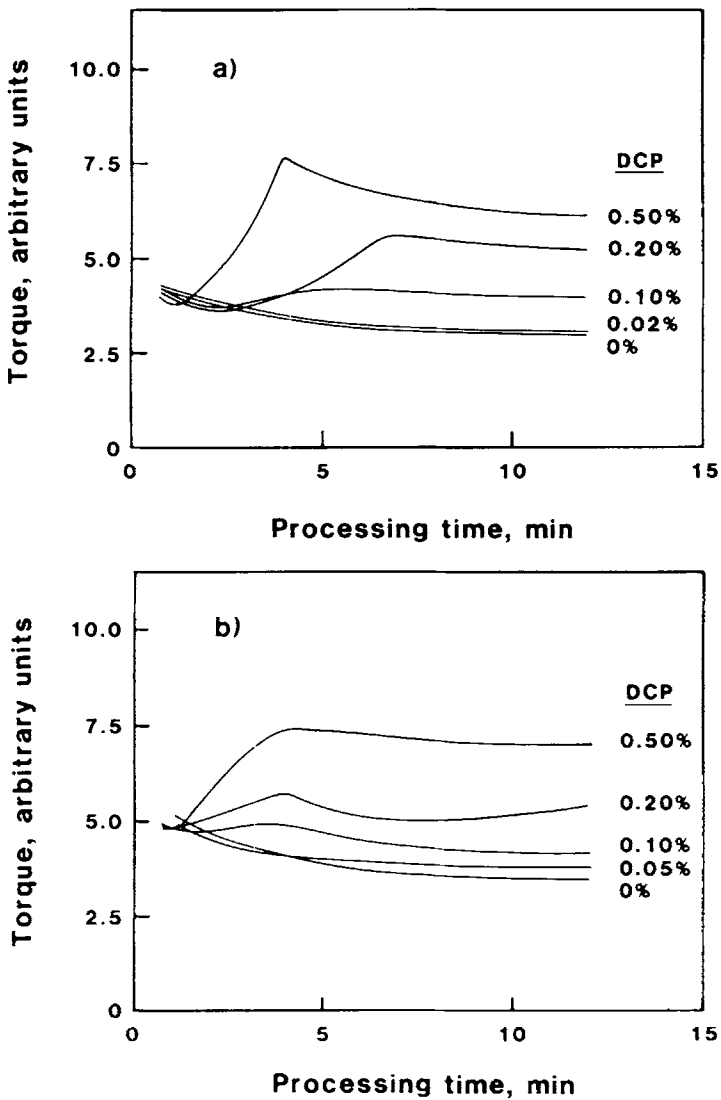
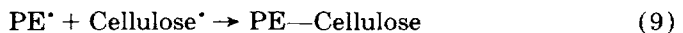


Fig. 5. Torque as a function of processing time for different amounts of DCP added: (a) LLDPE matrix, (b) LLDPE containing 50% cellulose.

(3) Grafting of polyethylene onto cellulose fibers by combining cellulose and polyethylene radicals



The efficiency of these reactions should increase with peroxide concentration, while reaction 9 also depends on the available cellulose surface and, therefore, on the concentration of cellulose fibers.

Reactions (4) and (9) should lead to increased molecular weight and thus to higher melt viscosities, while oxidative degradation should lead to a decrease

in molecular weight. These events may be expected to manifest themselves by variations in torque during processing. Figure 5 shows the torque vs. processing time for the LLDPE matrix and for composites containing different quantities of dicumyl peroxide. At DCP concentrations above 0.05%, the torque-processing time curves show a maximum value after about 4 min; both the maximum and final torque values increase with peroxide concentration. Such behavior, which is in contrast to the viscobreaking phenomenon,<sup>14,15</sup> may indicate that the oxidative degradation of LLDPE is not critical. On the other hand, the average molecular weight of the polymer appears to increase with the peroxide content. However, since the torque-processing time curves for the polymer matrix (Fig. 5a) and the composite (Fig. 5b) are similar, the increase in melt viscosity may be due to an increase in chain length, or to crosslinking of the polyethylene through reaction (4). Since the maximum in torque is not observed for polymers containing less than 0.05% dicumyl peroxide the crosslinking is negligible below this level of peroxide addition.

