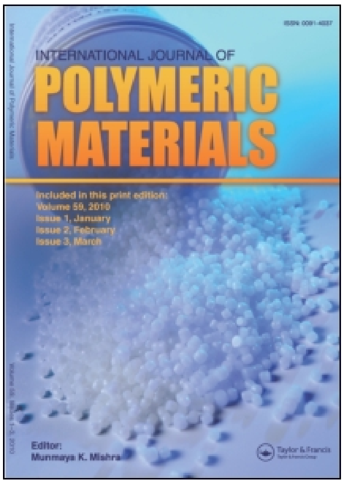

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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A. Boldizar[a]; C. Klason[a]; J. Kubát[a]; P. Näslund[b]; P. Sáha[c]
[a] Department of Polymeric Materials, Chalmers University of Technology, Göteborg, Sweden [b] Swedish Forest Products Research Laboratory, Stockholm, Sweden [c] Technical University Brno, Faculty of Technology Gottwaldov, Gottwaldov, Czechoslovakia

To cite this Article Boldizar, A. , Klason, C. , Kubát, J. , Näslund, P. and Sáha, P.(1987) 'Prehydrolyzed Cellulose as Reinforcing Filler for Thermoplastics', International Journal of Polymeric Materials, 11: 4, 229 — 262
To link to this Article: DOI: 10.1080/00914038708078665
URL: http://dx.doi.org/10.1080/00914038708078665

Intern. J. Polymeric Mater., 1987, Vol. 11, pp. 229–262
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Printed in the United Kingdom

Prehydrolyzed Cellulose as Reinforcing Filler for Thermoplastics

A. BOLDIZAR, C. KLASON and J. KUBÁT

Department of Polymeric Materials, Chalmers University of Technology, S-412 96 Göteborg, Sweden

P. NÄSLUND

Swedish Forest Products Research Laboratory, Box 5604 S-114 86 Stockholm, Sweden

and

P. SÁHA

Technical University Brno, Faculty of Technology Gottwaldov, CS-762 72 Gottwaldov Czechoslovakia

(Received September 26, 1986)

This paper presents the results of an experimental study of the mechanical properties of composites consisting of prehydrolyzed cellulose and thermoplastic matrices. The main feature of prehydrolyzed cellulose fibres is a high degree of brittleness, permitting the fibres to be finely comminuted in the shear field of normal compounding and processing machinery. Such an effect can be anticipated to improve the homogeneity and the mechanical parameters of the moulded samples. In the present work, this has been demonstrated with PP, HDPE and PS containing varying amounts of prehydrolyzed cellulose of different origin (bleached pulps). The tests were done on injection moulded samples. The compounding method (Buss-Kneader vs. twin-screw extruder) had only minor influence on the results. Theoretical assessment of the modulus values using the Tsai–Halpin equation gave somewhat lower values than those recorded on experimental samples. This was interpreted in terms of the disintegration of the cellulose component into submicroscopic fibrillar entities, so-called microfibrils, with a high aspect ratio and high modulus and strength values.

In another series of experiments suspensions of microfibrillar cellulose in water were prepared by intense mechanical treatment of prehydrolyzed cellulose. This fibrillar material was then incorporated into a thermoplastic matrix either directly by mixing with a latex (PVAC, PS), or after drying (freeze drying, solvent exchange (PP)). Contrary to what could be anticipated, the modulus and strength values of the composites obtained were inferior to those recorded with the composites prepared by conventional compounding of prehydrolyzed cellulose with the matrix material and subsequent injection moulding. This is interpreted in terms of excessive agglomeration of the fibrils resulting in a loss of the original aspect ratio.

The data obtained support the concept that cellulose has a significant potential, hitherto largely unexploited, as a reinforcing filler.

INTRODUCTION

The potential of cellulose materials as fillers for thermoplastics is reflected in an increasing number of publications dealing with the properties of such composites. Among the advantages of such fillers, one can mention low density, reduced wear of the processing equipment, the possibility of varying the L/D-ratio of the particles, and also their ability to absorb certain chemical substances which may act as coupling agents, plasticizers or blowing agents.

A systematic study of the mechanical properties of composites based on some major thermoplastics (HDPE, PP, PS, SB, PA6, PA12) and cellulose fillers (wood flour, cellulose flour and cellulose fibres) have been recently reported in two publications from this laboratory.[1,2] The first of these deals with the preparation of composites without the addition of coupling agents. In the second publication, a number of such agents, added to improve the mechanical properties, were described. To illustrate the effect of wood flour on the modulus it may suffice to mention that the E-value of PP increased from 1.1 GPa to 1.6 GPa and 2.6 GPa when it was compounded with 20% and 40% of soft wood flour. Adding the maleated PP-preparation did not increase the modulus further but the strength at yield increased ca. 20% for the two wood flour concentrations.

The breaking strength remained approximately constant when the filler concentration was increased. A downward trend was, as a rule, the result of using dispersants and elastomeric additives. As expected, the filling had an adverse effect on the fracture strain and the impact strength, but appropriate additives improved the adhesion between the two phases resulting in increased strength and impact strength.[2]

It is to be emphasized that the cellulose fibres used in the preparation of the composites were broken up during the compounding and injection moulding operations. Typically, the *L*/*D*-ratio of the cellulose particles in the final product was 5, to be compared with 30 in the starting material (shredded pulp).

The present paper is a continuation of the work presented in Refs. 1, 2. Here we exploit a property of cellulose previously not utilized in composites, namely its embrittlement by a hydrolytic treatment.[3–5] Although this effect has been known for more than a hundred years, its potential in cellulose-containing composites has not attracted any attention.

The embrittlement brought about by the action of hydrolytic agents such as, for instance, mineral or organic acids, is caused by a decrease in the chain length of the cellulose molecules.[6] Typically, conventional hydrolysis as used here brings about a five to tenfold decrease in the DP-value (degree of polymerization) of the chains. In the present context the resulting embrittlement has some practically important aspects.

To start with, prehydrolyzed cellulose will be disintegrated in the processing equipment much more easily than the untreated material. One can speak here of a self-comminuting filler producing an improved homogeneity of the final product. It may also be expected that such an effect can boost the mechanical parameters.

Another important aspect of the hydrolytic pretreatment of cellulose, although more difficult to realize technically, is the possibility to disintegrate the original fibre into fibrillar entities normally known as microfibrils. Among the outstanding characteristics of such fibrils are their unusually high modulus[7–9] and strength values[9–10] (110–137 GPa and 0.8–2.0 GPa, respectively) together with relatively high L/D-ratios.[4–6] When properly utilized in a composite, a reinforcing filler of this type certainly offers a number of interesting applications.

These two possibilities offered by prehydrolyzed cellulose, that is

A) simple disintegration into irregular fragments, and
B) disintegration into microfibrillar entities,

also determined the division of the present investigation into two corresponding parts. With regard to part A, no difficulties were encountered in achieving the expected effects, the hydrolytic treatment both producing better homogeneity and improving the mechanical parameters.

The second part of this investigation, where we attempted to disintegrate cellulose fibres into microfibrils with a high reinforcing potential did not, however, produce the anticipated results. This was probably due to the agglomeration of the fibrils when incorporated into the plastic matrix, whereby the L/D-ratio and, consequently, the reinforcing action were significantly reduced. A problem in this connection was the transfer of the fibrils, available as a water dispersion, into the matrix.

The use of cellulose fillers in thermoplastics has been reviewed in Refs. 1, 2. In a recent investigation various types of chemical and mechanical wood pulps and newsprint waste were used as reinforcing fillers in HDPE and PP.[11] Compounds containing more than 50% wood pulp were difficult to injection mould. The measured strength values were lower than the theoretically-predicted ones, probably due to the presence of voids created by the volatiles formed during processing. The modulus was almost independent of the pulp used; at 40% filler content it was about 4.5 GPa for both HDPE and PP. Carboxylic dispersion agents were used to improve wetting between fibres and resin. In another paper, the use of plywood grindings as fillers in LDPE is reported to result in an increase in stiffness from 105 MPa to 230 MPa at 30% filler content without loss of ductility.[12] The use of talc and $CaCO_3$ in combination with wood flour in PP based composites gave a higher bending stiffness and better gluability than wood flour alone.[13] The low stiffening effect of lignin appears to be related to the low modulus value of this material.[14] When using cotton fibres instead of phenolic impregnated cellulose flour as fillers in HDPE, an increase in ductility was recorded, probably due to good adhesion between the cotton fibre and the HDPE-matrix.[15]

The use of prehydrolyzed cellulose in composites based on a thermoplastic matrix has not been reported in available literature.

