

Conversion of Plastic/Cellulose Waste into Composites.

I. Model of the Interphase

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SYNOPSIS

This article proposes a mechanism for a significant improvement in the mechanical performance of a simulated waste fraction, composed of an immiscible low-density polyethylene (LDPE) and high-impact polystyrene (HIPS) blend (70:30 proportion), when chemithermomechanical pulp (CTMP) fibers and maleic acid anhydride grafted styrene-ethylene/butylene-styrene block copolymer (MAH-SEBS) were added. SEM micrographs of composites showed an increased contact between the continuous LDPE phase and CTMP fibers when the functionalized compatibilizer (MAH-SEBS) was used. By employing a model study using LDPE and regenerated cellulose, we investigated the interphase properties between the plastic phase and the cellulosic component. The model study utilized ESCA, FTIR, and contact angle analysis to follow the reaction between the cellulose surface and the functionalized compatibilizer. All three methods showed that MAH-SEBS was bonded to the surface of the cellulose. The single-fiber fragmentation test showed that the adhesion between cellulose fibers and the plastic matrix was significantly improved for MAH-SEBS-modified samples. The effect of enhanced adhesion on increased mechanical properties of cellulose composites is also discussed, and a prediction of composite strength given, based on interfacial adhesion promotion and fiber properties. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recycling is proposed as a desirable way to reduce the amount of waste deposited in landfills and minimize exploitation of natural resources. Plastic materials contribute about 5–10% by weight to the total waste deposited and are composed mainly of polyolefins, PET, PS, and PVC.¹ Plastic waste collected almost inevitably consists of several different plastics, and the separation of pure fractions poses practical problems. Normally, in the case of thermoplastics, the production of new details from used materials is limited to plastics with pure, single-phase qualities. This is explained by the fact that, in addition to the difficulties in finding markets for products made from mixed recycled plastics, many polymeric blends also suffer from inferior mechanical performance owing to the lack of miscibility and poor adhesion between the components.^{2–4} However,

the need for improved miscibility in many polymeric systems has prompted the development of chemical compatibilizers that improve interactions between plastic phases, and a variety of products for different systems are now commercially available.⁵

Unfortunately, however, in the case of waste plastics, separated fractions and industrial waste also often consist of varying amounts of metal or cellulosic impurities, originating from laminates, etc. Basically, cellulosic materials offer certain properties that make them attractive for use in the reinforcement of thermoplastics. High specific strength and stiffness, desirable fiber aspect ratio, low density, low cost per unit volume basis, biodegradability, and a mild effect on processing equipment are among the advantages.⁶ An attractive approach in producing useful products from mixed plastics would, thus, be to induce the cellulosic components in plastic waste to act as a reinforcement instead of simply remaining impurities. Yet, the use of cellulose fibers for this purpose is restrained because of some deteriorating effects, of which the poor dispersion characteristics in polymer melts and the mismatch

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with polyolefin matrices seem most important.^{7,8} There are reports in the literature of several routes of surface modification on both materials developed to increase interactions between cellulose and polyolefins.⁸⁻¹⁴ Functionalized compatibilizers, often consisting of a polymer backbone grafted with reactive species, have particularly been seen to provide a convenient interphase modification in plastic/cellulosic systems. Maleic acid anhydride (MAH) grafted in this way on synthetic polymers has been proved to form both ester linkages and hydrogen bonds when reacting with hydroxy groups at the cellulose interface, resulting in a surface modification of cellulose.^{15,16} In full-scale, injection-molded plastic/cellulose composites, the addition of a few percent of a reactive compatibilizer is effective in gaining strength and stiffness for materials composed of cellulose and plastics.¹⁷ This is, of course, very important for the creation of useful composite materials and stands in contrast to materials with unmodified cellulosic fillers, in which increasing filler content often decreases the mechanical strength. Although the improvement of mechanical properties can clearly be designated to the modification procedure, there is still a lack of information concerning the basic mechanisms explaining the enhanced performance of the composite. To gain better understanding of this improvement, this research had as its major goal to perform a model study of the interphase between the components in a simulated waste plastic/fiber system.

EXPERIMENTAL

Materials

Low-density polyethylene (LDPE), NCPE 1800 with no additives, was supplied by Neste Polyeten AB, Sweden. Specific gravity: 0.921 g/cm³. MFI: 2.0 g/10 min (ASTM D1238).

High-impact polystyrene (HIPS), Polystyrol 456 M was supplied by BASF. Specific gravity: 1.05 g/cm³. MFI: 2.5 mL/10 min (ISO/IEC 1133).

Maleic acid anhydride grafted styrene-ethylene/butylene-styrene block copolymer (MAH-SEBS) was used as functionalized compatibilizer. The block copolymer, Kraton FG 1901X, was supplied by the Shell Chemical Company. The SEBS main chain is functionalized with MAH to an extent of 2% by weight. Specific gravity: 0.91 g/cm³. MFI: 22 g/10 min.

The specifications above are all according to the suppliers. Molecular weights were determined by size exclusion chromatography, SEC (Table I). The

Table I Molecular Weights as Determined by Size Exclusion Chromatography

	M_n	M_w	M_{peak}
LDPE	18,200	73,400	
HIPS	80,500	223,500	
MAH-SEBS			39,000

samples were dissolved overnight with 1,2,4-trichlorobenzene (135°C) for LDPE and MAH-SEBS and tetrahydrofuran (25°C) for HIPS. Filtration (0.45 mm metal filter) was performed before injecting the samples to the Waters 150CV, equipped with refractive index and viscometer detectors. Molecular weights were determined using polystyrene standard calibration for HIPS and polyethylene standard calibration for LDPE and MAH-SEBS.

