Thermal Degradation of Cellulose-Containing Composites during Processing

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Synopsis

The strength properties of composites made of untreated cellulose fibers and linear low density polyethylene were investigated as a function of processing parameters. Studies have shown that the strength properties of composites increase with processing time and temperature. The increase in strength is accompanied by the appearance of new infrared absorption bands at 1718 and 1735 cm^{-1}. A linear relationship between the absorbance and yield strength of composites indicates that oxidation, possibly directly at interfaces, takes place and enhances adhesion between the cellulose and polyethylene.

INTRODUCTION

The interest in composite materials based on olefinic thermoplastics and cellulose remains high due to the attractive combination of economic and technical advantages inherent in these materials. Processing of cellulose-containing composites requires exposure of the components to relatively high temperatures, typical of those used in the processing of thermoplastic polymers. When cellulose is heated, it undergoes physical and chemical changes; physical properties affected include the enthalpy, weight, strength, color, and crystallinity; chemical changes include reduction of the degree of polymerization by bond scission, creation of free radicals, formation of carbonyl, carboxyl, and peroxide groups (especially in the presence of air), evolution of water, carbon monoxide, and carbon dioxide and finally, at elevated temperatures around 300°C, decomposition.[1]

The thermal degradation of cellulose is strongly influenced by the ambient atmosphere and pressure. The rate of thermal degradation of cellulose depends on whether degradation products are present (sealed system) or are being removed continuously (open system). The presence of reaction products in turn can accelerate the degradation process.[2]

In view of the above, questions arise on how the degradation of cellulose affects the properties of cellulose-containing composites. During the processing of such composites the degradation products are, at least partially, localized at the cellulose–polymer interface or diffuse into the polymer melt where they may react with the polymer matrix and the cellulosic filler. One possibility is that the degradation products may oxidize the polymer matrix. Such oxidation, for example, is required to form strong adhesive bonds between cellulose and polyethylene and is usually achieved by flame,[3] corona,[3-6] or high temperature extrusion.[3,7,8] Several other oxidative treatments have enhanced bonding. Goring and Suranyi[9] used ozone to create carboxyl groups on cellulose

fibers, wood, and plastic surfaces, creating better bonds between these various constituents. Young[10] used dichromate in oxalic acid as an oxidant to enhance bonding between cellulose fibers. Allan et al.[11,12] studied the oxidative coupling of phenolics to lignocellulosic fibers in the presence of strong oxidants like potassium ferricyanide and ferric chloride.

This work, presents evidence that the mechanical properties of cellulose-containing composites are indeed affected by processing conditions such as time and temperature, which will influence the kind and concentration of degradation byproducts. Changes in the chemical structure of cellulose and possibly oxidation of the polyethylene matrix both contribute to the characteristic properties of the composites.

EXPERIMENTAL

Linear low density polyethylene (LLDPE) used in this work as matrix polymer was a commercial grade (ESSO Co., Escorene LL 3010) having a density of 0.918 g/cm^3 and a melt flow index of 0.8. Alpha-cellulose fibers (Sigma Chemical Co.) were used throughout this work. Supplementary studies on discoloration of the composites were performed using the cotton fibers and black spruce thermomechanical pulp. Composites were prepared by mixing molten polyethylene with 0–40% of cellulose on a Brabender mill at temperatures of 150–240°C. Processing time varied between 4 and 20 min. Test samples were compression molded at $T = 160°C$ under pressure of 7.5 MPa and then quenched rapidly in cold water. This paper considers only composite samples containing 30% cellulose.

The tensile stress–strain behavior of composites was measured as the average of at least five samples at 23°C and 50% RH using an Instron Instrument model 4201. The length, width, and thickness of samples was 15, 3.15, and 0.5 mm, respectively, and the strain rate 10 mm per min. The initial tensile modulus, yield stress, and elongation as well as the stress and elongation at rupture were evaluated.

Analytic data on composite specimens were obtained from infrared spectra, using the Perkin-Elmer 467 or Mattson Instruments Cygnus 25 FTIR spectrophotometers. Samples were typically 0.2 mm in thickness. Absorbance, A, was measured against a linear background in the usual manner from the magnitude of the absorption peak, $A = \log(I_0/I)$, where I_0 is the intensity of incident radiation (baseline) and I is the intensity of transmitted radiation. The spectra were not corrected for light scattering.

