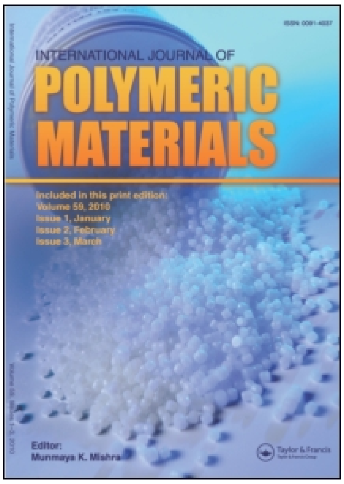

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Klason, C. , Kubát, J. and Strömvall, H. -E.(1984) 'The Efficiency of Cellulosic Fillers in Common Thermoplastics. Part 1. Filling without Processing Aids or Coupling Agents', International Journal of Polymeric Materials, 10: 3, 159 — 187

To link to this Article: DOI: 10.1080/00914038408080268

URL: http://dx.doi.org/10.1080/00914038408080268

Intern. J. Polymeric Mater., 1984, Vol. 10, pp. 159–187
0091-4037/84/1003-0159 $18.50/0

Printed in the United Kingdom

The Efficiency of Cellulosic Fillers in Common Thermoplastics.
Part 1. Filling without Processing Aids or Coupling Agents

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(*Received January 3, 1983*),

The paper reports on the processing and properties of composites consisting of thermoplastics and cellulose-based fillers. The plastics used were HDPE, PP, PS, SB, PA 6, and PA 12; the fillers were wood flour (white spruce), cellulose flour (bleached sulphate, pine) and cellulose fibre (bleached sulphate, birch). The mixtures were homogenized (kneader, alternatively single-screw extruder) before being injection moulded into tensile test bars. The modulus increased with the filler content, while the yield and breaking stress remained relatively unaffected. For HDPE, SB, and PA 12 a moderate increase in the strength level was noted. The extension at rupture and the impact strength fell sharply when the filler content was increased. The compounding method had no influence on the modulus. Kneader compounding, producing a higher homogeneity, gave in general higher strength and impact values than compounding in a single-screw extruder. The temperature dependence of the modulus was highly reduced, as was also the mould shrinkage. At processing temperatures in excess of 200°C, severe discolouration was noted.

Cellulosic fillers may be regarded as low-reinforcing fillers comparable to untreated mineral products such as calcium carbonate. On the other hand, the materials used here have the advantage of a substantially lower density.

INTRODUCTION

The use of cellulose and lignocellulosic composites appears to gain in importance, at least judging from the increasing amount of literature in that area. The applications of such materials range from simple filling to more elaborate structures like laminates and chemically modified systems. Despite the large number of literature references, systematic studies of the various aspects of this area appear to be relatively rare. This is also the case with cellulose and various types of ligno-cellulosic materials used as fillers for thermoplastics.

In this paper, we present the results of an experimental study concerning the effect of filling on the mechanical properties of injection-moulded samples of high density polyethylene (HDPE), polypropylene (PP), and normal and impact-modified polystyrene (PS, SB). Additional experiments have also been carried out with polyamide 6 and 12 (PA 6, PA 12). Wood flour (white spruce), cellulose flour (bleached sulphate, pine) and bleached cellulose fibres (bleached sulphate, birch), were used as fillers. Apart from the mechanical parameters obtained from stress-strain measurements (modulus, breaking stress, and strain), also the impact strength was determined (Charpy). The experiments further comprised the determination of mould shrinkage and water absorption. In all cases, a substantial increase in modulus (E) was observed with increasing filler content, while the elongation at yield (ε_y) and rupture (ε_B), and impact strength (IS) decreased markedly.

The yield strength (σ_y) and the strength at rupture (σ_B) varied only moderately. The processing of the filled composites did not show any particular problems except for the styrene polymers and the polyamides, where degradation and discolouration occurred. The maximum filler content was 50–70% depending on the plastic and filler used. The properties of the mouldings were dependent on the degree of homogenization imparted to the material prior to injection moulding.

The polar nature of wood-based fillers and reinforcing agents affects adversely the adhesion to the plastic matrix.[1] In certain cases, the filler is therefore treated with adhesion-promoting agents (stearic acid etc.). In the present investigation, no such agents were employed.