Chemithermomechanical pulp (CTMP), consisting of 95% spruce and 5% pine, supplied by S.C.A. (Sundsvall, Sweden), was used for the preparation of composites. A Kajaani FS-100 instrument was used to determine the length distribution of the CTMP fibers. The length of the fibers was determined both as received from the supplier and after injection molding and testing of tensile properties. To obtain fibers from injection-molded samples, the plastic content in the test bars was dissolved in paraxylene. Fibers were separated from the solution by filtration, and fiber lengths were then determined without further treatment.

Regenerated cellulose, free from additives, was used for a model study of the interphase between cellulose and LDPE. Both fibers and membrane filters were used, owing to the experimental techniques. Svenska Rayon, Sweden, supplied the fibers, which had an average fiber length of 40 mm, a diameter of 12 μm, and a specific gravity of 1.59 g/cm³. The membrane filters came from Schleicher & Schuell, Germany, and were designated RC 58. The average pore diameter was 0.2 μm.

Preparation of Composites

Granulated LDPE and HIPS were blended to batches in a relative weight proportion of 70 : 30 (LDPE:HIPS); 0-30% of the batch weight was CTMP fibers, used as received without further purification or drying. The fibers were added to the batch by manual disintegration of the pulp into thin pieces (about 1 × 1 cm). MAH-SEBS was added to the mixture in two concentrations: 0 and 5%, based on batch weight.

The batches were compounded in a Buss Kneader PR 46 (screw diameter: 46 mm, L/D: 11, exit die: 15 mm) at 180°C to ensure good mixing and homogenization of the materials. The approximate residence time was 3–5 min. The room-temperated compound was then granulated in a rotating knife mill (Rapid GK20). The granulate was used to make tensile test bars by injection molding in an Arburg Allrounder 221E/170R. Machine parameters: 180°C at all three zones, injection pressure, depending on fiber content, 30–50 MPa (0.7 s), holding pressure 25–35 MPa (15 s), cooling time (29 s). The specimens were manufactured according to DIN 53455, and had an effective length of 75 mm and a cross-section of 3.5×10 mm. Measurements of tensile properties were performed with an Instron 1193 tensile tester equipped with an extensometer G51–15MA. The strain rate was 5 mm/min and the temperature 23°C. All mechanical tests were evaluated using at least five test bars for each composition. Scanning Electron Microscopy (SEM) was employed in the investigation of fractures, and the dispersion of the different phases in tensile tested composites. The instrument was a Jeol JSM 350 SM, operated at 5 kV.

Model System for Evaluation of Interfacial Adhesion

To remove impurities, the regenerated cellulose fibers were first boiled in water for 12 h, dried in an oven (70°C), and then soxhlet extracted in dichloromethane for 18 h. The functionalized compatibilizer was placed in an oven at 180°C for 15 min to transform maleic acid (MA) groups into the more reactive maleic acid anhydride (MAH) form by elimination of absorbed water. For the purpose of surface modification, the fibers were reacted for 10 min with “activated” MAH-SEBS dissolved in hot toluene (100°C). The concentration of MAH-SEBS was calculated as 5% by weight, relative to the regenerated fibers in atmospheric environment (fiber humidity about 3–5% by weight). After the reaction, fibers were soxhlet extracted in toluene for 12 h to eliminate unbonded material, and then finally dried.

The preparation of regenerated cellulose filter membranes for the surface characterization followed the same procedure as above, with some exceptions. The reaction was carried out by filtration of a 200 mL solution containing 2.4 g MAH-SEBS in toluene through a filter membrane (0.05–0.06 g). The filter membrane was then placed in an oven (180°C) for 1 h in order to aid the reaction of unreacted material. Soxhlet extraction subsequently took place to eliminate unbonded material. The intention in using this

procedure was to increase the cellulose surface area available for the MAH-SEBS solution, and was a necessity for a successful investigation by FTIR.

CTMP fibers for surface characterization were sufficiently clean after soxhlet extraction in toluene (12 h), but otherwise followed the procedure described for regenerated cellulose fibers. To prepare samples for the single fiber fragmentation (SFF) test, single regenerated cellulose fibers were placed between LDPE films, which were melted together in a press at 140°C. The total press time was 2 min, holding no pressure during the first and applying about 8 MPa during the second minute. The films were then placed between two aluminium plates (10 mm thick, 1.2 kg each) to ensure uniform cooling from melt. Dogbone-shaped specimens (Fig. 1) with single aligned-fibers were punched out from the film and mounted in a Minimat miniature tensile tester (Polymer Labs Thermal Sciences Inc.). The tensile tester was placed under an optical microscope (Olympus BH2-UMA) equipped with crossed polarizers, which made it possible to observe birefringent stress patterns in the thin matrix. The traction speed was 5 mm/min, and the sample was elongated until no further breakage of the fiber occurred. The evaluation of the interfacial shear strength is based on length measurements of 585 fragments of untreated fibers and 957 fragments of MAH-SEBS-treated fibers.

