

Cellulose-Induced Crosslinking of Polyethylene

Polymeric composites containing wood pulp fibers have recently attracted considerable attention due to their low cost and excellent mechanical properties.^{1,2} However, commodity thermoplastic matrixes, such as polyethylene, are incompatible with cellulose, a factor leading to inadequate property retention when the composites are exposed to hostile conditions like high humidity or subfreezing temperatures. Therefore, surface pretreatment of the cellulosic fibers or the incorporation of additives have become widely used methods to modify the weak interface. Silane coupling agent modification of fibers³ and the use of surface modifiers such as maleated waxes⁴ are examples of these methods.

An alternate route to improving the mechanical properties of polyolefins is to crosslink these using thermolabile peroxides. At concentrations in the range of 1 wt %, agents such as benzoyl peroxide have been reported⁵ as effective in crosslinking polyethylenes. Benzoyl peroxide has also been used in composite systems; it has been shown to increase the tensile properties of polypropylene/wood flour composites,⁶ and elsewhere^{7,8} to promote grafting onto cellulose. The mechanisms whereby peroxides affect composite properties are not well understood, motivating current research in our laboratories. The present brief report is a result of that continuing study.

EXPERIMENTAL

Linear low density polyethylene (LLDPE) was the polymeric matrix, and highly bleached hardwood pulp the reinforcing fibers used in this work. The LLDPE was a commercial grade resin (LL-3010, courtesy of Esso Chemical Canada), with a melt index of 0.8. Samples containing 30 phr of cellulose were prepared by first dispersing the components using a Brabender mixing head (temperature range 160 ÷ 240°C), and then compression molding at 160°C. The pressed plates were cooled by quenching rapidly in cold water. Small amounts of benzoyl peroxide (up to 0.1%) were premixed with polyethylene and cellulose fibers before processing in the Brabender mixing head. The gel content in composites was determined by extraction in a Soxhlet apparatus using *para*-xylene as solvent. The extraction was performed for 24 h at 130°C, and the gel was collected on Whatman #4 filter paper.

Mechanical properties of composites were measured at room temperature using an Instron Instrument Model 4201. The length, width, and thickness of the samples were 27 mm, 3.2 mm and 0.6 mm, respectively. The rate of elongation used was 20 mm/min.

RESULTS AND DISCUSSION

The stress/strain characteristics of cellulose fiber-containing, crosslinked composites reveal interesting features, a particular aspect being shown by yield strength data in Figure 1. In Figure 1, the reference curve for the LLDPE matrix (A) shows that its yield strength is essentially independent of processing temperature. Thus, in the range 160 ÷ 240°C, the matrix polymer may be considered as thermally stable. The addition of benzoyl peroxide (curve B) produces yield values some 10 ÷ 15% higher than for the control polymer. The yield strength, again, is independent of cure temperature, suggesting that the peroxide is fully activated and consumed in the experimental temperature range. Curves C and D are in sharp contrast to the above; the former, presenting the effect of cellulose fiber addition, shows no significant influence of the fiber up to approximately 170°C, followed by a sharp rise in yield strength, which reaches a maximum at processing temperatures in the vicinity of 220°C. The data pattern suggests that a reaction takes place above a threshold temperature of about 170°C and that reaction driving the yield characteristics of the polymer in the same direction as peroxide-decomposition initiated crosslinking (curve B), but with results that exceed significantly those obtained with peroxide alone. Curve D may then be regarded as evidence for synergism between the cellulose and peroxide compo-

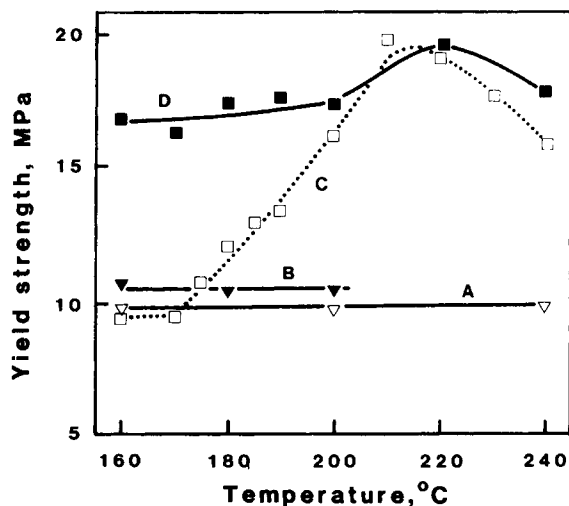


Fig. 1. Yield strength of polymers as a function of processing temperature. Cellulose content 30 phr. Processing time: 12 min. (a) LLDPE matrix; (b) LLDPE matrix with 0.1% benzoyl peroxide added; (c) untreated cellulose/LLDPE composite; (d) cellulose/LLDPE composite with 0.1% benzoyl peroxide added.

nents. Yield strength is now roughly doubled in comparison with the control polymer, and the strengthening effect is produced uniformly in the range $160 \div 190^\circ\text{C}$.

It is presently not feasible to offer detailed mechanisms for the observed effects. The fact that both the presence of cellulose fibers and peroxide-initiated crosslinking increase the resistance of the LLDPE to the permanent deformation, however, suggests that mechanically stronger network structures may be contributing to that mechanism. These networks seem to be generated more efficiently and at greatly reduced expenditures of energy, when fibers and peroxide are used in combination. Further diagnostic work will be needed to account for the observations and therefore to permit exploiting the consequences fully.