A survey of the literature dealing with wood-based fillers and reinforcing agents before 1975 is given in an earlier paper[2] reporting on injection moulding of wood flour filled PE, PS, and PVC. According to Ref. 2, there was an increase in E with the filler content, while σ_B remained practically unchanged; the impact value fell sharply. At 30% filler content, the E-value for LDPE was *c.* 1.6 GPa, for HDPE and PP *c.* 2 GPa, and for SB and PS *c.* 3 GPa.

The following literature notes supplement the references given earlier.[2] According to Ref. (3), pulp mill residues (southern yellow pine) at 20% filling left the E-value of PS nearly unchanged, while this value was doubled for HDPE; σ_B did not change much, and IS was substantially reduced. The properties of the injection-moulded samples were not affected by the aspect ratio in the range of 3–19. A 2.5 GPa E-level for PP containing 30% wood flour is reported in Ref. 4.

Straw flour increased the value of the flexural modulus of a PP copolymer from 1.4 to 2 GPa, while wood flour (in another type of PP copolymer) gave an increase from 1 to 3.7 GPa[5] at 40% filling level. This may be compared with 4.1 and 2.6 GPa as obtained with talcum and $CaCO_3$, respectively. The unnotched Charpy value fell from NB to 4.5 and 6.5 kJ/m^2 for wood and straw flour, respectively. The corresponding values for talcum and $CaCO_3$ were 3.5 and 8 kJ/m^2. The dart drop value was practically unaffected by increasing temperature for the wood-filled composite, while for the talcum-filled samples it increased markedly.

Only a small effect of varying the fibre length is reported in Ref. 6, which reports on the use of fibres with varying lignin content in PP, PS, an SAN (thermomechanical pulp). An unusually low reduction in IS was observed with styrene acrylnitril copolymer (SAN) containing both low and high lignin fibres; PP and PS, on the other hand, behaved regularly. The results in Ref. 6 were restricted to loadings in the range of 0 to 9 weight-%. The processing temperature was 240–290°C.

Some wood flour containing composites (extruded sheet or profiles) are available commercially (Elastogran, Woodstock, Sonwood).[4,7–10] At 40% filling the E-value of Elastogran is in the vicinity of 4 GPa (*c.* 1.5 for pure PP), σ_B is approximately unchanged, while ε_B falls from *c.* 600 to 4–6%. The impact strength remains unaffected by temperature (c. 8–10 kJ/m^2, corresponding to the value for PP at −20°C). The thermal expansion is reduced by c. 50%. Water absorption (21 d. at RT) increases from 0.2 to 0.5%. The mould shrinkage is reduced to practically zero. The heat deflection temperature increases from 54 to 106°C.[7] For 50:50 PP:wood flour composites (Woodstock) a modulus value of 2.5 GPa has been reported.[8–10] The value of a 3:1 PVC:wood flour mixture (Sonwood) is c. 6 GPa. The flexural strength values are c. 30 and 67 MPa in the two cases.[9–10]

Bagasse-filled ABS was tested as a roofing material; its nailability was, however, poor.[11] Wood flour filling of PE, PP, and PS reduced the mouldability.[12] Discolouration of PE/wood flour was reported to occur above 180°C.[13]

An important group of lignocellulosic fillers are various nut shell flours and similar materials. Peanut hull[14] filling of HDPE produced only a minor increase in E; σ_B decreased somewhat, smaller particles giving higher σ_B-values (also higher melt viscosity). With PP the modulus increased c. 50% at 35% filler; there was a certain increase in IS (notched Izod).[15–17] Similar results are reported for filling HDPE, PP, and ABS with walnut shell flour.[18] Among other fillers of this group, various soybean[19] preparations, rice-hull[20] fractions, corn cobs[1] and cocoa pod[21] powder may be mentioned.

Literature data thus indicate that the addition of lignocellulosic fillers to common thermoplastics produces a substantial increase in the modulus. This increase is higher, the lower the E-value of the matrix material. The changes in σ_B and σ_y are relatively small and do not obey any simple rules, while IS and σ_B fall sharply with increasing filler content. On the whole, the behaviour observed is similar to that recorded when using conventional mineral fillers. This is also true of the reduced warpage and other characteristic features of filled systems.

The lack of possible reinforcing action is due to the geometrical shape of the filler particles as present in the final product. Also, when fibres are used as the starting material, a substantial decrease in fibre length is noted during the processing step. The reinforcing effect normally expected with cellulose fibres is thus lost. In certain cases, the fibre structure is preserved with an improvement of the strength parameters as a result. Ref. 22 reports a doubling of IS (Izod) of PP when 20% of Douglas fir bark fibre is incorporated.