Water content of composites was determined gravimetrically as described elsewhere.[13]

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows initial parts of the stress–strain curves for the 30% alpha-cellulose-containing composite prepared at different processing temperatures and times. It is seen that the stress and elongation at yield are a function of preparation conditions. Figure 2 presents yield strength vs. processing temperature, for constant processing time (11 min). The strength remains constant
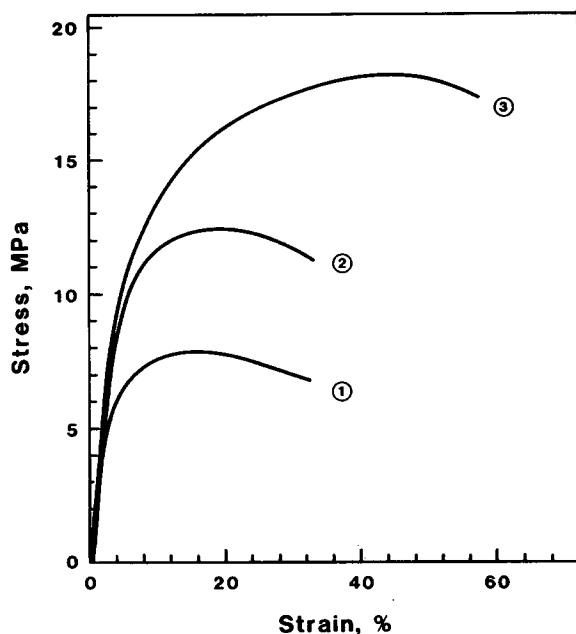
Fig. 1. Initial parts of the stress–strain curves showing the increasing yield strength for samples prepared at different processing conditions: (1) 160°C, 11 min; (2) 205°C, 11 min; (3) 205°C, 20 min.

up to 180°C then increases rapidly with the processing temperature. The maximum yield strength is reached at approximately 225°C. Also, the yield stress increases with processing time. The increase in strength of the composite is accompanied by some discoloration and the appearance of new infrared absorption bands at 1718 and 1735 cm^{-1}.
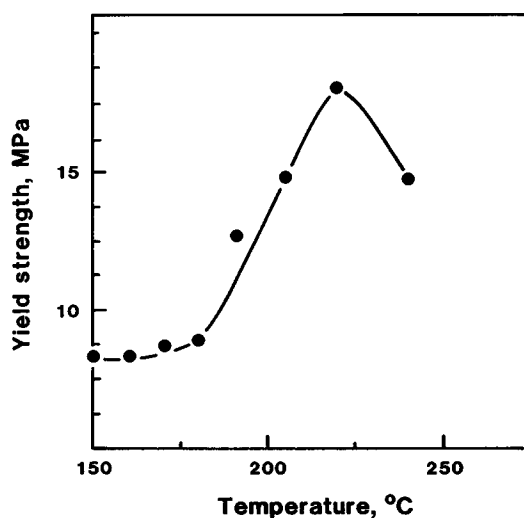

Fig. 2. Yield strength vs. processing temperature. Cellulose content 30%. Processing time 11 min.

The intensity of discoloration depends on the type of fibers used. Cotton fibers were found to be the most resistant and did not change color up to 200°C. Thermomechanical black spruce pulp produced composites with dark brownish color even at the lowest processing temperatures (150°C). Composites prepared with alpha-cellulose changed gradually from colorless to light brown when processing temperatures varied from 150 to 240°C. The degree of discoloration was found to be dependent on the water content in cellulose. Fibers with higher moisture content produced darker composites, frequently containing bubbles.

Infrared Spectra

It is inherently difficult to obtain clearly interpretable infrared spectra for composite materials. To begin with, the infrared analysis required relatively thin samples, usually with thicknesses comparable to those of cellulosic fibers alone (i.e., of the order of 10 μm or less). Secondly, due to the large number of cellulose–polyethylene interfaces contributing to light scattering, the infrared spectra can be characterized only semiquantitatively. Obviously light scattering produces a higher opacity in composites as compared with clear polyethylene.