Surface Characterization of Materials

The effect of the MAH-SEBS treatment on the surface chemistry of cellulose was investigated by Electron Spectroscopy for Chemical Analysis (ESCA), contact angle analysis, and Fourier Transform Infrared Spectroscopy (FTIR). The instrument used for the ESCA was an AEI ES200 Spectrometer, and

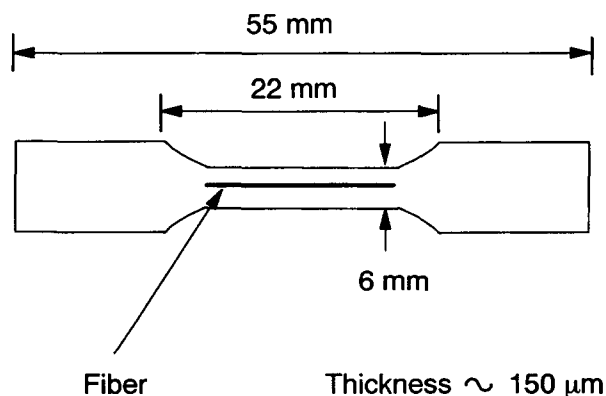


Figure 1 Dimensions of a specimen for evaluation of interfacial shear strength.

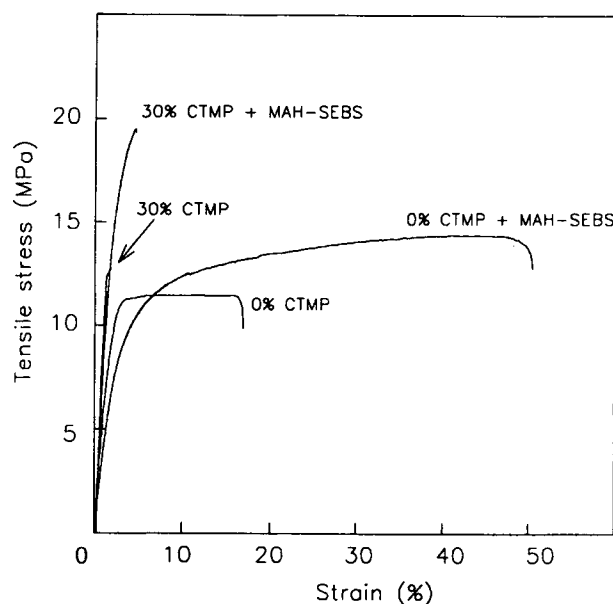


Figure 2 Characteristic stress/strain profiles for LDPE/HIPS/CTMP composites.

a Mg (K_{α}) x-ray source (12 kV, 20 mA) was used for the quantitative determination. An Al (K_{α}) x-ray source (15 kV, 20 mA) was used for the detailed spectrum.

Contact angles of distilled water on regenerated cellulose filter membranes and CTMP sheets were determined by a Dynamic Absorption Tester Fibro 1100 DAT. In this test, the change in contact angle for a 5 mL droplet was registered photographically as a function of time. Ten measurements were performed for each sample, which gave a standard deviation between 5 and 15% for each point in time. Initial values of the contact angle were then determined by extrapolation to the intercept where time equals zero. The aim of this procedure was to minimize errors resulting from absorption etc. All measurements were performed at room temperature.

Fourier Transform Infrared Spectroscopy (FTIR) was performed on regenerated cellulose filter membranes with a higher specific area than fibers. The instrument, a Perkin Elmer FTIR System 2000, was

equipped with a KRS-5 crystal in order to use the Attenuated Total Reflectance (ATR) technique (500 scans, MCT detector).

RESULTS AND DISCUSSION

Mechanical Properties of Composites

The addition of both cellulose fibers and functionalized compatibilizer to the LDPE/HIPS mixture shifts the mechanical characteristics of the system towards a stiffer and stronger material with decreased elongation (Fig. 2). The increase in both strength and stiffness cannot be explained solely by the expected effect of the SEBS main chain to "act as an ordinary compatibilizer," improving interactions between the immiscible LDPE and HIPS phases (Table II). It is known that the strength of short fiber composites is dependent on the transfer of load from the matrix to the fibers. Well-developed interactions between the stronger cellulose fibers and the plastic phase are, thus, required for this type of mechanical behavior, which suggests that MAH-SEBS promotes adhesion between the fibers and the plastic components. It is proposed that the following mechanism is responsible for the enhancement of adhesion: maleic acid anhydride grafted on SEBS chains is highly reactive towards hydroxyl groups at the cellulose surface and, when compounding at elevated temperatures or reacting in solution, both covalent and hydrogen bonds develop between the functionalized compatibilizer and the cellulose surface (Fig. 3). Further, MAH-SEBS covers the cellulose surface and, thus, wetting by the polyolefinic LDPE and HIPS phases is simplified, and better contact between cellulose and plastics is achieved. We also suggest that entanglements by different parts of the block copolymer may play a prominent role in the adhesion improvement between all components.¹⁸⁻²⁰ Matching parts of the block copolymer are able to diffuse into the separated LDPE and HIPS domains and, hence, connect them through an interphase region consisting of MAH-

Table II Mechanical Properties of LDPE/HIPS/CTMP Composites

	Strength at Break (MPa)	Elongation at Break (%)	Elasticity Modulus (GPa)	Impact Strength (kJ/m ²)
0% CTMP	9.8	32.9	0.53	20.0
0% CTMP + MAH-SEBS	12.4	71.5	0.40	21.1
30% CTMP	11.3	2.1	1.73	15.3
30% CTMP + MAH-SEBS	17.4	5.1	1.48	16.7

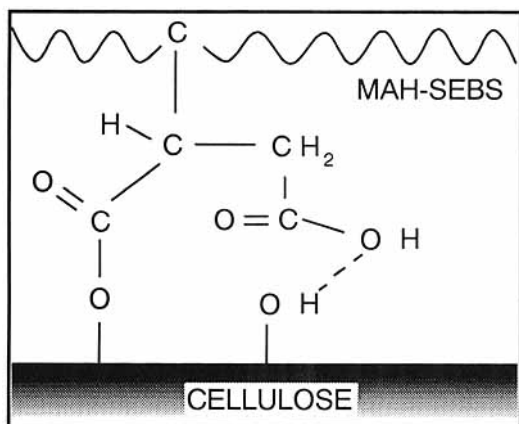


Figure 3 Proposed chemical reaction between MAH-SEBS and the cellulose surface.