EXPERIMENTAL

Materials

Matrix materials The polymers used were injection moulding grades of PP (copolymer type, GYM 621, ICI, density 0.905 g/cm^3,

$MFI_{230/2.16}$-value 13, broad MW-distribution with $\bar{M}_n$ 6500, $\bar{M}_w$ 83600, as determined by GPC), and clear PS (N 4001, Hoechst, density, 1.05 g/cm^3, $MFI_{200/5}$-value 4.5, $\bar{M}_n$ 134000, $\bar{M}_w$ 335000 from GPC-measurements). Also, a HDPE-material having a high melt viscosity was used (blow moulding grade, DMDS 2215, Unifos Kemi, density 0.956 g/cm^3, $MFI_{190/2.16}$-value 0.2, $\bar{M}_n$ 22000, $\bar{M}_w$ 286000 with GPC-curve showing a marked peak at the high MW-end). The HDPE and PP-grades represent matrix materials with high and low viscosity, respectively.

To facilitate the incorporation of the fibrils from a homogenized suspension (gel) into a polymer matrix, a PS-latex (B134-52B, anionic, General Tire & Rubber) and a PVAC-latex (Bg 389, anionic, Borregaard), were used.

Cellulose fillers In most experiments, the cellulose component was subjected to a prehydrolytic treatment in aqueous acid solutions. The hydrolyzed pulps were

a) dried and ground before being compounded with the matrix material, or

b) treated as suspension in a slit homogenizer or a Valley beater in order to disintegrate the fibres into a microfibrillar dispersion (gel) in water. This dispersion was then used together with a PVAC or PS-latex to produce the composites (wet method). In other experiments, this dispersion was dried (freeze-drying or solvent exchange), whereafter it was incorporated into the plastic material using common compounding techniques.

Since this paper is divided into two parts, one on unhomogenized (not treated mechanically in the wet state) cellulose compounded with the matrix material in the as hydrolysed state (a), and the other on homogenized (i.e. mechanically treated pulps) microfibrillar dispersions, we characterize, to start with, only the unhomogenized samples. The various methods of homogenization together with a characterization of the resulting materials will be described in the second part of this work.

The pulps used (all bleached) were as follows; DP-values in parenthesis relate to hydrolyzed samples, cf. below.

Softwood sulphate (pine 50%, spruce 50%)	DP 1260 (370)
Softwood sulphite	DP 1390 (170)

Birch sulphite	DP 1404 (350)
Dissolving pulp	DP 764 (239)

(Ultra, Billerud, R18 94.2%, R10 89.8%, ethanol extract 0·2%, ash 0.04%).

Commercial microcrystalline cellulose (Avicel PH-101, FMC, 60 mesh, average L/D-value 2, average length 50 μm, DP 150) was also used. This material is not mechanically treated after the hydrolysis.

The hydrolysis of the pulp samples was carried out using 3% oxalic acid solution in water at 0.2 MPa pressure, temperature 121°C, for 1 h. The resulting DP-values are listed above. With the dissolving pulp sample, a more intense hydrolysis was also carried out with 6% oxalic acid for 6 h. This treatment gave a DP-value of 154.

After hydrolysis, the pulps were washed to pH 7, and dried at 70°C until a moisture content of 5% was reached (3 days in oven with recirculating air).

Both the hydrolyzed and untreated cellulose samples were disintegrated in a rotating knife mill (Rapid GK 20, screen 4 mm) in order to facilitate the feeding of the compounding machine. After milling, the samples were dried twice at 100°C for 9 h in vacuum in order to reduce the humidity to below 0.1% prior to compounding. Between the two last drying steps the cellulose was remilled in the Rapid-mill (screen 1 mm in this case).

The hydrolyzed cellulose pulps are denoted HC-pulps in the following text.

The results obtained with the cellulosic fillers were compared with glass fibres (Scandinavian Glassfibre, FR 1396, length 3 mm, diameter 10 μm, density 2.55 g/cm^3) in PP (30% GF by weight). The glass fibres were used both untreated (the sizing was removed by heat treatment at 400°C) and treated with a silane coupling agent (PC1A : PC1B in the relation 1 : 4, Union Carbide).

COMPOUNDING AND TESTING

The components were homogenized in a twin-screw extruder (Werner & Pfleiderer ZSK 30). The screw configurations and the

TABLE I

Screw configuration in the twin-screw compounding extruder (ZSK). Total length of screw elements = 967 mm. M—metering, S—shear (kneading), P—pressure blocks

Screw nr.	M	S	P	Degassing
1	77%	19%	4%	closed
2	69%	30%	1%	open
3	70%	30%	0	open
3B	70%	30%	0	vacuum

Melt temperatures: PE 180°C, PP 180°C, PS 180°C, PA6 250°C.

temperature of the barrel are given in Table I. Three different screw geometries were evaluated in order to minimize the miscolouration of the cellulose component. A few pressure blocks (reverse flights) (screw No. 2) gave a good compromise between homogeneity and brightness of the compound. Local increases in pressure resulted in miscolouration. However, the best results were obtained by screw configuration No. 3 consisting of only conveying and kneading blocks. When vacuum was applied to the degassing zone, screw No. 3 is called No. 3B.

It was also found that the moisture content had to be kept as low as possible (less than 0.1%), otherwise miscolouration occurred together with the formation of small voids in the test samples. Therefore, the extrudate strands were dried carefully (100°C in vacuum for PP, 80°C for PS) before injection moulding. During compounding, a degassing zone had to be included at the end of the mixing zone.

In some experiments, a Buss–Kneader (Model PR46) was used for compounding the mixtures.[1,2]

The injection moulded (Arburg 221E/17R) test bars (Din 53455) had a cross-section of 10 × 3.5 mm and an effective length of 75 mm. The injection moulding conditions are given in Table II.

The tensile tests were performed according to ASTM D 638 at an extension rate of $0.1\,\mathrm{min}^{-1}$ (Instron 1193, extensometer G51-15MA). From the stress-strain curves, the strength at yield and rupture, σ_y and σ_b, and the corresponding deformations, ε_y and ε_b, were determined. The impact strength was measured with a Frank instrument (Model 565 K, unnotched and notched Charpy, DIN 53453).

TABLE II

Injection moulding parameters. Arburg Allrounder 221/170R, locking force 250 kN

	HDPE	PP	PS	PA6
Melt temperature °C	180	180	190	240
Mould temperature °C	40	35	30	60
Injection pressure MPA	130	100	90	100
Holding pressure MPA	120	90	60	70

Test bar according to Din 53 455.

The flow curves of the filled melts were measured with a CEAST Rheoscope 1000.

After impact testing some of the fracture surfaces were studied in SEM (Jeol JSM 35). The SEM was also used to determine the fibre dimensions. The samples were dissolved in hot o-dichlorobenzene for PP and toluene for PS. The solution was applied onto a glass plate and the solvent evaporated. The fibres were covered with a 200 Å thick gold-layer. The state of the filler particles was also observed using light microscopy.

Filling levels are given as weight percentages unless otherwise stated.

Remarks on the influence of screw geometry and repeated treatment in the twin-screw extruder

Some changes in the properties of the test bars were noted when the compounds were treated repeatedly in the twin-screw extruder. For instance, when letting a PP-compound containing 40% hydrolyzed softwood sulphate (3% oxalic acid, 121°C, 1 h) pass the extruder four times, the modulus fell linearly from 4.7 to 4.3 GPa, using the screw configuration No. 1 dominated by metering blocks (normal screw shape). When the configuration No. 2 containing a majority of kneading blocks was used, the opposite effect was observed (modulus increasing from 3.8 to 4.3 GPa). The value of σ_b varied at the same time from 24 to 21 MPa, and 24 to 27 MPa, respectively. Although the reasons for this are not known, these results show that the compounding process influences the properties of the injection moulded parts.

The influence of screw geometry was also evident from the impact strength values. After one compounding step, screw No. 3 gave the highest IS-values (16 kJ/m^2, notched Charpy), as compared to screws No. 1 and 2.

The absolute values of the various properties mentioned here should not be compared with the bulk of the results presented below, since they have been obtained under slightly different conditions, e.g. a different humidity content of the compounds (degassing zone under vacuum).

Applying vacuum to the degassing gate of the ZSK-compounder (this condition is referred to as screw No. 3B) had a distinctly beneficial effect on the mechanical properties of the moulding. Not only were the E and σ_b-values some 10–20% higher, but also the scatter of the results was significantly reduced. These effects are likely to be associated with microscopic cavities caused by the water content of the cellulose phase, such cavities acting as crack initiators.