Laminate-type composites based on paper have, in general, an improved property profile. For instance, a 2:1 paper:PE laminate had an E-value of 10.8 and 4.8 GPa in the machine (MD) and cross direction (CD), respectively. For laminates stacked alternately in MD and CD, E was 7.7 GPa (σ_B 78 MPa).[23] Ref. 24 reports data on sheets compression moulded from a mixture of pulp and PP-fibres. Substantial improvement was obtained when the sheet was formed from a water suspension prior to the moulding step (E 3.8 GPa wet, 1.7 GPa dry, both at 33% RH; σ_B behaved similarly). Laminates based on paper and PMMA are treated in Ref. 25. The E-value for a 30% paper composite was 7.2 GPa.

Among the various methods to improve the adhesion between the filler and the matrix are impregnation with a monomer and subsequent polymerisation (sawdust–PMMA composites),[26] and grafting and impregnation with the corresponding polymer (bagasse),[27,28] resulting in a substantial property improvement. Acetylation and crosslinking with formaldehyde had only limited effect on paper/PE laminates.[29] Water absorption was reduced when PE in fibre/PE composites was corona treated.[30] Treating the wood flour with non-polar rosin[31] used for paper sizing increased the tensile strength and the notched Izod impact strength in PP composites *c.* 50%.

The patent literature reports on a variety of cellulosic or lignocellulosic fillers, including lignin, combinations with inorganic fillers, adhesion improvement, etc. Only a few examples will, however, be given here: press-moulded sheets of PP/wood particles;[32] panels etc. based on polyolefine fillers with sawdust or straw;[33] PP/wood particles (Woodstock);[34] addition of rubber to such products;[35] PVAC-composites for floor coverings, show soles, etc.;[21] injection-moulded drinking cups from wood flour filled PE;[36] PS compositions containing processing oil and rubber;[37] incombustible polyolefine compositions;[38] impregnation of the filler with a suitable plastic prior to compounding;[39] or using an acrylic acid-propene graft copolymer in wood flour filled composites for improved toughness.[40] A particular product group is cellular plastics filled with a lignocellulosic component.[41–44]

There are further a number of articles and patents on the utilization of agricultural and plastics waste in boards, building materials, and similar products. Such products, however, fall outside the scope of the present paper.

EXPERIMENTAL

Materials used

The polymers used were injection moulding grades of HDPE (DMDS 7006, Unifos Kemi; density 960 kg/m^3; MFI 190/2.16, 7.0), PP (copolymer GYM 121, ICI, density 905 kg/cm^3, MFI 230/2.16, 13.0), PS, clear (Hostyren N 4001, Hoechst; density 1050, kg/m^3; MFI 200/5, 4.5), impact-modified PS, SB (Hostyren S 4200, Hoechst; density 1040 kg/cm^3, MFI 200/5, 9.5), PA 6 (Grilon A28 GM, Emser; density 1130 kg/m^3, $T_m = 215°C$), and PA 12 (Grilamid L 22 G, Emser; density 1010 kg/m^3; viscosity number, (DIN 53727) 235, melting range 176–180°C).

The properties of the fillers used, i.e. wood flour (white spruce), cellulose flour (bleached pine sulphate), and cellulose fibres (defibrated bleached birch sulphate), are given in Table I.

The aspect ratio varied from 6 for the wood flour (WF) to 12 and

TABLE I

Properties of fillers used

	Softwhite spruce wood flour (from AB Lignitverken, Sävsjö, Sweden)[a]	Bleached sulphate cellulose (birch) flour (Cepo S 100, Svenska Trämjölsfabriken, Gothenburg, Sweden)[b]	Bleached sulphate woodpulp (pine)
Sieving, mesh	120	100	—
Acidity, pH	5.7	5.0	5.0
Colour	light yellow	white	white
Bulk density (approx.) kg/m^3	200	330	150
Particle length L, max	500	600	2000
min	50	50	80
average	180	300	800
Particle width D, max	150	40	50
min	15	15	15
average	30	25	25
L/D aspect ratio, average	6	12	32
Price (approximate) SEK/kg (1982)	1.0	4.2	4.0

[a] Ash 0.25%, extractibles: 2.55% in diethyl ether, 3.03% in acetone.

[b] Cellulose content >99%, alpha cellulose 80%, lignin nil, resin 0.2%, ash 0.35%.

32 for cellulose flour (CF) and pulp fibres, respectively. The shape of the wood and cellulose particles was different, the wood particles consisting of fractured fibre bundles with a fairly large thickness variation, Figure 1. The amount of fines in the wood flour was relatively large. The softwood fibres (fluff) had a length of *c.* 0.8 mm. The wood flour was light yellow, while the cellulose fillers were white.