Despite the fact that crosslinking of polyethylene is expected to increase with peroxide content, the yield stress reaches a plateau value at DCP concentration of 0.03% (Fig. 1). This indicates that at this level of peroxide addition the crosslinking of polyethylene plays a negligible role in the modification of composite properties. Indeed, soxhlet extraction of the peroxide modified composites (up to 0.1% of DCP) revealed only a negligible amount of insoluble polyethylene (less than 3% by weight of polyethylene matrix). Similar behavior, independent of crosslinking, was also observed in our previous study, where a small amount of benzoyl peroxide was added to cellulose/LLDPE composite;<sup>17</sup> the formation of insoluble gel was found only at processing temperatures above 170°C, while the yield stress of composites already increased significantly at 160°C. A plausible explanation is that the average molecular weight between chemical crosslinks is more important than the molecular weight between physical entanglements. Therefore, the mechanical properties of solid composites are determined by entanglements. However, the increased molecular weight and the presence of chemical crosslinks strongly affect the melt viscosity of composites.

SEM micrographs of fracture surfaces of the peroxide-modified-composites indicate clearly that polyethylene is grafted onto cellulose surfaces. The treated fibers adhere well to the polymer matrix and break and delaminate during stretching (Fig. 6a). In contrast, the untreated fibers are pulled out from the matrix practically intact (Fig. 6b). Obviously, such fibers have no significant reinforcing effect in the composites. Micrograph of the soxhlet extracted fibers (Fig. 7) from the DCP modified composites also show the existence of polyethylene deposits on the fiber surfaces. Using electron beam as a probe, we observe melting rather than the surface cracking which would be typical for pure cellulose fibers.

The results presented demonstrate that peroxide-induced modification of composite properties is due mainly to the grafting of polyethylene chains onto the cellulose fiber, which subsequently promotes interfacial adhesion. It appears that only a small quantity of peroxide, corresponding approximately to the critical concentration,  $C_{crit}$ , contributes to the grafting reactions. An excess of peroxide may eventually result in crosslinking the polyethylene matrix with little effect on the composite's properties. According to this mechanism, one

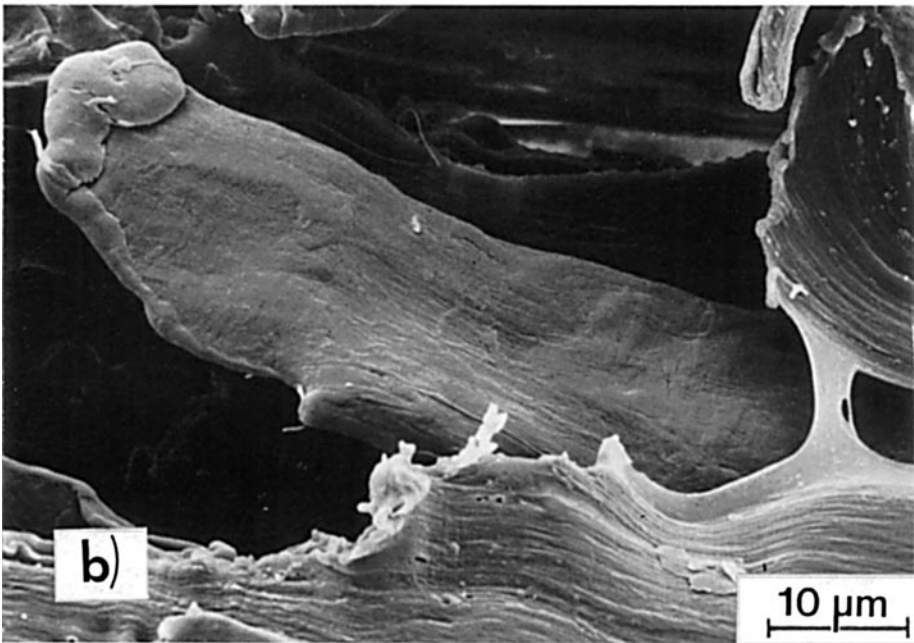
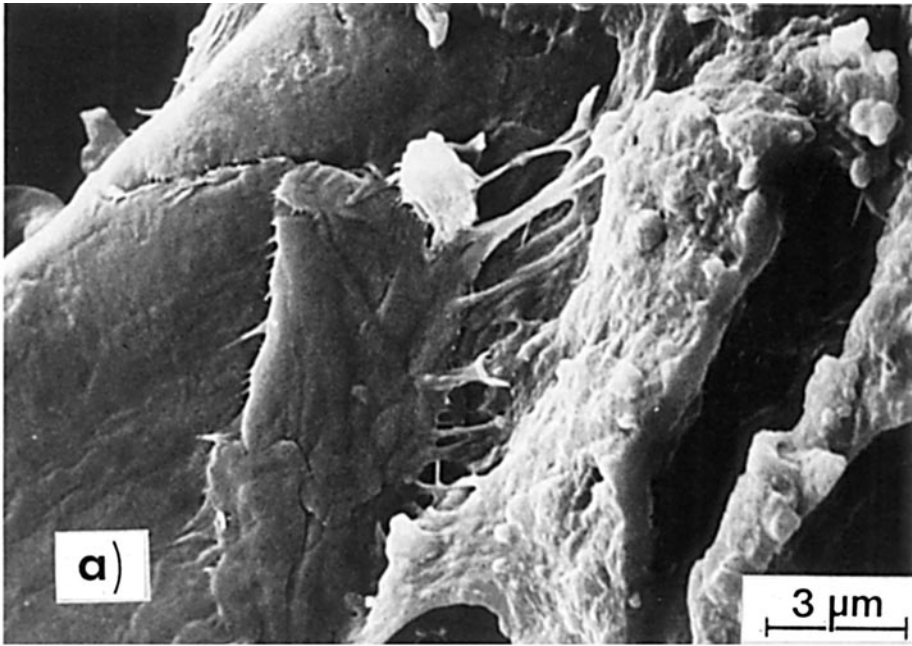