SEBS. Similar arguments may be used in suggesting that such entanglements will also be present in an environment close to the fibers, originating from the functionalized compatibilizer bonded to the cellulose surface. This means that the fibers would be merged to the plastic phase (Fig. 4). As mentioned, good contact and adhesion between phases and, in particular, to the stiffer and stronger fibers, yield an improvement in mechanical performance.

Scanning electron micrographs support this theory. When studying tensile fractures of both MAH-SEBS-modified and -unmodified LDPE/HIPS/cellulose composites, the changes in microstructure become obvious. First, the addition of the compatibilizer decreases the diameter of the HIPS droplets and enhances their dispersion in the continuous LDPE phase, which is in agreement with previous reports.^{3,4} Of greater interest is that SEM micrographs also show that the functionalized compatibilizer facilitates the direct contact between the cellulose fibers and the LDPE/HIPS plastic phase. In unmodified samples [Fig. 5(a)], holes and spacings commonly occur along the fiber, resulting in poor contact and inferior stress transfer between the phases. Figures 5(b) and 5(c) show samples that have been modified with MAH-SEBS. As the plastic phase more or less covers the fiber surface, it can be concluded that the contact between the plastic and cellulose phases is improved by the functionalized compatibilizer. The better miscibility of the phases also enhances mechanical mixing, which explains the improved dispersion of the fibers in the matrix material. Enhanced dispersion is, in addition to the earlier discussed adhesion promotion, probably responsible for further improvement in the mechanical properties of the composite. Another observation made in Figure 5(b) and (c) is that the

major component surrounding the modified fibers seems to be the continuous phase, LDPE, while the HIPS droplets are scattered in the bulk phase. This is useful information for the design of a model study of the interphase.

Model of the Cellulose/Plastic Interphase

A model study was performed to experimentally quantify the role of MAH-SEBS in the interfacial adhesion between fiber and matrix and to outline a connection with the improved mechanical properties in composites. The study involved a single cellulosic fiber embedded in a plastic matrix, in which surface characteristics were evaluated by ESCA, FTIR, and contact angle measurements and interfacial adhesion by the single fiber fragmentation (SFF) test. The SFF test was performed using regenerated cellulose fibers, as the test requires a fiber with uniform properties and a low variation in dimensions, i.e., constant diameter. CTMP fibers, which are relevant to recycling of industrial significance, were not sufficiently homogeneous to fulfill the demands of the SFF test. As the model study deals only with interfacial adhesion between the matrix and the fibers, we suggest that the same modification mechanism is reproducible for the two types of cellulose fibers. The surface characterization presented below support this assumption. Still, pronounced differences

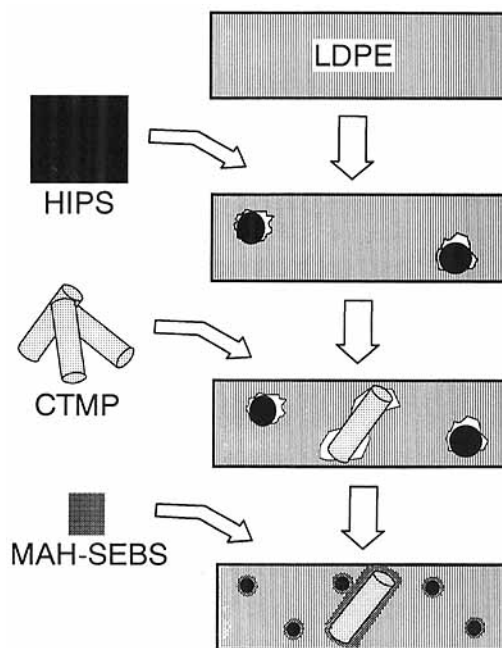


Figure 4 Proposed mechanism for the improvement in mechanical performance of MAH-SEBS-modified composites.

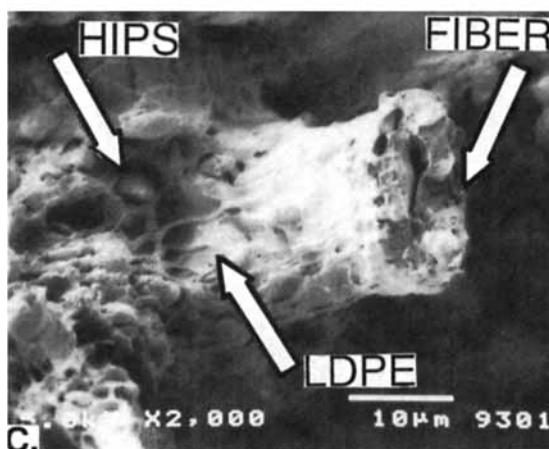
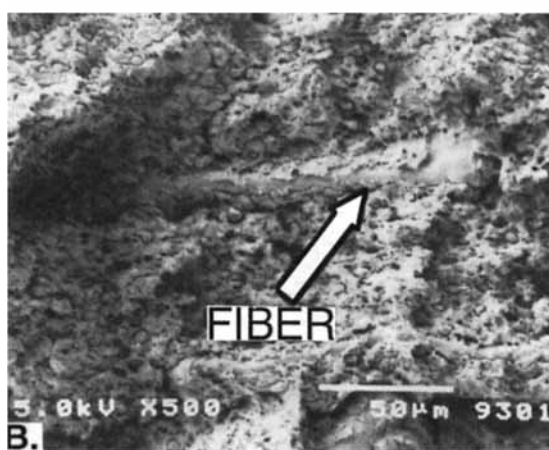
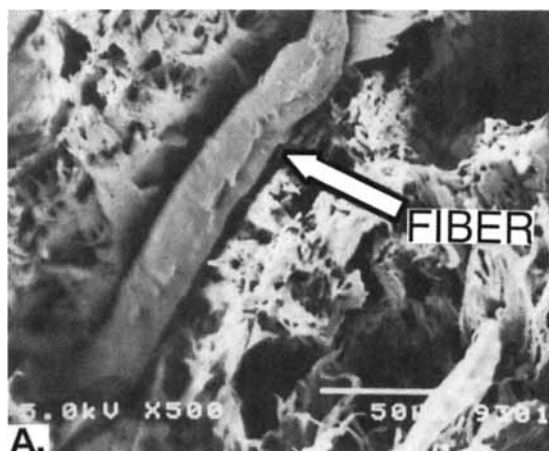