Comparisons between the Buss–Kneader and twin-screw (ZSK 30) compounding

In comparing the efficiency of various compounding machines, several criteria can be used. In the present case, we chose the usual mechanical parameters of injection moulded test bars after compounding in a Buss–Kneader(PR 46) and a twin-screw extruder (ZSK 30, screw No. 1).

The compounds were based on PP(GY 621 M) and cellulose fibres (dissolving pulp) treated in two different ways; one was hydrolyzed for 1 h in 3% oxalic acid, while the second was not subjected to any hydrolytic treatment. After compounding, the materials (cellulose content 40%) were injection moulded at 180°C (same as compounding).

On the whole, the differences between the two compounding methods are rather small. Moreover, they depend on the cellulose preparation used.

The values of E, σ_y, and σ_b appear to be largely independent of the compounding method chosen. With regard to ε_y and ε_b, the twin-screw machine gave slightly higher values (4% and 5% for ε_y and ε_b, respectively) than the Buss–Kneader (corresponding values 3% and 4%) for the unhydrolyzed cellulose. There was no difference in the ε-values measured on samples containing hydrolyzed cellulose.

On the other hand, the ZSK-machine appeared to produce consistently higher values of impact strength (notched, Charpy, 14 kJ/m^2 as compared to 11 kJ/m^2 with Buss for the unhydrolyzed sample). Again, the difference noted with the hydrolyzed preparations was markedly smaller (10 kJ/m^2 with ZSK, 9 kJ/m^2 with Buss).

The variation in the impact strength, and to some extent, also in the ε-values seems to indicate that twin-screw compounding produces a better homogeneity of the samples.

RESULTS

The account of the experimental results obtained in this work will be divided into two parts, the first relating to samples containing hydrolyzed and dried cellulose, the second to samples where the cellulose phase has been subject to the action of a homogenizer or a Valley beater before being incorporated, as a dispersion of fibrils, into the suitably dispersed matrix material. Screw No. 3B has been used during all the experiments presented below.

MECHANICAL PROPERTIES OF COMPOSITES BASED ON UNHOMOGENIZED HYDROCELLULOSE

The samples referred to in this section were prepared by conventional melt compounding of hydrolyzed and dried cellulose, followed by injection moulding. The basic mechanical parameters measured were evaluated from stress-strain curves; they were supplemented by impact stress data. The bulk of the data relates to a PP-matrix.

It will be shown further below that the reinforcing efficiency of the cellulose phase depends on its DP-value (PVAC-films prepared from a PVAC-latex and homogenized microfibrillar dispersion of cellulose in water). It was found that such a dependence may be present also in composites prepared by compounding a thermoplastic matrix with unhomogenized, prehydrolyzed cellulose. In general, the DP-value should be within the range 200–400 for optimum reinforcing effect. It is to be pointed out, however, that these results originate from different experimental series relating to various pulps, hydrolysis methods and matrix materials (PP and HDPE).

Figure 1 shows the variation of the modulus, *E*, with the filler concentration for a number of cellulose grades incorporated into the PP-matrix in both hydrolyzed and untreated state. A commerical HC-grade (Avicel) has been included for comparison together with a glass-fibre based sample (30%). The results show that, in general, the hydrolyzed cellulose grades produce a higher stiffening effect. Among the pulp grades used bleached softwood sulphate tends to

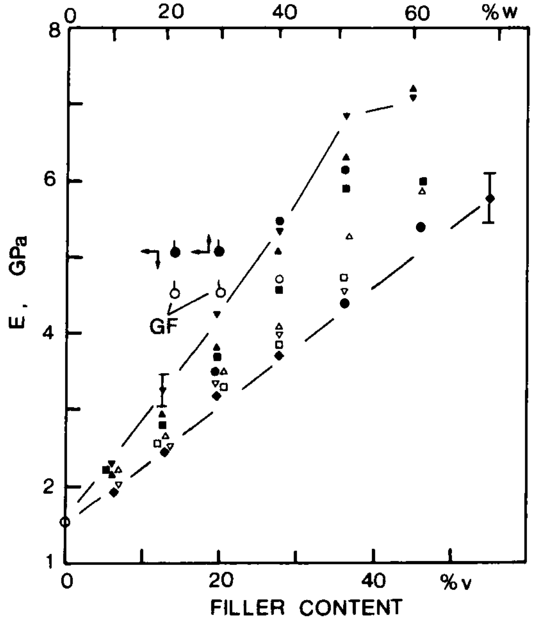

FIGURE 1 Variation of the initial modulus with cellulose concentration in PP (by volume—lower abscissa, by weight—upper abscissa). Filled symbols—hydrolyzed, open symbols—untreated cellulose. ∇—bl. softwood sulphate, △—bl. softwood sulphite, □—bl. hardwood sulphite, ○—dissolving pulp, ◆—commercial microcellulose (Avicel). The two symbols ○ denote the E-value of the uncoupled glass fibre composite (30% GF by weight) as relating to the volume (left) and weight (right) concentration (different density of glass and cellulose), ●—coupled glass fibre composite. The scatter of E amounts to about ±0.3 GPa.

give higher modulus values. The same is true of softwood as compared with the hardwood pulp. The lowest E-levels are obtained with the commercial microcellulose (Avicel PH-101), which is a particulate filler consisting of aggregated microfibrils.

With regard to glass fibres, one notes that they produce a more marked stiffening than the cellulosic materials, especially for the coupled GF-samples. The difference is clearly visible in a comparison by volume, while at equal weight, glass fibres are not significantly better. Considering the significantly higher E-value of the glass fibres and also their higher average fibre length ($\bar{l}_n$ = 300 μm, aspect ratio 30), the hydrolyzed cellulose grades must be characterized as highly efficient stiffening agents for this type of thermoplastics.

The results showing the variation of the yield stress value, σ_y, with the filling level are reproduced in Figure 2. On the whole, σ_y appears to remain approximately constant up to about 30% cellulose. For bleached hydrolyzed soft wood sulphate, there is a slight initial increase in σ_y. Above 40% filling level, σ_y falls with increasing cellulose concentration.

The differences between untreated and prehydrolyzed fibres are

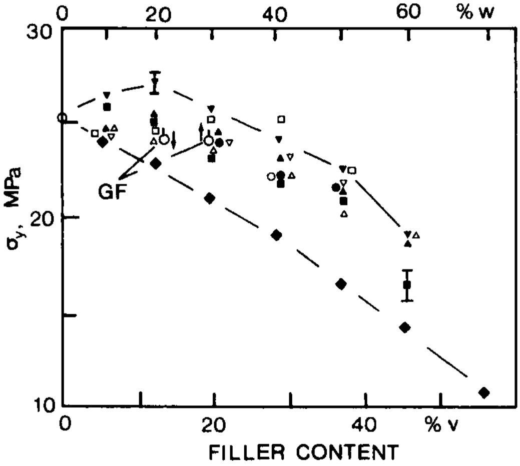

FIGURE 2 Variation of the yield stress with cellulose concentration in PP. Filled symbols—hydrolyzed, open symbols—untreated cellulose, cf. Figure 1. Scatter approximately ±0.4 MPa. The σ_b-value for sized GF-composite is 30 MPa (not shown in Figure).

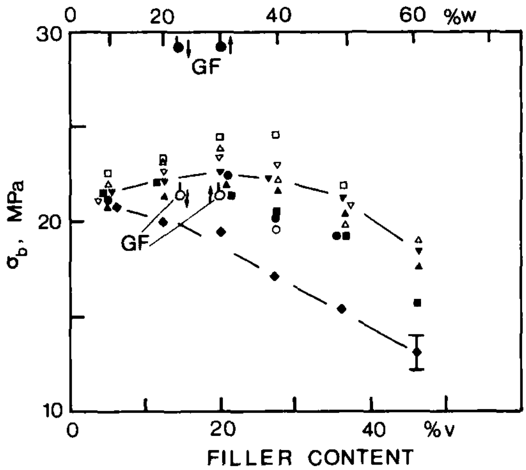

FIGURE 3 Variation of the stress at rupture, σ_b, with cellulose concentration in PP. Filled symbols—hydrolyzed, open symbols—untreated cellulose, cf. Figure 1. Scatter approximately ±0.8 MPa. The σ_b-value of unfilled PP not reproduced (necking of the sample, $\varepsilon_b > 250\%$); that of sized GF/PP is 29 MPa.

rather small. An exception is the commercial product Avicel, characterized by a sharper, monotonous fall in σ_y as the filling level is increased. The untreated glass fibres showed no strengthening effect. However, for the sized glass fibres the strength increased from 24 to 30 MPa.