Due to excessive sample thickness, not all of the infrared absorption bands could be measured. However, in general, the infrared spectrum of composites is a superposition of the spectra of polyethylene and cellulose as exemplified by absorption bands at 1430, 1160, 895, and 665 cm^{-1} for cellulose and 1470, 1380, 720 cm^{-1} for polyethylene (Fig. 3). The magnitude of peaks characteristic of cellulose is a function of relative cellulose content.

Infrared absorption bands located at 1635, 1718, and 1735 cm^{-1} are not typical of either cellulose or polyethylene and were found to be sensitive to
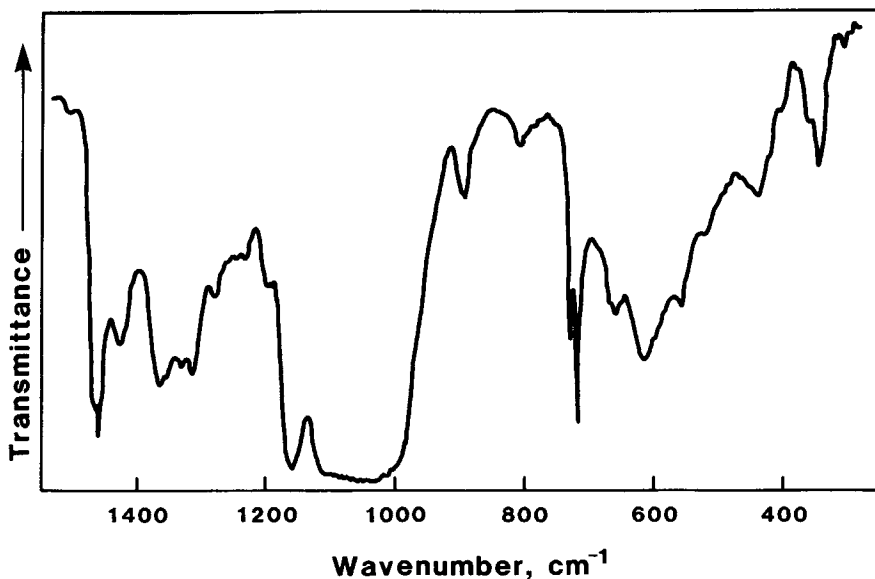

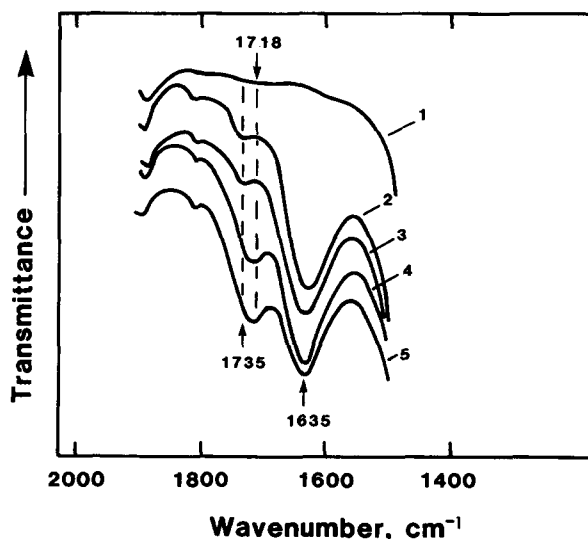Fig. 3.   IR spectrum of cellulose containing composite. Cellulose content 30%.

Fig. 4. The dependence of infrared spectra on processing conditions. Samples as prepared, without drying. Spectra were shifted to provide better readability. Processing conditions: (1) Polyethylene matrix 240°C, 16 min; (2) composite 160°C, 4 min; (3) composite 160°C; 16 min; (4) composite 205°C, 16 min; (5) composite 240°C, 16 min.