The average moisture content of the fillers before drying was 7–9%; drying at 105°C for 24 h resulted in a moisture content <0.1% before compounding. Upon exposure of the fillers to air in the hopper of the machine, the moisture uptake was approximately 0.5% (exposure time *c.* 10 min).

Compounding

Two methods were used to homogenize the polymer/filler blends, one of which consisted of homogenizing the blends in a mixing

FIGURE 1 Scanning electron micrograph of the wood flour used. The original magnification was 1000×.

extruder (Buss–Kneader PR46, diameter $D = 46$ mm, D/L = 11) using a 6-mm exit die. The average residence time was of the order of 100 s, the temperature 180°C for all polymers, except PA 12 (195°C) and PA 6 (235°C). In certain cases, the blends were treated several times.

The second method used a small single-screw extruder (Dolci, diameter 25 mm, L/D = 20) with a 6-mm exit die. The residence time was similar to that of the Buss-equipment.

The moisture uptake by the filler during feeding to the Buss equipment (0.5%) was eliminated in the degassing zone of the machine (vacuum). On the extruder, this moisture could not be removed, resulting in a certain die swell (foaming).

The extrudate from the Buss- and extruder equipment was hot-pelletized whereafter it was kept dry until injection moulded. It was found necessary to keep the moisture content of the blends below 0.1%, as otherwise a discolouration of the material took place together with a decrease in the surface gloss of the moulded test bars.

No compounding difficulties were noted with the Buss-machine except with the polyamides, where 20% and 30% were the maximum filler contents for PA 6 and PA 12, respectively (severe degradation of the compound at higher filling). With the polyolefines, it was possible to achieve filler contents of 70%. The styrene polymers were difficult to compound at >30%, due to degradation (discolouration). The compounds were treated on the Buss-machine twice in order to achieve a good dispersion. Wood flour was more easily dispersed than cellulose flour; the fibres showed moderate degree of dispersion even after two compounding passages.

Extruder compounding was more difficult, with regard to both feeding and the degree of homogeneity achieved. Normally, feeding problems arose at filler concentrations exceeding 20%, especially with cellulose fibres, where flocks, 1.5–3 mm in diameter, were found in the moulded samples. The Buss machine gave a substantially better dispersion of the fibrous filler, although even in this case about 1 mm large flocks were found in the samples.

Some improvement of the dispersion took place during injection moulding, due to the combined effect of the screw and the narrow gates of the mould.

The influence of the temperature during the compounding step will be discussed below.

Injection moulding

The compounded and granulated blends were injection moulded on a conventional machine (Arburg 221E/17/R) into test bars (DIN 53455) having a cross-section of $10 \times 3.5\,\mathrm{mm}^2$ and an effective length of 75 mm. A rectangular gate (4 × 2 mm) was arranged at the side of one end of the test bar. The flow direction thus coincided with the longitudinal direction of the bar.

Because of the high viscosity and the pseudoplastic character of the highly filled blends, the injection had to be relatively rapid (with high injection pressure, up to 140 MPa) in order to ensure good mould filling. With PE and PP, at filler content >50%, *c.* 5% of a viscosity reducing additive (AC-Polyethylene 6A, Allied Chemical), had to be used. With the styrene polymers, difficulties with mould filling and release (low shrinkage) appeared already at 20% filler, and problems with discolouration arose as well. Thus, the *practical* limit for styrene polymers was 20%. The other polymer blends could be moulded without difficulties at filler contents up to 30%.

The melt temperature was 180°C, except for PA 12 (195°C) and PA 6 (235°C).

The residence time in the barrel was *c.* 2 min.

Mechanical testing

Stress-strain curves were measured with an Instron tensile testing device (Model 1193) according to ASTM D638 at 23 ± 0.5°C. The strain rate was $4.2 \times 10^{-3}\,\mathrm{s}^{-1}$. From the stress-strain curves, Young's modulus of elasticity, E, the yield stress, σ_y, and the corresponding strain, ε_y, were evaluated. The nominal stress and strain at rupture, σ_B, ε_B, were also determined.

The samples were tested after conditioning at RT and 50% for 24 h, i.e. as practically dry samples containing 0.04–0.2% moisture. The polyamide-based samples were tested in a dry (as moulded) as well as a conditioned state (15 h in water at 60°C).