Fig. 6. SEM micrographs of the fractured surfaces: (a) composite with 0.5% DCP added, (b) unmodified composite.



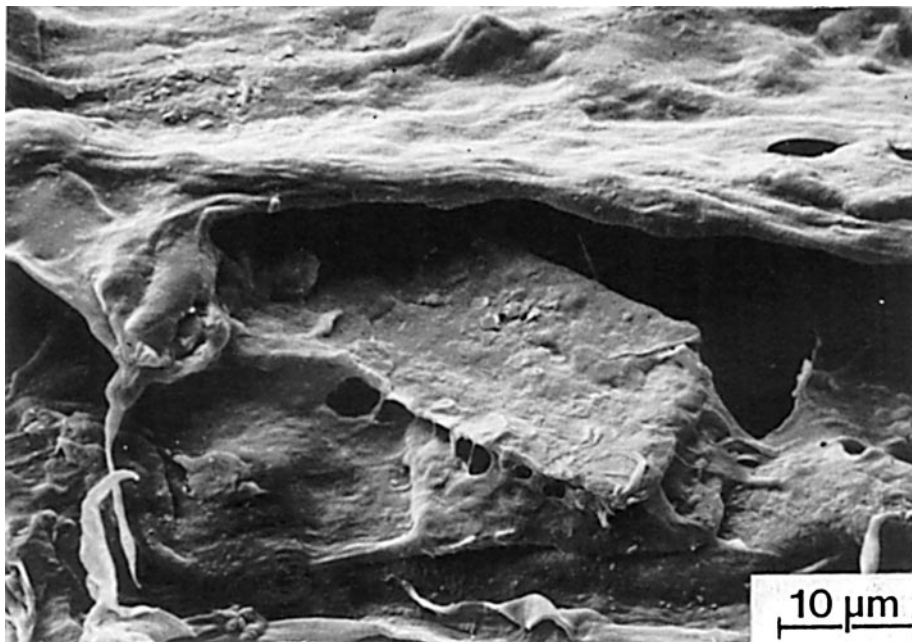


Fig. 7. SEM micrograph of the soxhlet-extracted fiber.

would expect  $C_{\text{crit}}$  to increase with the fiber concentration. Indeed, this is the trend shown in Table I, thus supporting the proposed mechanism.

## CONCLUSION

It has been demonstrated that the addition of a small amount of peroxide during processing significantly improves the mechanical properties of cellulose fiber-LLDPE composites. At the lowest levels of addition, dicumyl peroxide was found to be more effective than benzoyl peroxide. Improvement of mechanical properties is attributed to the peroxide-induced grafting of polyethylene onto cellulose surfaces, as demonstrated by SEM micrographs of fracture surfaces and of the surfaces of soxhlet-extracted fibers. The existence of a critical concentration of peroxide suggests that grafting reactions terminate when the fibers are covered with grafted polyethylene. Excess of peroxide causes some crosslinking of the polyethylene. This, however, has only minor effects on the overall mechanical properties of composites.

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