the preparation condition. They lie in the region of low intrinsic absorption of both polyethylene and cellulose. They are presented in Figure 4. The absorption band at 1635 cm^{-1} corresponds to adsorbed water in cellulose.[14] Such water might play a significant role in degradation processes. Klason et al.[15] observed that moisture content higher than 0.5% increased the degree of discoloration of composites. Figure 5 presents the absorption bands at 1635 cm^{-1} for samples with different water contents. Curve 1 refers to a freshly prepared composite. Despite careful drying of cellulose before mixing this peak was always present in composites. Moisture content can be somewhat diminished by long treatment at high vacuum, or more rapidly by simultaneous heating and pumping. Results to be published elsewhere[16] indicate that the composites, after removal from vacuum, sorb water rapidly up to 0.5%, whereupon the rate of sorption slows down. This may be due to fibers located at surfaces or at cross sections. Typically, for composites containing 30% cellulose, about 20% of the cross-sectional area is occupied by cellulosic fibers. Thin samples of cellulose-containing composites have high surface to bulk ratios and the number of fibers located at surfaces is often very high compared with the total number of fibers. Further, fibers located at surfaces or cross sections are easily accessible to water, i.e., water can be quickly absorbed or desorbed. If infrared absorption is measured using a conventional spectrophotometer, the samples are subjected to high intensity irradiation and the sample temperature increases. As a result, the investigated sample loses some of its water. In this respect FTIR is much superior as an analytic process, as scanning times are much shorter and the radiation energy absorbed is significantly lower. Figure 6 shows the dependence of absorbance at 1635 cm^{-1} as a function of water content. In the investigated composites it was found to be a linear function of water content.
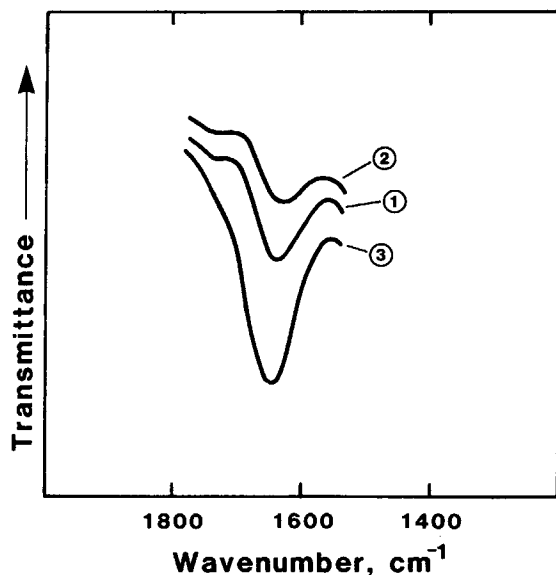
Fig. 5. The absorption band 1635 cm^{-1} for different water contents. 30% cellulose-containing composite. Processing conditions: 160°C, 4 min; (1) freshly prepared composite; (2) after 24 h vacuum treatment; (3) after 7 days immersion in water.

The absorption bands at 1718 and 1735 cm^{-1} (Fig. 4) are not present in pure polyethylene even when processed at 240°C for 20 min. The presence of cellulose in polyethylene leads to the appearance of the absorption band located at 1735 cm^{-1} (Fig. 4, curve 2). For samples processed at 160°C this peak only slightly increases with processing time. If the processing tempera-
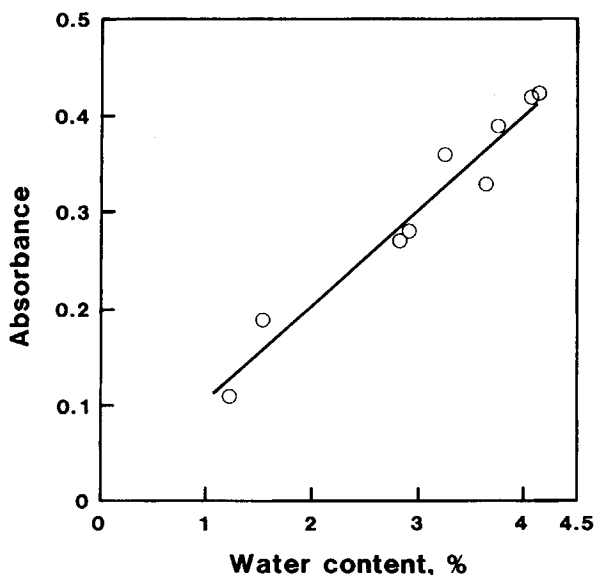