For the PE, PP, and PS-based samples the moisture content during testing (0.04–0.2%) was dependent on the filler content (cf. the section of Moisture uptake). After several months of conditioning at 50% RH, a moisture content of 0.5–2% at 40% filler content was reached, however without attaining an equilibrium state. As the mechanical parameters were not significantly influenced by such an extended exposure to 50% RH, one-day conditioning was applied.

The impact strength was tested with a pendulum device (Zwick, Model 565K) according to the Charpy-method (unnotched). This method appeared to reflect well the variations in the composition of the samples and differences in their preparation.

RESULTS

Discolouration

In a series of experiments the temperature in the compounding step (Buss–Kneader, single-screw extruder) was varied between 150°C and 200°C for PE and the styrene polymers and between 180–200°C for PP. On the whole, the melt temperature had a comparatively small effect on the mechanical properties of the moulded samples. However, a highly significant correlation was found between the temperature during compounding and the colour of the compound (Table II). The darkening also depends on the filler content, as increased filling results in increasing sheer heating. The temperature limit during compounding may be set at 200°C, appreciable darkening occurring above this temperature. Considerable darkening also results from a prolonged residence time in the machines. Both the compounding and injection steps contribute to the final colour.

Below 150°C, no filler discolouration was noted. Normally, bleached sulphite gives a higher brightness than sulphate grades. Wood flour, on the other hand, darkens somewhat even at <150°C. It was, however, not possible to injection mould the filled compounds at such low temperatures.

During compounding, thermal degradation of the extrudate core (low thermal conductivity) was a source of discolouration. Also, a moisture content exceeding 0.5% increased the degree of discolouration. The values given in Table II are approximate assessments

TABLE II

Discolouration observed on moulded test bars. Melt temperature during moulding 180°C except for PP and PA 12 (195°C) and PA 6 (235°C).
CF = cellulose flour: WF = wood flour
YE = light yellow; BR = brown; BL = black

Compound	Buss–Kneader barrel temperature °C	Colour Filler content, % 10	20	30	40	60
HDPE/CF	150		YE		YE	YE
	180		YE		YE	BR
	200		BR		BR	BR/BL
HDPE/WF	150		YE/BR		YE/BR	BR
	180		BR		BR	BR
	200		BR		BR	BR/BL
PP/CF	180		BR		BR	BR
	200		BR		BR	BR/BL
PP/WF	180		BR		BR	BR
	200		BR		BR	BR/BL
Styrene polymers	180		BR		BR/BL	BR/BL
(PS, SB)/CF	200		—[a]		—[a]	—[a]
Styrene polymers/WF	180		BR		BR/BL	BR/BL
	200		—[a]		—[a]	—[a]
PA 6/CF	235	YE/BR	BR	—[a]	—[a]	—[a]
PA 6/WF	235	YE/BR	BR	—[a]	—[a]	—[a]
PA 12/CF	190	YE/BR	YE/BR	BR	—[a]	—[a]
PA 12/WF	190	YE/BR	BR	BR	—[a]	—[a]

[a] Severe degradation.

of the discolouration resulting from increasing the filler content. By yellow is meant the colour of natural wood (pine), while brown refers to the colour of hardboard of the Masonite-type. Both these colours may be concealed by dark colouring (red, green, black).

Although normally not mentioned in the literature, these effects appear to be more important than commonly believed. Ref. 13 reports that discolouration occurs at 180°C, while no mention of the colour is made in Ref. 6, dealing with melt temperatures in the range of 240–290°C.

Plate-through

The plate-through effect, i.e. the disruption of the continuous film of the matrix material at the surface of the moulded part appears at a critical filler content. Above this filling level a rough surface pattern is obtained, which is unacceptable in many applications. Under the conditions used here, the critical filling level was *c.* 30% for HDPE, and 40% for PP and the styrene polymers, the moulded parts losing their surface gloss at these filler contents. The surface finish of the PA-samples was acceptable (max 30% filler was tested).

Mould shrinkage

As normally found when filled polymers are used the mould shrinkage was reduced when the filler content was increased. Table III shows the data for HDPE, PP, and SB filled with 20–60% WF and CF (Buss-compounded).

Moisture uptake

In equilibrated samples, the moisture content is proportional to filler concentration, as the sorption by the matrix may be neglected. At 23°C and 50% RH, several months were needed to reach equilibrium. Figure 2 shows the sorption curves for filled PP. Samples containing wood flour consistently attained a somewhat higher moisture content than those filled with cellulose flour. The other polymers behaved similarly to PP, as illustrated in Table IV. At 40% filling, the quantity absorbed after 1 month was about 0.5% for HDPE and PP, and 0.7–0.9 for SB.