Some of the trends exhibited by σ_y, weakly discernible in Figure 2, are more clearly shown by the variation of the corresponding rupture parameter σ_b. As Figure 3 shows, there is a significant increase in the σ_b-value up to about 30% filling level. This effect is especially pronounced with the unhydrolyzed fibres. At higher concentrations, the difference between hydrolyzed and untreated cellulose appears to be reduced. Again, Avicel shows a behaviour different from that of the other materials, while the untreated GF-sample has a σ_b-value similar to that of some of the hydrolyzed pulps. Sizing of the GF increased σ_b to 29 MPa.

Without going into details with regard to the differences between the various fibres, one finds that softwood sulphate pulp appears to give somewhat higher σ_b-values among the hydrolyzed grades, while hardwood sulphite produces the best results when used in its untreated form.

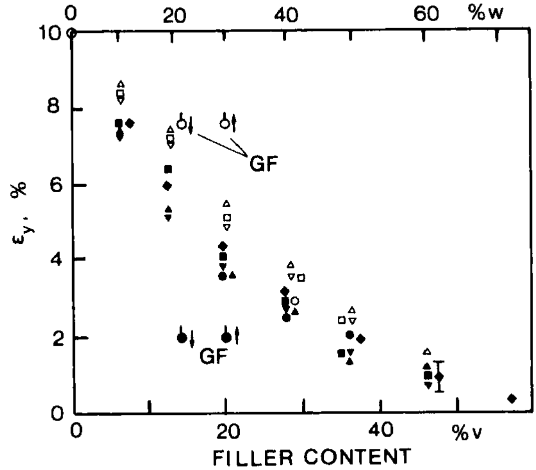

FIGURE 4 Variation of the yield deformation, ε_y, with cellulose concentration in PP. Filled symbols—hydrolyzed, open symbols—untreated cellulose, cf. Figure 1. Scatter ±0.2%.

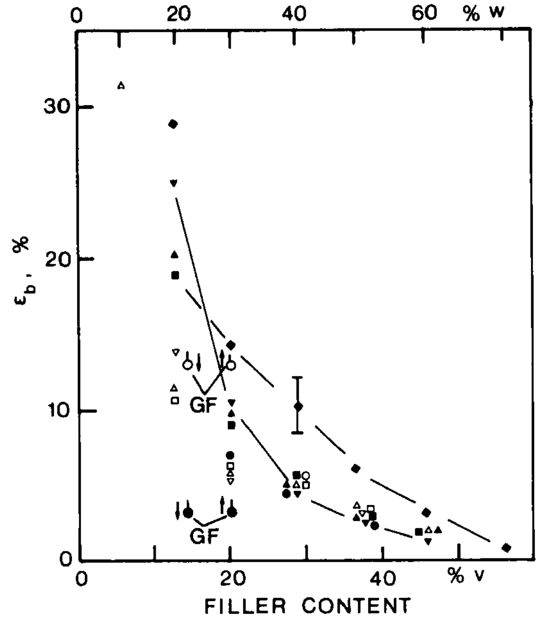

FIGURE 5 Variation of the deformation at rupture, ε_b, with cellulose concentration in PP. Filled symbols—hydrolyzed, open symbols—untreated cellulose, cf. Figure 1. Scatter ±2%. $\varepsilon_b > 250\%$ for unfilled PP and >30% for 10% filling level.

The deformation at yield, ε_y, falls markedly when the filling level is increased, Figure 4. Untreated pulps appear to produce slightly higher ε_y-levels. Avicel is equivalent to the hydrolyzed fibre grades. The ε_y-level was very low for the sized GF-samples.

The values of ε_b, the deformation at rupture, do not indicate any significant effect of the hydrolytic treatment, Figure 5. Avicel, however, produces somewhat higher ε_b-values, an effect which may be related to the lower *L*/*D*-ratio of this material. Again, the ε_b-value for the treated glass fibres was very low.

With regard to impact strength, IS, unnotched Charpy values did not differentiate between hydrolyzed and untreated fibres in a significant manner. This is evident from Figure 6. There was a marked decrease in IS with increasing filling level, as could be expected for composites of this type. The second part of Figure 6 shows the IS-values for notched samples. In this case, the untreated

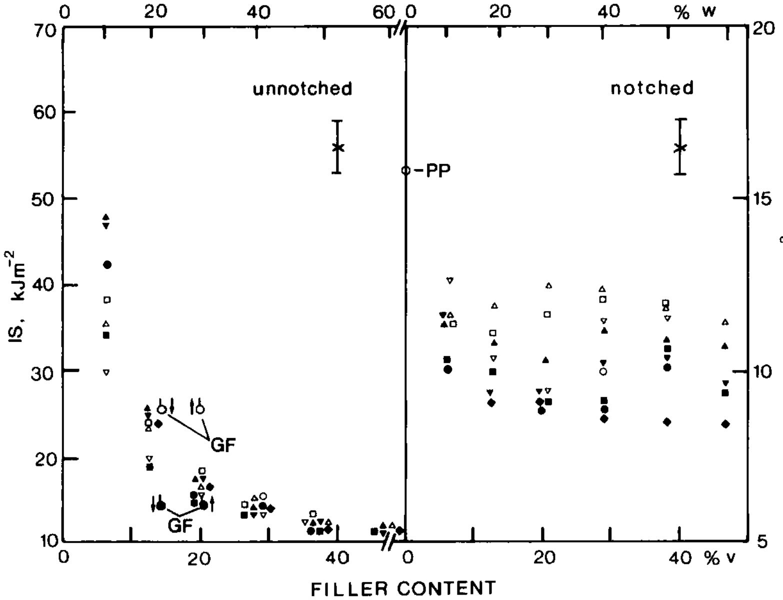

FIGURE 6 Unnotched (left) and notched (right) impact strength (Charpy) for PP samples with varying cellulose content. Filled symbols—hydrolyzed, open symbols—untreated cellulose, cf. Figure 1. Scatter: unnotched ±1.5, notched ±0.8 kJ/m^2. Notched values not recorded for GF-sample. No break for unfilled PP (unnotched).

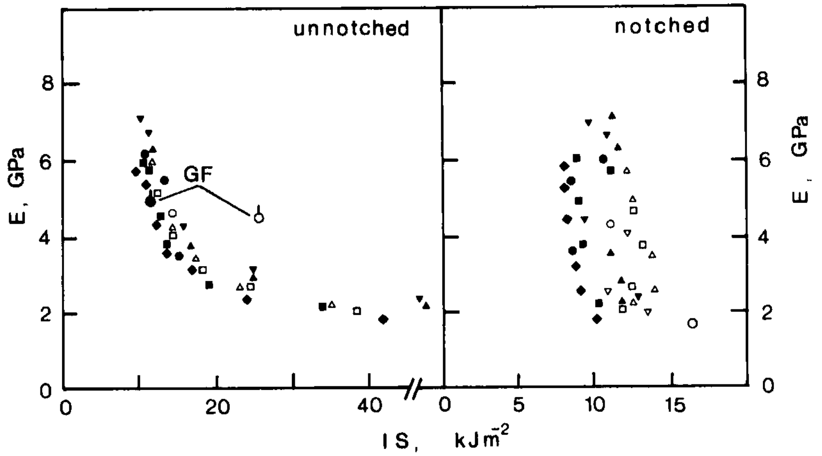

FIGURE 7 Modulus vs. impact strength for unnotched (left) and notched (right) samples. Filled symbols—hydrolyzed, open symbols—untreated cellulose, cf. Figure 1.

fibres produce composites with slightly higher IS-levels. There is practically no variation of IS with the filler content, apart from the initial fall from the level corresponding to the unfilled material.

Figure 7 illustrates the *E* vs. IS relationship for the unnotched (left) and notched (right) samples. The hydrolyzed and untreated fibres behave similarly when tested in unnotched samples. For notched samples, there is a significant shift to higher IS-levels for the untreated fibres. In the former case uncoupled glass fibre gives a higher IS; after treatment with a coupling agent, the behaviour of cellulose is approached. Avicel is equivalent to the other cellulose materials in unnotched samples; when a notch is introduced, Avicel produces somewhat inferior results.

Filling of a HDPE-matrix with cellulose

In experiments where the PP-matrix was replaced by HDPE, results largely similar to those reported above for PP were recorded. Primarily, this applies to the relative change of the various properties upon filling with the different cellulose materials. This is in good agreement with the results reported by Woodhams.[11]

Filling of a PS-matrix with hydrolyzed pine sulphate

In this section, we report on the effects of filling a matrix of a standard (clear) polystyrene with hydrolyzed, bleached softwood sulphate, a material which consistently appeared to produce somewhat better results than the other fibres. The filler content was varied up to 30% by weight. There was no yield point in the stress-strain curves, implying that only σ_b and ε_b were measured. Unhydrolyzed cellulose can hardly be used as filler for PS due to the large number of fibre agglomerates in the resulting composites.