Fig. 6. Plot of absorbance at 1635 cm^{-1} vs. water content for composite prepared at 160°C. Cellulose content 30%. Processing time 4 min.
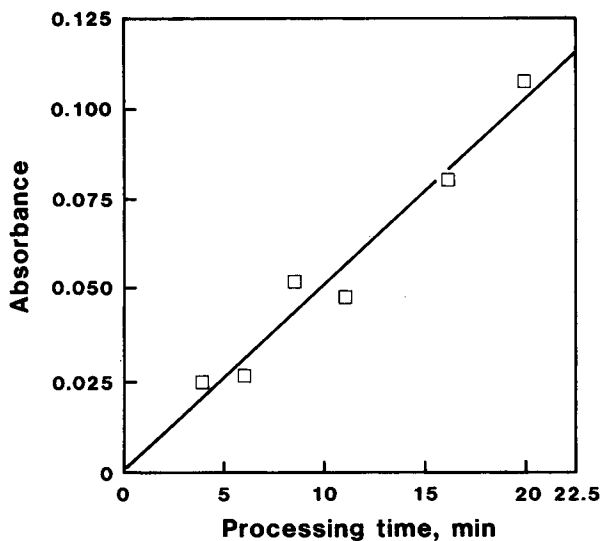
Fig. 7. Plot of absorbance at 1718 cm^{-1} vs. processing time. Cellulose content 30%. Processing temperature 205°C.

ture is increased, a new overlapping peak appears at 1718 cm^{-1} and becomes dominant at about 205°C. At any given temperature the magnitude of this peak increases with processing time as shown in Figure 7. The presence of these absorption bands may be due to ketonic, acidic, and ester groups attached to polyethylene[17] and /or cellulose.[18] These may result from thermal degradation of cellulose[18] or the oxidation of polyethylene. At present, however, we do not have any direct evidence to support the formation of carbonyl or carboxylic groups in the polyethylene matrix during processing.
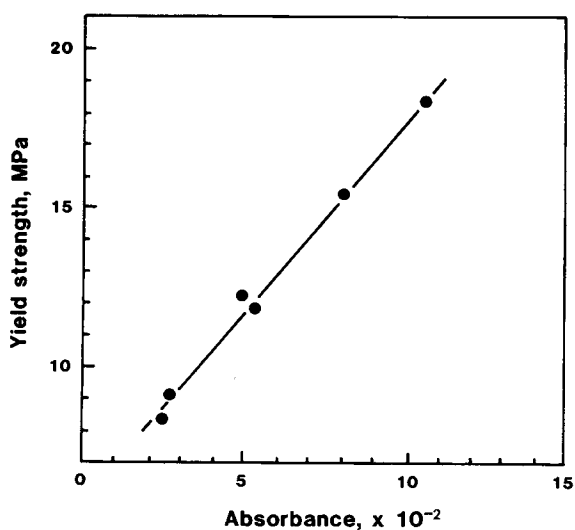

Fig. 8. Dependence between yield stress and absorbance at 1718 cm^{-1}. Cellulose content 30%. Experimental points correspond to different processing times.

Finally, Figure 8 shows the relationship between the total absorbance at 1718 cm^{-1} and the yield strength of the composite for samples prepared at different processing times. Such behavior would be consistent with increasing interfacial adhesion. The linear relationship between absorbance and yield strength indicates that oxidation processes, possibly directly at interfaces, occur and give rise to some adhesion between the untreated cellulose and polyethylene. We feel that a more detailed study is needed to identify the origin of the improved adhesion, including a study of the possible influence of shearing conditions during processing. Therefore, we intend to carry out such a systematic studies of cellulose-containing composites based on variety of polyethylenes and untreated and treated celluloses.

CONCLUSION

The data presented show that mechanical properties of composites respond to processing conditions. The increase in strength is probably due to oxidation at interfaces which enhances adhesion between the cellulose and polyethylene matrix. Also indicated is the possible optimization of ultimate strengths of such composites through the exercise of stringent controls over process time/temperature variables. Yet to be shown is the broader range of composite properties that may be affected by processing variables.

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