Figure 2 presents the yield strength of composites as a function of benzoyl peroxide concentration in the LLDPE matrix. As little as 0.025% peroxide is seen to induce a dramatic increase in the yield strength. A similar relationship has been observed for elongation at yield. These effects resemble those obtained for composites using high density polyethylene (HDPE) as matrix material. The improvement was smaller than in the case of LLDPE,⁹ however, raising the possibility that the presence of tertiary carbons in the olefinic copolymer contributes to the fiber/peroxide-initiated reactions. These reactions, responsible for the increased yield strength of composites treated with benzoyl peroxide, may be due to crosslinking or grafting steps. Alternatively, the combination of peroxide groups and high temperatures could introduce polarity in the host polymer, thereby increasing the adhesion at polymer/fiber contacts. To clarify this, the insoluble fraction of composite materials was determined by extraction. Figure 3 shows that gel formation starts at about 170°C and that the gel fraction reaches a maximum of some 18% at 220°C . No gel formation was detected in composites or in the matrix LLDPE prepared without benzoyl peroxide, even when these were processed above 200°C . Comparison of the gel content (Fig. 3) and yield strength data (curve C of Fig. 1) as a function of processing temperature shows a strong similarity. Both increase strongly, and the increase coincides with the inception of rapid thermal degradation of cellulose. This and the fact that no gel was detected in polyethylene at low levels of benzoyl peroxide addition may suggest that cellulose alone, and its degradation byproducts, play a similar role to peroxide in fostering the modification of polyethylene matrixes. We have pointed out previously¹⁰ that chemical changes occur in cellulosic fibers when these are subjected to typical polyolefin processing temperatures, thereby substantiating the link. Additional experimental data are needed to resolve such questions as whether the gel formation is induced by the pure cellulose, by its degradation byproducts, or by low molecular weight products migrating out of the cellulose fraction during processing. Another point to question is whether the

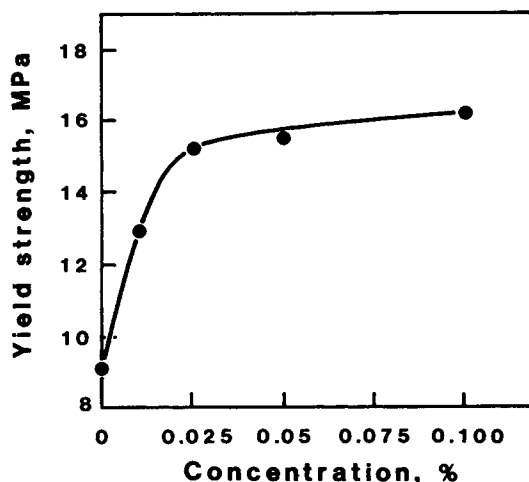


Fig. 2. Effect of benzoyl peroxide concentration on the yield strength of composite. Processing temperature, 160°C; processing time, 12 min.

gel formation occurs within the polyethylene matrix or through grafts of polyethylene components to the fiber surface.

Work presently underway will examine the influence of mixing rate and melt viscosity on the quantity and distribution of gel in the composite. This reflects on the apparent scattered spatial distribution of crosslinks within the composite. Presumably, the degree of dispersion of the peroxide, or its preferential localization at fiber interfaces, may be a factor in the matrix modification process, and the variables noted above should be important in that context. A further focal point of interest is the precise nature of the cellulose/matrix interface. Given the major mechanical property responses at low processing temperatures, it seems possible that the formation of free radicals may lead to the formation of strong adhesive bonds at these low temperatures. As several reaction schemes are possible, the exact nature of such bonds cannot yet be well defined. For example, benzoyl-peroxide-initiated radicals may attack the cellulose backbone generating cellulosic radicals which may subsequently promote the grafting of cellulose to the polymeric matrix. Alternatively, grafting of peroxide on polyethylene could take place through attack on tertiary carbons and on the few double bonds usually present on the backbone chain. Crosslinking of polyolefins is known to be sensitive to side reactions occurring with benzoyl peroxide, as it generates chain-transfer reactions. It is also possible that the presence of polar

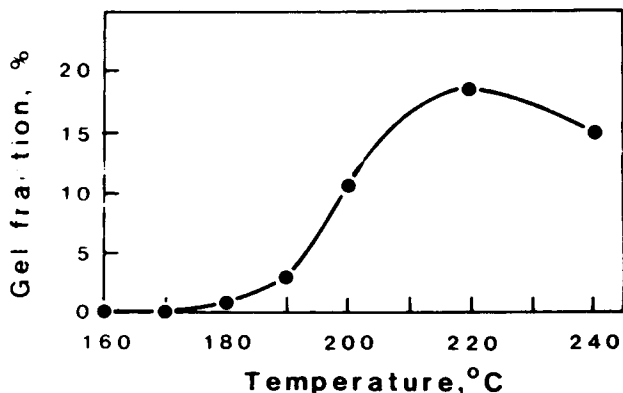


Fig. 3. Gel fraction in composites vs. processing temperature. 0.1% benzoyl peroxide added.

groups on cellulosic fibers modifies the nature and the life span of the reactive species generated, thus facilitating the crosslinking of the polymeric matrix. A more detailed discussion of the possible mechanisms leading to the improvement of mechanical properties and the formation of gel will be published elsewhere.⁹

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