The parameters E, σ_b, and ε_b are reproduced in Figure 8. For the hydrolyzed fibres the variation of E with the volume concentration of the filler is strictly linear. Also σ_b shows an increase upon filling, albeit a relatively small one. There is further the expected reduction in ε_b. It is interesting to note that at low filling levels (approximately 1%), there is a significant initial increase in ε_b, before the falling linear branch of the ε_b-diagram is reached. As could be expected, the unhydrolyzed cellulose gives a poor reinforcing effect in PS.

The reduction of the IS-values (unnotched Charpy) with the filler

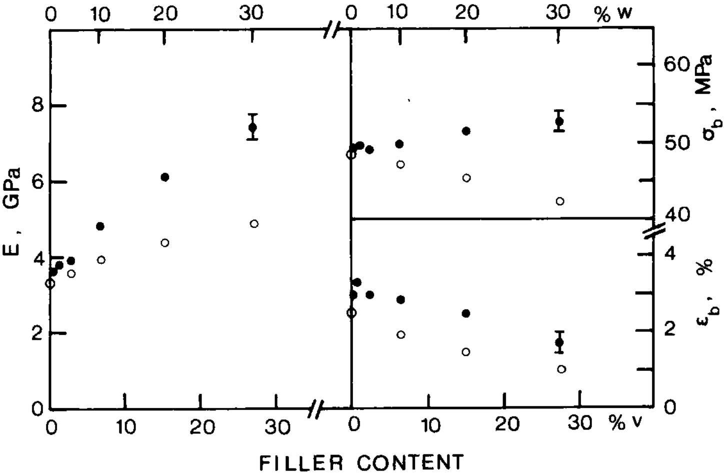

FIGURE 8 Variation of E, σ_b, and ε_b for a PS-based composite filled with hydrolyzed softwood sulphate pulp. Scatter: E ± 0.3 GPa, σ_b ± 0.5 MPa, ε_b ± 0.15% Filled symbols—hydrolyzed, open symbols—untreated cellulose.

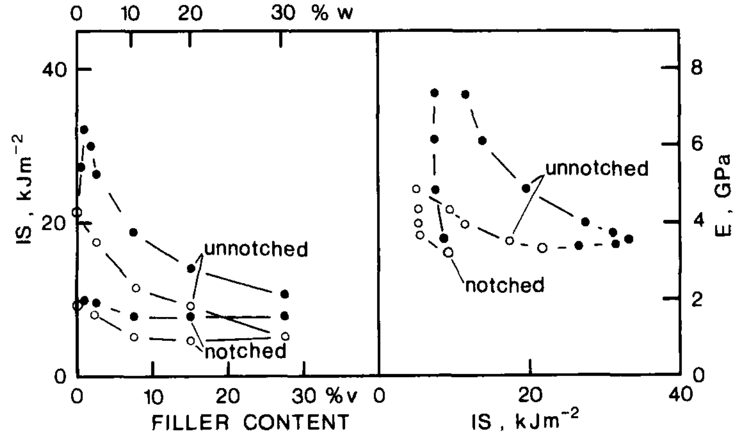

FIGURE 9 Unnotched and notched impact strength (Charpy) of PS filled with hydrolyzed softwood sulphate (left). E vs. IS (right). Symbols as in Figure 8.

content is shown in Figure 9. This general trend does not apply, however, to the initial part of the diagram, where a pronounced maximum in IS with the filler concentration can be seen for the hydrolyzed fibres. This effect reflects the corresponding variation in ε_b as shown in Figure 8. Figure 9 further shows the variation of the IS-values obtained with notched samples. In this case, one notes a monotonous, although very limited decrease in IS.

The right-hand part of Figure 9 shows the usual *E* vs. IS diagrams for the two kinds of samples. For unnotched samples, the maximum in IS shown in the left-hand part of the figure is reflected in a reversal of the order of the points belonging to the various filler concentrations. The initial increase in IS is not reflected in the modulus.

Melt rheology and processing

To supplement the above data on the mechanical properties of the various composites, it may be appropriate to comment on the rheological characteristics of some of the melts, since the design of moulds has often to be based on such parameters. Measurements of this type are commonly accounted for in many reports dealing with filled composites.

There is, on the other hand, very little information on the influence of fillers and reinforcing agents on the production rate, even though it is generally accepted that such additives may produce a marked reduction in the cycle time (injection moulding). In the present case we supplement the rheological data with diagrams showing the reduction in sealing time upon filling.

Figure 10 gives the variation of the apparent viscosity, η_a, with the filler content for the PP and PS-based melts. As can be seen, untreated fibres produce a slightly higher viscosity in the PP-compounds than fibres subjected to hydrolysis (bleached softwood sulphate). The differences are, however, small; they tend to disappear at higher filling levels. The variation of η_a with the filler content shows the expected behaviour.

The PS-compounds containing hydrolyzed pine sulphate show a remarkably low dependence of η_a on the filler content, Figure 10. The reason for this was not found. It is known, however, that PS has a high T-sensitivity around 200°C. No difference was found between hydrolyzed and untreated fibres.

The practically important reduction in the sealing time, t_s, for the PP and PS compounds containing varying amounts of hydrolyzed softwood sulphate pulp is shown in Figure 11. As can be seen, the

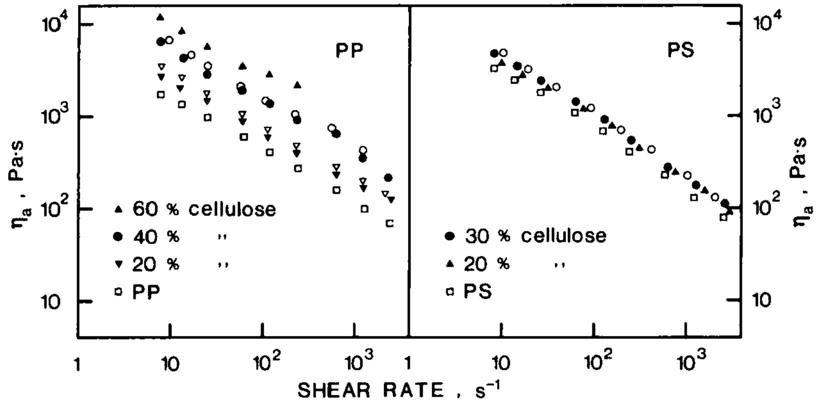

FIGURE 10 Variation of the apparent viscosity η_a with the shear rate as determined in a capillary viscometer. Left—PP compounds containing hydrolyzed and untreated softwood sulphate, right—PS compounds with hydrolyzed and untreated softwood sulphate. Filled symbols—hydrolyzed, open symbols—untreated cellulose.

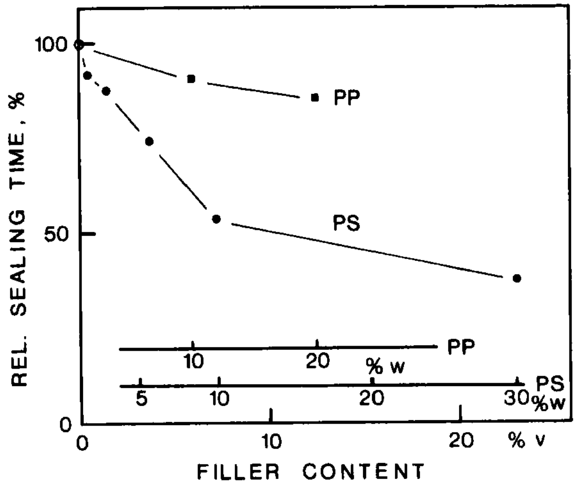

FIGURE 11 Sealing time t_s vs. filler content (by volume and by weight) for the PP and PS-based compounds containing hydrolyzed softwood sulphate pulp. t_s given as percentage of the value measured for the unfilled matrix material.

reduction is significantly higher for the PS-based composites. While for PP there is a 15% reduction in t_s upon adding 20% cellulose, the reduction for PS is 45% at only 10% addition (by weight). Filling with 2% leads in PS to a t_s-reduction of 12%.

It may be added that the t_s-period accounts for approximately 40% of the total injection moulding cycle (t_s determined gravimetrically).