Figure 5 (a) SEM micrograph of a tensile fracture in a LDPE/HIPS/CTMP composite without MAH-SEBS. Magnification: $\times 500$. (b) SEM micrograph of a tensile fracture in a LDPE/HIPS/CTMP composite with 5% MAH-SEBS. Magnification: $\times 500$. (c) SEM micrograph of a tensile fracture in a LDPE/HIPS/CTMP composite with 5% MAH-SEBS. Magnification: $\times 2000$.

in crystallinity, morphology, and mechanical properties must be carefully considered, and we, thus, recommend that only relative measurements of different treatments should be evaluated.

Bonding of the Functionalized Compatibilizer to Cellulose

Regenerated cellulose and CTMP fibers were treated with MAH-SEBS, as described in the experimental section. All fibers and membranes were extracted with solvent prior to analysis. ESCA results (Table III) of extracted regenerated cellulose fibers show that the MAH-SEBS is present on the cellulose surface. The oxygen content for regenerated cellulose fibers, displayed as the O/C ratio at the cellulose surface, decreased from 0.63 to 0.38 when fibers were treated with a 5% by weight, MAH-SEBS solution. The atomic mass concentration of species representing the carbon-carbon bond increased from 17% to 44% in treated samples [Fig. 6(a)].

Similar changes are seen for the CTMP fibers as the O/C ratio decreases from 0.42 to 0.27 for MAH-SEBS-treated samples [Fig. 6(b)], which shows the ability of the functionalized compatibilizer to be bonded to the different types of cellulose. Further indications of the presence of MAH-SEBS onto cellulose are received from contact angle measurements, shown in Table III. The contact angle between water and regenerated cellulose changes from 29° to 88° when the cellulose has been treated with a solution of the functionalized compatibilizer. A similar change is registered for the CTMP fibers as the contact angle is increased from 85° to 101° by the MAH-SEBS treatment. The wetting of a surface with a water droplet is dependent on the presence

Table III Surface Properties of Cellulose

	O/C	Contact Angle
Regenerated cellulose (Untreated)	0.63	29°
Regenerated cellulose (MAH-SEBS treated)	0.38	88°
CTMP (Untreated)	0.42	85°
CTMP (MAH-SEBS treated)	0.27	101°
MAH-SEBS		95°

Oxygen/carbon (O/C) atomic composition ratio as determined by ESCA. Contact angle between water and different surfaces as determined by DAT.