Calculated vs. measured modulus values

The modulus is one of the properties of a composite containing a particulate or fibrous phase which may be calculated in a relatively easy way using the theoretical model of Tsai–Halpin[16] or its simplified form proposed by Lewis–Nielsen.[17] In the present case, we use the latter formula which has the following form

$$\frac{E_c}{E_1}=\frac{1+ABv_2}{1-B\psi v_2}. \tag{1}$$

Here, E_c and E_1 denote the elastic moduli for the composite and the matrix, respectively, v_2 the volume fraction of the filler, A is a constant dependent on the Poisson's ratio of the matrix and the aspect ratio of the filler, while $B = (E_2/E_1 - 1)/(E_2/E_1 + A)$ takes into account the moduli of the matrix and the filler. The common upper and lower bounds of the rule of mixtures correspond to $A \rightarrow \infty$ and $A \rightarrow 0$, respectively. In this investigation it is assumed that the constant A could be expressed as $A = 2(L/D)$, where L/D is the aspect ratio of the rodlike fibres. If the stress is acting perpendicular to the fibre orientation, A equals 0.5. The factor ψ takes into account the packing fraction of the filler, v_m, at maximum filler concentration, and ψ is expressed as

$$\psi = 1 + \left(\frac{1 - v_m}{v_m^2}\right) v_f. \tag{2}$$

In Figure 13, Eq. (1) has been applied to PP containing hydrolyzed and untreated pine sulphate fibres, to PS with the hydrolyzed fibres, and finally to the PP/Avicel composite. The calculations are based on the following assumptions and measured values. The fibrous elements are assumed to be maximally oriented and evenly distributed over the cross-section, which gives a maximum packing density ϕ_m of 0.82. The E-value of the fibres is taken as 20 GPa[18], that of the PP- and PS-matrix (measured) as 1.55 and 3.4 GPa, respectively.

The L/D-values of the cellulose phase have been obtained by microscopic investigation of the dissolved middle part of the test bars. The distribution of the length and width of hydrolyzed and untreated softwood sulphate fibres is shown in Figure 12. It is found that the hydrolyzed fibres are more damaged than the unhydrolyzed fibres. Furthermore, they have been cut both transversally and longitudinally.

The average aspect ratio ((L/D) was 3.7 and 6.5 for hydrolyzed and unhydrolyzed fibres in PP, respectively. The fibre damage was almost independent of the matrix material used (PP or PS) or of the filling level. However, for PS a large number of long fibres were found agglomerated in networks up to 2 mm in diameter when unhydrolyzed cellulose was used. It has to be emphasized that the microfibrils cannot be seen in the microscopes used. Thus, the composites with hydrolyzed cellulose may contain a limited number of these reinforcing microfibrils.

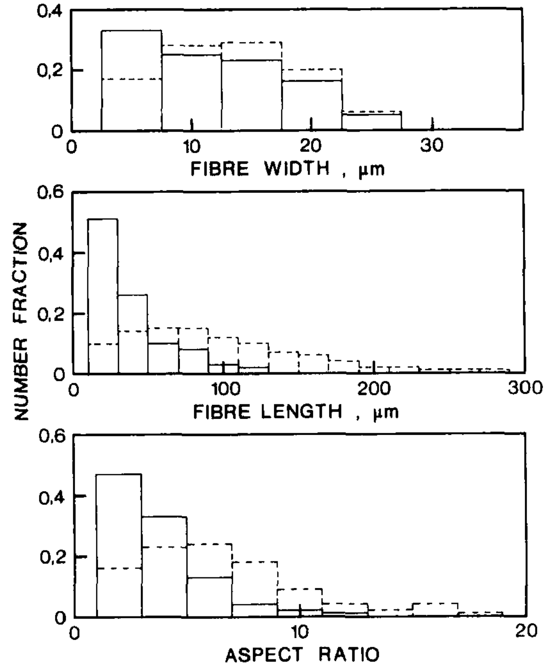

FIGURE 12 Fibre dimensions for hydrolyzed (solid line) and untreated (dashed line) bleached softwood sulphate in PP (60% PP). The fibres were dissolved from test bar; size determined from SEM-pictures. Average aspect ratio 6.5 for untreated and 3.7 for hydrolyzed fibres. Number of analyzed fibres: 200 per sample.

The values for Avicel were: $L \approx 45\,\mu m$, aspect ratio ≈ 3, i.e. Avicel is a particulate filler with an ellipsoidal form.

The solid lines in Figure 13 represent theoretical values of the relative modulus for assumed values of the L/D-ratio of 2, 5 and 10 as applied to cellulose fibres in a PP-matrix. The dashed line relates to PS and a L/D-value of 10.

When comparing experimental data with the theoretical predictions, as reproduced in Figure 13, one arrives at the following conclusions. The system PP/Avicel with its particulate filler phase gives a fair agreement with Eq. (1) for the measured L/D-value of around 3.

When comparing the two types of fibres in the PP-matrix, one

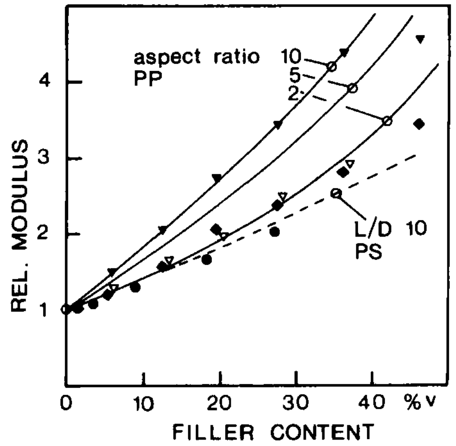

FIGURE 13 Comparison of theoretical values of the relative modulus according to Eq. (1) with experimental data for some of the composites at varying filler content. Symbols showing experimental results: ▼—hydrolyzed pine sulphate pulp in PP, ▽—untreated pulp, ◆—Avicel in PP, ●—hydrolyzed pulp in PS. Solid line: PP with fillers having aspect ratios 2, 5 and 10; dashed line for PS with aspect ratio 10 of the filler (theoretical values).

finds some irregularities. To start with, untreated fibres produce a significantly lower increase in modulus than what could be expected in view of their L/D-ratio. For the hydrolyzed variety, the opposite is true. Without going into details as to the possible causes of this behaviour one may note, that Figure 13 clearly demonstrates the beneficial effect of the hydrolytic treatment on the modulus increasing efficiency of the fibres, at least in a PP-matrix. One may speculate that this is due to a partial comminution of the fibres into cellulose microfibrils which, although invisible during the miscroscopic inspection used, may contribute significantly to the ultimate reinforcing effect. It may also be noted that the hydrolyzed fibres ($L/D \approx 4$) had a ribbon-like shape with a width of 15 μm and a thickness of 5 μm (average values).

The experimental values of the PS-samples are not in agreement with theoretical predictions, the hydrolyzed fibres producing a higher increase in modulus than that anticipated on the basis of their aspect ratio ($L/D \approx 5$).

SEM-micrographs

Although no coupling agents were used in the present work, some differences in the adhesion between the cellulose phase and the matrix were discernible in SEM-micrographs of surfaces obtained by breaking the injection moulded test bars. For instance, the adhesion between hydrolyzed fibres and the PP-matrix appeared to be better than in the composite containing untreated fibres, Figures 14a–b. Another feature of the hydrolyzed fibres, Figures 14a, is a certain tendency to fibrillate and to loose the original fibre character.

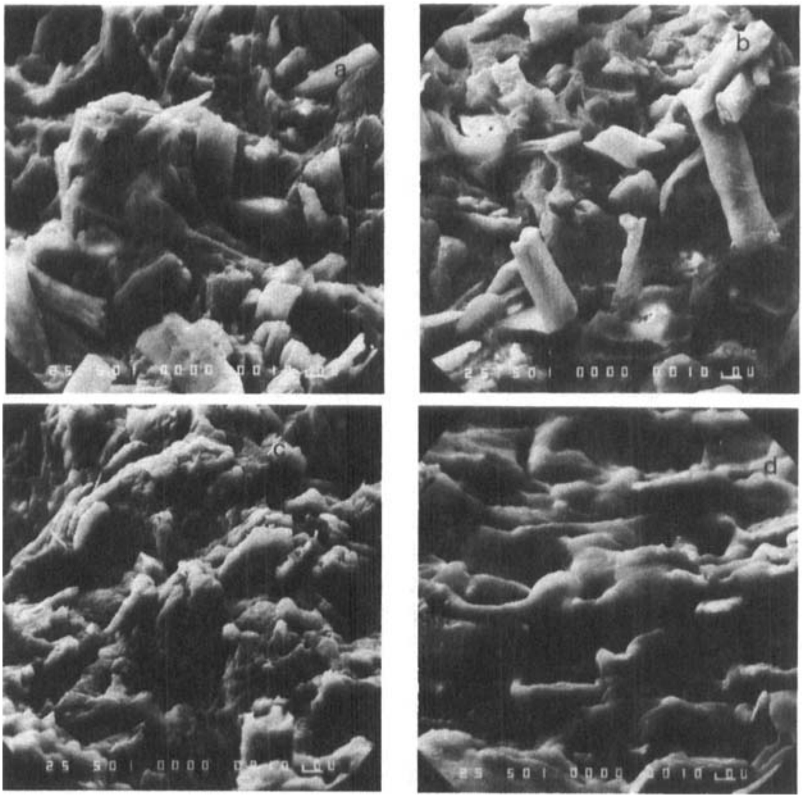

FIGURE 14 SEM micrographs of fracture surfaces of some of the composites. a—PP with HC-fibres, b—PP with untreated fibres (40%), c—PP with Avicel PH-101, d—PS with HC-fibres. Pulp: bleached softwood sulphate; 40% in PP and 10% in PS. Length of white line: 10 μm.