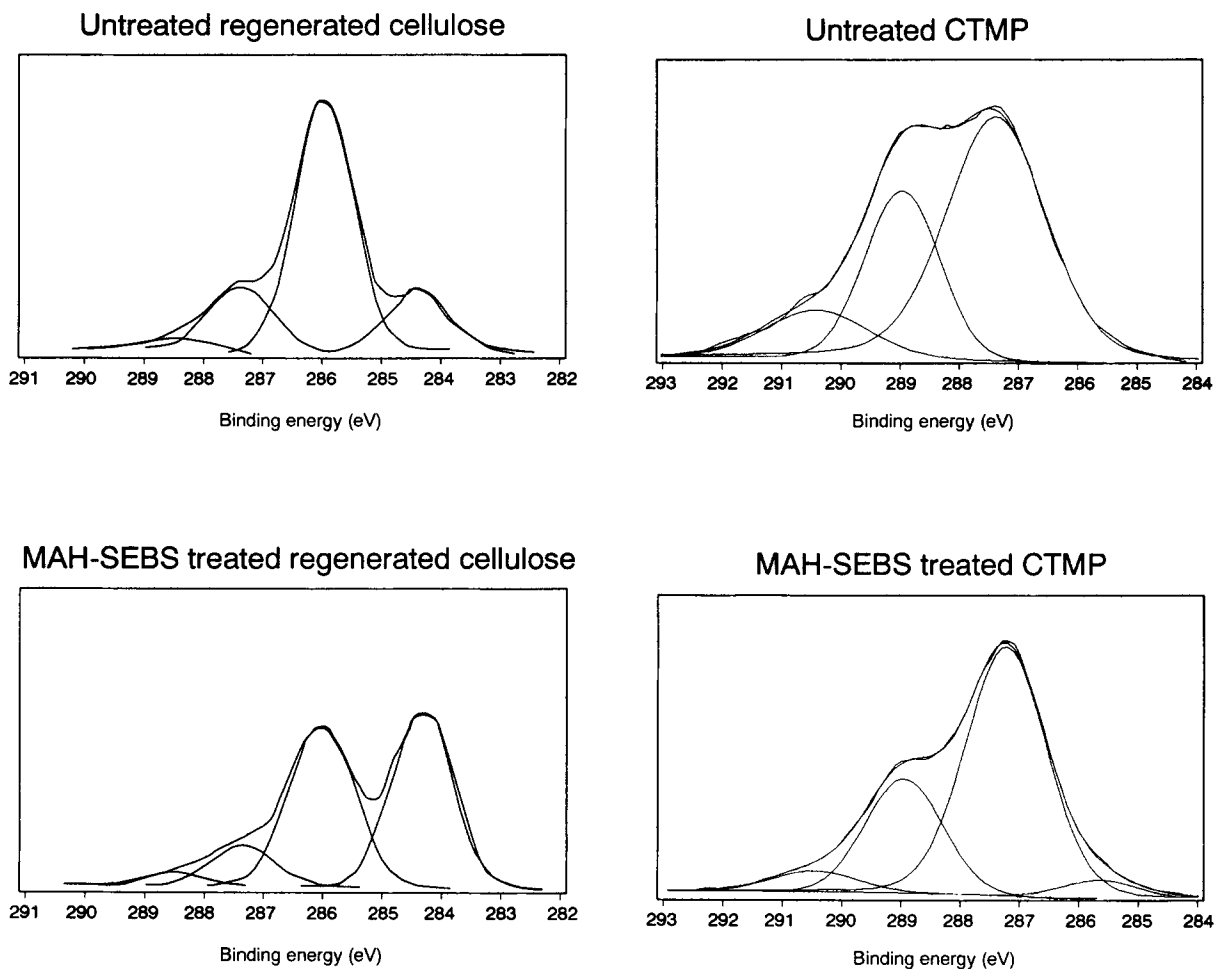


Figure 6 (a) ESCA spectra of the atomic species representing the carbon content. Untreated and MAH-SEBS-treated regenerated cellulose fibers. (b) ESCA spectra of the atomic species representing the carbon content. Untreated and MAH-SEBS-treated CTMP fibers.

of oxygen species on the surface. Good wetting and low contact angles are associated with oxygen-rich surfaces. The oxygen content in the MAH-SEBS chain is low in comparison with the oxygen content in the cellulose chain (about 1 and 50% by weight, respectively). Hence, the contact angle for a water droplet on a cellulosic material will be increased when cellulose is covered with MAH-SEBS. The contact angle measurements are, thus, in accordance with the ESCA results, showing that the MAH-SEBS bonds to CTMP fibers as well as regenerated cellulose surfaces.

Covalent bonding between cellulose and MAH-SEBS was detected by FTIR spectroscopy. The characteristic peak at 1739 cm^{-1} , develops for MAH-SEBS-treated regenerated cellulose, and is designated as being an ester bond (Fig. 7). The peaks at 1717 cm^{-1} and 1785 cm^{-1} arise from unreacted maleic acid and maleic anhydride, respectively. Hence,

the esterification of the maleic acid anhydride group with the cellulosic hydroxyl group takes place as proposed.

Measurement of Interfacial Adhesion

Table IV, summarizing a large number of test data, shows a 70% increase in the interfacial shear strength between LDPE and a regenerated cellulose fiber when MAH-SEBS is used for fiber surface treatment. Thus, the SFF test confirms that the improvement in strength seen on the MAH-SEBS-modified LDPE/HIPS/cellulose composites is strongly dependent on the interfacial adhesion between the fibers and the matrix material. A completed SFF test yields a broken fiber with a distribution of fragment lengths, which can be used to determine the critical fiber length, l_c . The critical fiber length, inserted in Eq. (1), enables the calcu-

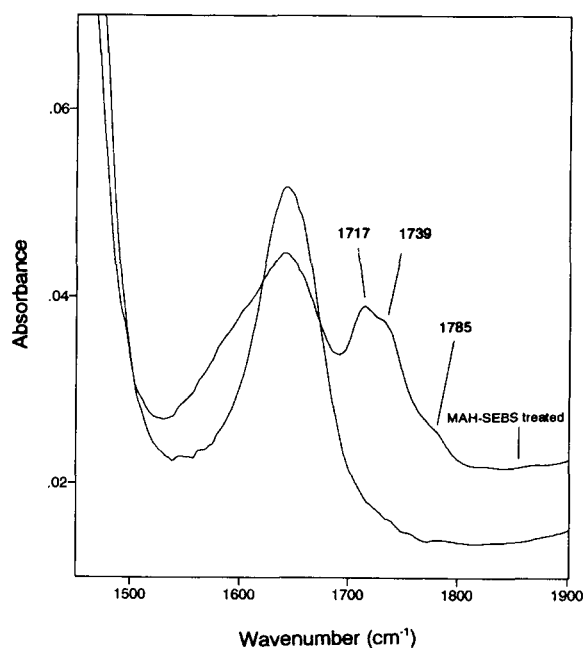


Figure 7 FTIR spectra of untreated and MAH-SEBS-treated regenerated cellulose membrane filters.

lation of the interfacial shear strength, τ , as a measurement of adhesion. The theoretical background is described elsewhere.^{8,21-23}

$$\tau = \frac{\sigma_{fu} \times d}{2 \times l_c} \quad (1)$$

where d is the fiber diameter and σ_f is the ultimate fiber tensile strength at the critical fiber length.

In order to achieve the most relevant calculation, different distribution models have been employed that fit the lengths of the fiber fragments to the critical fiber length.²³⁻²⁶ However, partially, as Eq. (1) was originally developed by Kelly and Tyson based on studies of a metallic fiber/matrix system, some systems have been seen to exhibit a lack of fit to the common models. Some authors have, thus, assumed a normal distribution of fiber fragments in order to obtain a relative measurement of the adhesive strength.²³⁻²⁶ For our model system, the critical fiber length was obtained by dividing the arithmetic mean of all fragment lengths by 0.75, as though they were normally distributed between l_c and $l_c/2$. From this, the interfacial shear strength was calculated, which yields a relative measurement that suits our model study.

Micrographs taken through an optical microscope during the tensile stretching of specimens support the numerical values of the interfacial shear strength. The shear transfer is more effective when

Table IV The Critical Fiber Length and the Interfacial Shear Strength between Regenerated Cellulose Fibers and LDPE

	Critical Fiber Length (μm)	Interfacial Shear Strength (MPa)
Untreated fibers	660	3.3
MAH-SEBS treated fibers	410	5.6

using MAH-SEBS-treated fibers, as large and well-developed triangular stress patterns are generated along the fiber fragments [Fig. 8(a)]. These patterns are much less significant in the unmodified samples, where it also is possible to see an indication of debonding between the fiber and the matrix [Fig. 8(b)]. Debonding is detected as the stress patterns seem

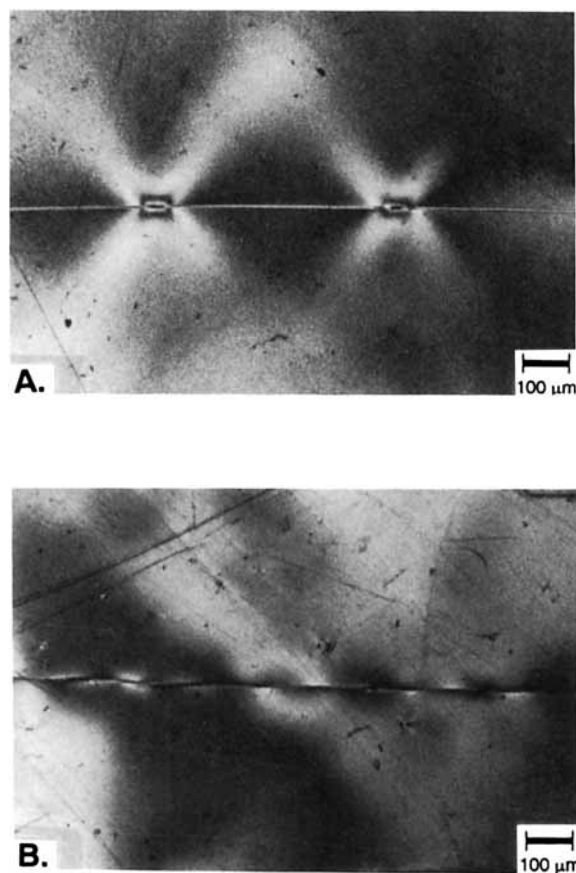


Figure 8 (a) Micrograph from optical microscope showing stress concentrations in LDPE along the axis of a regenerated cellulose fiber treated with MAH-SEBS. (b) Micrograph from optical microscope showing stress concentrations in LDPE along the axis of a regenerated cellulose fiber (untreated).

to move towards the middle of the fiber axis after breakage, thus indicating insufficient stress transfer at the fiber ends.

The model study, together with the evaluation of the mechanical properties of composites, satisfies the suggested mechanism for improved mechanical performance in LDPE/HIPS/CTMP blends. The experiments stipulate that a major part of the improvement in composite performance can be contributed to the MAH-SEBS-promoted adhesion between the plastic phase and fibers.

Limits of Improvement

As seen here and explained in numerous reports, it is possible to utilize several different methods to improve mechanical characteristics in composites and blends in which there is a lack of interaction between the components. Although the degree of improvement may vary in different systems, one question is often left to answer: what is the maximum limit of improvement? One way to provide a theoretical prediction of the ultimate strength of composites was given by Kelly and co-workers,^{22,27} who stated that the ultimate axial tensile strength, σ_{cu} , in an aligned short fiber composite with the fiber volume fraction V_f , can be expressed as:

$$\sigma_{cu} = \sigma_{fu}(1 - l_c/2l)V_f + \sigma'_{mu}(1 - V_f) \quad l \geq l_c \quad (2)$$

and

$$\sigma_{cu} = \sigma_{fu}V_f l/2l_c + \sigma'_{mu}(1 - V_f) \quad l \leq l_c \quad (3)$$

where l is the uniform length of fibers in the composite and σ'_{mu} is the stress in the matrix at the failure strain of the composite.