The PP/Avicel composite also appears to show a fair degree of filler/matrix adhesion, Figure 14c.

Figure 14d illustrates the structure of the PS-based composite containing hydrolyzed pine sulphate pulp, indicating good adhesion between the two phases.

SOME COMPOSITES BASED ON MICROFIBRILLAR CELLULOSE

In this section we present the results of a series of experiments aiming at incorporating microfibrillar cellulose into some thermoplastic matrices. Cellulose in microfibrillar form was obtained by exposing prehydrolyzed cellulose to the intense shear force field of a slit homogenizer or a Valley mill as described below. The resulting material was a gel consisting of a dispersion of microfibrils in water. In some of the experiments, this gel was mixed with an emulsion of the polymer particles in water (PVAC, PS). In other experiments, the gel was dried according to various methods in order to obtain the microfibrillar matter in a dry state, and to allow its incorporation into the plastic matrix by usual compounding techniques (PP).

The results to be presented do not reflect the reinforcing potential of the microfibrils which could be ascribed to them on grounds of their assumed modulus and strength values. This appears to be due to the strong tendency of the fibrils to form agglomerates, thereby reducing the value of the original L/D-ratio which is the basic prerequirement in obtaining a reinforcing action in a composite.

Due to the special character of the microfibrillar cellulose samples we include here a section on their preparation and properties before presenting the results relating to the corresponding composites.

As a rule, the hydrolysis method used in this section was based on boiling the cellulose samples in 2.5 M HCl at 100°C for 1 h at a cellulose concentration of 7% (see below). The disintegration of the hydrolyzed material was performed using either a Valley-beater or a slit homogenizer. The methods used for drying the samples were freeze-drying and solvent exchange.

The pulps that have been treated in a slit homogenizer or a Valley-beater are referred to as homogenized cellulose.

Preparation of homogenized, microfibrillar cellulose

Method A. Bleached softwood sulphite, DP 1390, was hydrolyzed in 2.5 M HCl for 1 h at 100°C (pulp concentration 7%). It was washed and neutralized with ammonia to pH 7. After hydrolysis, the DP-value was 267. The material was homogenized in a Valley-beater for 2 h at 2 kg load, whereafter it was freeze-dried (Modulys freeze drier, type EF4), ground (Wiley-mill) and sifted through a 40 mesh sieve. The dry material was compounded with PP.

Method B. The pulp (as in A) was swollen in 3% NaOH at 50°C for 10 min before being hydrolyzed in 2.5 M HCl for 2 h at 90°C to give a DP-value of 343. After a 2 h homogenizing treatment in a Valley-beater (as in A), the material was dried after solvent exchange at 40°C (iso-propanol to *n*-hexane). The resulting powder was compounded with PP.

Method C. The sample of Method B, hydrolyzed in the same way, was subjected to the homogenizing action of a slit homogenizer (Manton Gaulin MC18-5TBS) at 1% concentration. The pressure was 30 MPa; the sample was passed through the slit 10 times. The DP decreased to 310. Thereafter, the sample was freeze-dried, ground, and sifted as in Method A and compounded with PP.

Method D. Softwood sulphate pulp was hydrolyzed to DP 300 in 1 M HCl at 70°C for 4 h at 7% pulp concentration, then washed and homogenized in the Valley-beater for 2 h at 2 kg load. It was added in the wet state to a PS-latex (General Tire & Rubber, B134-52B, anionic type), dried at 40°C, ground before injection moulding.

Method E. As in Method C with only 3 passages through the slit homogenizer, DP-value 330 before compounding with PP.

Method F. In this case, unhydrolyzed bleached birch sulphite was treated as in Method C (slit homogenizer, 55 MPa, 10 times through the slit, freeze-drying) before compounding with PP.

Method G. Softwood dissolving pulp was hydrolyzed in 1.5 N H_2SO_4 at 90°C for 4 h (DP160) before washing and neutralization, followed by spray drying in Niro Atomizer. The resulting powder was similar to the Avicel PH-101-product, and it was compounded with PP.

Some of the above samples (Methods A, D, and G) were characterized with regard to their composition and DP. The saccharide components were determined by GC after complete hydrolysis in 72% sulphuric acid and acetylation (Method AH 23-4, Swedish Forest Products Lab., Stockholm). The DP-values were obtained from viscosity measurements in CED-solutions using the relation $DP^{0.905} = 0.75 \cdot [\eta]$. The results are summarized in Table III. It is evident that the content of some of the hemicellulosic saccharides is reduced by the hydrolysis, the content of glucose being increased correspondingly.

The results of Table III, including the DP-values given therein, are, however, somewhat ambiguous. The reason for this is the sensitivity of the hydrolytic reaction to the pretreatment of the samples. Significant differences in, for instance, the DP-values are obtained when hydrolyzing never-dried vs. dry pulp samples. The influence of alkaline pretreatment on the ultimate DP-value is another example.[19]

To supplement the physical characterization of the microfibrillar material, we determined the sorption isotherm at RT of dry, homogenized HC pulp, hydrolyzed and treated according to Method C above (DP 310). As expected, the hydrolyzed material exhibits an over-all lower moisture absorption (5% compared with 8% at 50% RH), an effect likely to be associated with a higher crystallinity. This was confirmed in direct determinations of the

TABLE III

Composition and DP-values of some of the pulp samples used (untreated and hydrolyzed). Commercial microcellulose (Avicel PH-101) included for comparison. Lignin content negligible in all samples

	Pine sulphate		Pine sulphite		Diss.	pulp	Avicel PH-101
	untr	hydr	untr	hydr	untr	hydr	
Arabinose, %	0.9	0.4	0.4	0.4	0.3	0.3	0.4
Xylose, %	8.5	7.3	5.5	2.4	2.4	1.9	1.6
Manose, %	7.0	7.0	7.7	6.6	3.5	2.9	1.7
Galactose, %	0.3	—	—	—	—	—	—
Glucose, %	83.3	85.3	86.4	90.5	93.8	95	96.3
DP	1260	300	1390	267	764	150	145
Method of hydrolysis and homogenization; cf. Preparation		D		A		G	

crystallinity level of the hydrolyzed samples using X-ray diffractometry. Typically, figures in the vicinity of 76% were obtained in this case (Method B, bleached softwood sulphite), to be compared with 69% for the untreated cellulose. The crystallinity was determined in an X-ray diffractometer using the technique described in Ref.[20]

To complete the characterization of the microfibrillar cellulose, Figure 15 shows a TEM-picture of dissolving softwood pulp treated according to Method C. The dimensions of the microfibrils together with a certain extent of agglomeration are clearly visible in the picture.

Films based on PVAC-latex containing homogenized HC Blending of polymer latices with microfibrillar cellulose gels appears to be a relatively simple way of preparing composites based on the two components, especially when the samples have the form of films prepared by drying thin layers of such mixtures. In a series of experiments, a PVAC-latex was mixed with various aqueous dispersions of microfibrils. The concentration of cellulose was 40% by weight of the total solids content. The fibrillar material was obtained by different mechanical treatments of various pulps, which had been prehydrolyzed in boiling hydrochloric acid to varying DP-levels.

FIGURE 15 TEM-picture of microfibrillar cellulose. Dissolving pulp softwood, hydrolysis in 2.5 M HCl at 105°C for 1 h, thereafter 10 passages through the slit homogenizer. Philips EM 400, magnification 10.000 x. Uranium acetate shadowing. Black line 1 μm.