Regardless of several limitations pointed out in the literature, the theory suits our purpose of performing a relative estimation of the maximum strength, which can theoretically be obtained in our model system.²⁸⁻³⁰ Studying Eqs. (2) and (3), it becomes clear that the maximum strength of a composite with fixed filler proportion is reached when either the fiber lengths increase towards infinity or when the critical fiber length is infinitesimally small. As the name implies, short fiber composites suggest that the fiber length is limited to a certain value. Therefore, increased composite tensile strength is achieved by decreasing the critical fiber length, i.e., enhancing adhesion between the matrix and the fibers. However, even with "perfect" adhesion, the critical fiber length is limited. This is explained by the fact that the maximum shear stress that can theoretically be transferred to the fiber is restricted

by the maximum shear stress in the matrix before yielding. Thus, the minimum critical fiber length is calculated from Eq. (1), assuming that the interfacial shear strength, τ , is equal to the shear yield strength of the matrix material. The SFF test determined the critical fiber length for MAH-SEBS-modified samples to be 409 μm . Consequently, provided that the shear yield strength for the LDPE is higher than 5.6 MPa, additional enhancement of the matrix/fiber adhesion will further improve the strength of a model system composite. The significant effect of adhesion (critical fiber length) on the ultimate strength of an aligned short fiber composite is illustrated in Figure 9. Obviously, the relative effect of the adhesion improvement is most pronounced for fibers shorter than 1 mm in our model study. Cellulosic fillers are normally supplied as the CTMP in our composites as a broad distribution of fiber lengths, often containing a large portion of relatively short fibers (Fig. 10). This distribution will be shifted to even shorter fiber lengths when the composites are produced by processing, which is followed by injection molding, as the result of the breaking of fibers by wear in the processing equipment. The composite may now have a large volume fraction of fibers that are not able to contribute optimally to the total strength, i.e., are below the critical fiber length. As the variation in tensile strength of CTMP fibers is considerable, it is impractical to estimate the ultimate tensile strength for composites, as was done for our model system above. Still, when study-

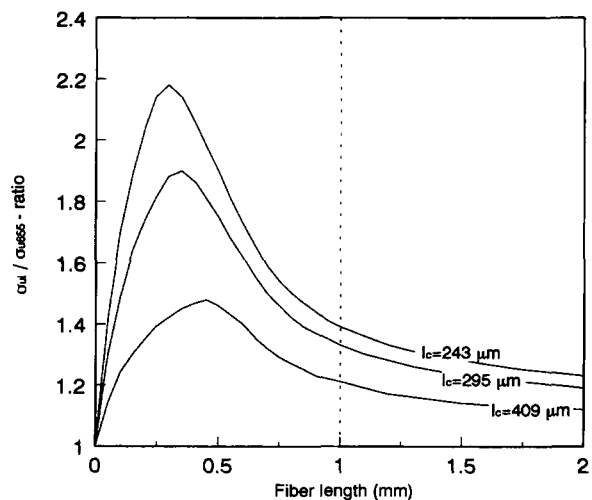


Figure 9 The relative effect of various critical fiber lengths (adhesion) on the ultimate short fiber composite strength. Index 1 represents the ultimate strength of a regenerated cellulose fiber composite with the critical fiber length 655 μm (unmodified samples).

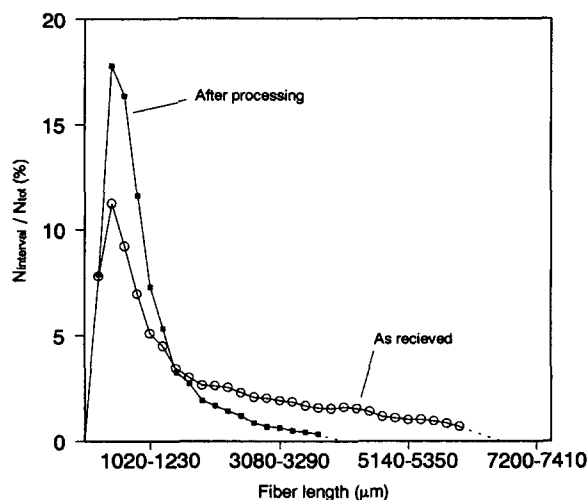


Figure 10 Population distribution of CTMP fibers displayed through fiber length intervals.

ing the fiber length distribution for CTMP fibers together with tensile strength values from the literature (600–1500 MPa before recycling), it becomes apparent that a large fraction of fibers will be within the zone in which adhesion is crucial for the composite strength.³¹ This would correspond to the “1 mm limit” for the regenerated cellulose (about 350 MPa). Consequently, further improvement of adhesion, together with better alignment of the fibers, would yield a material with significantly increased mechanical strength. This points out the need for additional research on improved adhesion, alignment of fibers, and reduction of processing wear in cellulose/plastic composites.

CONCLUSIONS

Tensile tests of LDPE/HIPS composites showed an increased stiffness when cellulose fibers were added. Increased strength is furthermore provided when, in addition to the cellulose fibers, a functionalized compatibilizer, MAH-SEBS, is added. SEM micrographs of fracture surfaces indicated good contact between cellulose fibers and the continuous phase (LDPE) in samples containing MAH-SEBS. A model study representing the LDPE/cellulose fiber interphase investigated the effect of MAH-SEBS. ESCA and contact angle analysis showed the ability of MAH-SEBS to react with the cellulose surface. It is proposed that the bonding of MAH-SEBS to hydroxyl groups at the cellulose surface is possible, owing to the reactive maleic acid anhydride, which is grafted onto the backbone of the compatibilizer.

FTIR spectroscopy established the development of ester bonds between the cellulose and MAH-SEBS. The SFF test showed that the adhesion between LDPE and cellulose fibers was improved when MAH-SEBS was bonded to the cellulose surface. It is concluded that the significantly enhanced mechanical properties in the LDPE/HIPS/cellulose composites owes principally to the ability of MAH-SEBS to improve adhesion between the plastic phase and the fibers, together with increased dispersions. Furthermore, a theoretical prediction suggests that the composite strength may be increased even more by further improvement of adhesion, together with better alignment of fibers. It is our opinion that specially designed functionalized compatibilizers have a great potential as modifiers for systems with mixed plastics containing impurities and may aid in creating products with marked improvements in mechanical properties.

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