TABLE IV

Variation of the modulus of a microfibril-containing PVAC-film (PVAC content 40%) with the DP-value of the cellulose component. Samples prepared by evaporating thin layers of an aqueous dispersion of the two components. Cellulose pulps treated with different methods. Modulus of unfilled PVAC 63 MPa

Pulp, treatment	DP	E, MPa (±scatter, MPa)
Bleached softwood sulphite, no hydrolysis	1260	750 (100)
Diss. pulp, no hydrolysis	764	650 (100)
Diss. pulp, milled in Valley-beater	550	1300 (200)
Softwood sulphate pulp, treated according to method C	310	1800 (300)
Different pulps, method C with different time of hydrolysis	200–400	1600–2900 (500)
As above, but with DP <200	140–200	1300–1600 (300)

Although the results in Table IV are rather uncertain (differently treated pulps), there seems to be an optimum stiffening effect for pulps having a DP-value within the range 200–400. The experimentally observed E-values for the homogenized HC-pulps can be estimated by Eq. (1) with an aspect ratio of 50 (real aspect ratio >100). The fair agreement is due to some agglomeration of fibrils into flakes having a very low aspect ratio. These experiments do, however, show the inherent stiffening properties of cellulose microfibrils.

Injection moulded samples based on PS-latex containing homogenized HC In the above experiments, softwood sulphate pulp hydrolyzed to a DP-value of 300 was mixed with a PS-latex. The mixtures were dried, whereafter they were ground and injection moulded. (Sample preparation according to Method D above).

Table V gives the results of tensile test on the injection moulded samples containing 16 and 40% HC. For comparison, values for a composite with 40% Avicel PH-101 are included. As can be seen, the admixture of the commercial Avicel-grade produces results

TABLE V

Modulus, E, breaking strength, σ_b, and elongation, ε_b, of injection moulded PS-based composites containing 16 and 40% homogenized HC (softwood, DP 300), and 40% Avicel PH-101. Samples prepared by moulding a disintegrated, dried mixture of PS-latex and HC. E_{rel} denotes the modulus ratio filled/unfilled

%cellulose	E, GPa	E_{rel}	σ_b, MPa	ε_b, %
0	2.4	1.0	45	2.0
16	3.5	1.5	42	1.5
40	5.2	2.2	35	0.8
40 (Avicel)	4.1	1.7	36	1.0

somewhat inferior to those obtained with the homogenized HC-pulp at 40% admixture level. On the whole, the increase in modulus upon incorporating the cellulose phase is relatively low. The decrease in σ_b is moderate. There is further the expected decrease in ε_b.

The reason behind the rather small stiffening effect seems to be insufficient disintegration of the dried HC-phase into fibrillar entities with a sufficiently high L/D-value. Such a disintegration in the shear field of the processing machinery (injection moulding) is probably prevented by the hardness of the cellulose after drying. This was supported by the microscopic observations on 5 μm thick microtome slices of a test bar containing 40% HC. The cellulose particles had an aspect ratio lower than 5. Also, a certain extent of agglomeration (dimensions 10 × 50 μm) was observed.

PP containing homogenized HC This section reports the results of mechanical tests on injection moulded samples of PP containing 20% or 40% homogenized HC. Included are also samples containing unhydrolyzed cellulose treated in the slit homogenizer (method F), and samples with Avicel PH-101.

After converting the HC-material to a microfibril dispersion, three methods to obtain the cellulose phase in dry form were used, namely

Freeze drying (methods A, C. E. F, cf. Materials),
solvent exchange (method B), and
spray drying (method G).

The freeze drying procedure was in some instances modified by adding certain chemical intended to prevent agglomeration of the microfibrils. These were carboxymethyl cellulose (CMC, Billerud, type PF20), dodecanol-(1), and poly(ethylene oxide) (PEO, Berol, molecular weight 200).

After drying, the material was compounded with PP in the usual way and injection moulded into tensile test bars. The mechanical parameters of the test bars are shown in Table VI.

As can be seen, the differences between the various methods used in drying the homogenized microfibrillar dispersions of HC are rather small. The samples based on HC dried by solvent exchange exhibit somewhat better mechanical properties. Neither is there any significant difference between hydrolyzed and unhydrolyzed cellulose in this case (freeze drying). It is also interesting to note that the commercial product Avicel (agglomerated microfibrils) produces results largely similar to those obtained by freeze and solvent exchange of homogenized HC. The results found for the unhomogenized and spray-dried HC are almost identical to the Avicel-values, as could be expected. On the whole, the modulus

TABLE VI

Mechanical properties of PP composites containing dried, homogenized HC. The drying methods are identified by letters referring to the corresponding heading under Materials. Homogenized, unhydrolyzed cellulose, and Avicel included for comparison. $\sigma_h = \sigma_y$ (no yield point)

Cellulose treatment	Cellulose content %	E GPa	σ_b MPa	ε_b %	IS unnotched kJ/m^2	Remark
Freeze-drying Method						
A	20	2.9	26	2.6	50	
C	20	3.0	26	5.2	40	
C	40	3.8	26	3.4	12	
E	20	2.8	25	2.5	45	
F	40	3.9	27	2.4	15	Unhydr
Solvent exchange						
B	20	2.5	26	3.6	50	
B	40	4.6	27	2.0	24	
Spray drying						
G	20	2.8	25	3.5	28	
G	40	4.0	21	2.5	10	
Avicel PH-101	20	3.2	26	5.3	30	
Avicel PH-101	40	4.1	22	3.4	12	

and strength values attained here are significantly below the levels reached when using unhomogenized HC in the corresponding composites.

The results reported in Table VI can be interpreted in terms of an extensive agglomeration in the fibrillar matter into entities with a rather low L/D-ratio. The particles were ellipsoidal in form with an aspect ratio of approximately 2. This aspect ratio did not change to any large extent during compounding in the ZSK-machine or during injection moulding. The cellulose particles, consisting of thousands of microfibrils, are apparently too hard to be disintegrated during melt compounding.

Adding the substances mentioned above (CMC, dodecanol, PEO) to the fibrillar gel before drying did not improve the mechanical features of the samples. On the contrary, a significant embrittlement reflected in low ε_b-values was noted.

DISCUSSION

The results shown above represent but a small fraction of the total experimental effort in connection with this project. Among the composites which have not been discussed, one may mention those based on various polyamides (PA6, 66, 11, and 12). Contrary to what could be anticipated with regard to the hydrogen bonding capability of both polyamides and cellulose, the results obtained were not very encouraging. Among other things, the moduli of the composites relative to the unfilled matrix, especially for conditioned samples, were consistently lower than those recorded with PP and HDPE-matrices. Further, small differences only were noted for the hydrolyzed pulps as compared to the untreated ones. A brief account of these results can be found elsewhere.[21]

Since cellulose microfibrils are obtained from prehydrolyzed (or untreated) cellulose by the action of intense shearing, an attempt was made to subject the cellulose phase to the shearing action of the twin-screw extruder before compounding with the matrix material. Different screw configurations were used, and the water content of the fibres (both hydrolyzed and untreated pine sulphite) was also varied. Unexpectedly, composites prepared from cellulose pretreated in this way always showed inferior mechanical properties.

These effects were not pronounced when considering the E-values. For instance, with PA12 moduli between 2 and 3 GPa were obtained with such pretreatment, while the normal procedure (disintegration in a Rapid mill) gave 5 GPa (hydrolyzed pulp). With unhydrolyzed pulp, the results were similar.

The main result of this work is the demonstration that a hydrolytic treatment of the cellulose fibre and the resulting embrittlement produces a significant improvement in the modulus when incorporated into a polyolefin or a polystyrene matrix by using the conventional melt compounding technique. The E-values observed for such composites greatly exceed the values obtained with inorganic particulated fillers and almost equals the values recorded for glass fibre or mica reinforced polymers. Obviously, only a small fraction of the HC-fibres have been converted into microfibrillar entities. The main fraction has a very low aspect ratio and a very low length (less than 50 μm). Still, the reinforcing effect is higher than predicted by the Tsai–Halpin equation.

It is also interesting to note that the impact strength is rather high for the level of E-values obtained. If the fibres could be disintegrated into microfibrils, the E vs. impact behaviour could be improved even more.

From the processing point of view, the reduction in sealing time and, consequently, of the moulding cycle certainly appears important. In this respect, cellulosic fillers compare favourably with their inorganic counterparts.[22]

When using hydrophilic fillers like cellulose great care must be taken to prevent the formation of voids caused by residual moisture absorbed in the hopper of the machine. Keeping the hopper hot or under vacuum helps to reduce this effect, but some voids are still formed by the volatile components produced due to degradation of cellulosic fillers at the processing temperatures used. A careful selection of the processing conditions is therefore imperative, especially with regard to avoiding unnecessary thermal loads and shear heating.

Acknowledgements

Financial support from the National Swedish Board for Technical Development is gratefully acknowledged.

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