Upon immersion of the samples in hot water (90°C), a moisture content of 8–10% was measured after 7 days. The HDPE and SB-based samples showed severe cracking above 30% filler content, while only minor surface defects appeared on the PP-bars with a filler content of up to 40%. The cracking tendency appears to be related to the plate-through effect (see above).

TABLE III

Mould shrinkage in percent for different filler contents. Dry as moulded

Filler content %	Mould shrinkage, % HDPE/CF	HDPE/WF	PP/CF	PP/WF	PS/CF	PS/WF	SB/CF	SB/WF
0	2.0	2.0	0.9	0.9	0.5	0.5	0.5	0.5
20	1.2	1.0	0.8	0.6	0.3	0.3	0.3	0.3
40	0.9	0.7	0.6	0.3	0.1	0.1	0.2	0.1
60	0.4	0.4	0.6	0.3	0.1	0.1	0.1	0.1

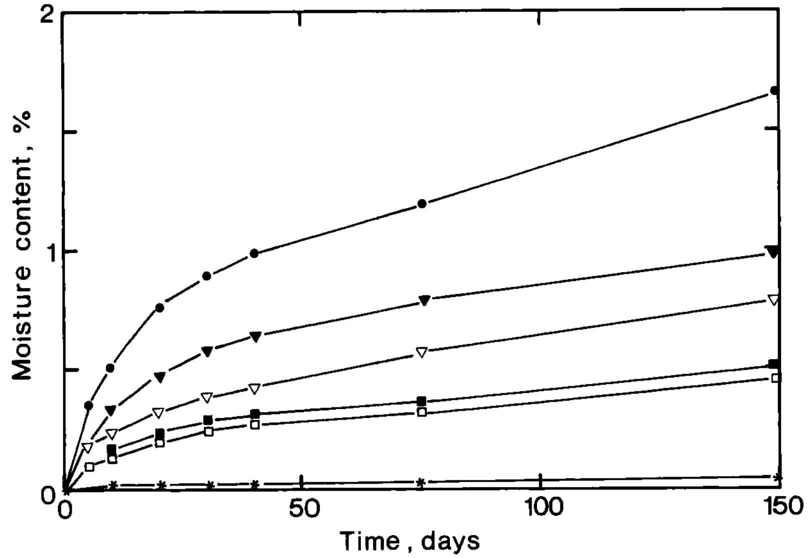

FIGURE 2 Moisture content vs. storage time at 23°C and 50% RH for filled PP. Injection moulded test bars. * unfilled, ■ 20%, ▼ 40%, ● 60% filler. Open symbols, cellulose flour (CF); filled symbols, wood flour (WF).

Density

The density of the moulded bars (HDPE, PP, and SB containing WF and CF) was calculated from the weight divided by the volume of the bar; the results are shown in Figure 3. Using 1540 and 1420 kg/m^3 for CF and WF, respectively, the calculated values for the composites fall clearly above the observations. This is due to gaseous occlusions and inefficient packing of the filler. In view of the complicated structure of the fillers used, this is hardly surprising.

Melt viscosity

As expected, the melt viscosity increases with the filler content (reduced mouldability). This was observed in all cases (Instron Capillary Rheometer, Model 3211). The degree of pseudoplasticity did not change with the filler content, cf. Ref. 2, 45–47. If the power law was used to describe the viscosity in the shear range of

TABLE IV

Moisture absorption in percentage vs. absorption time at 23°C and 50% RH. Injection moulded test bars (approx. weight 7 g, width 10 mm, thickness 3.5 mm)

	Moisture absorption, % Absorption time, days		
Compound	1	30	150
HDPE/CF 20%	0.04	0.23	0.43
HDPE/CF 40%	0.10	0.44	0.82
HDPE/WF 20%	0.04	0.26	0.49
HDPE/WF 40%	0.12	0.48	0.89
PP/CF 20%	0.04	0.25	0.48
PP/CF 40%	0.08	0.42	0.80
PP/WF 20%	0.07	0.29	0.49
PP/WF 40%	0.12	0.58	0.89
SB/CF 20%	0.18	0.87	1.10
SB/CF 40%	0.22	0.88	1.63
SB/WF 20%	0.22	1.20	1.25
SB/WF 40%	0.33	0.68	1.10
PA 6/CF 20%	0.18	1.23	2.30
PA 6/WF 20%	0.18	1.28	2.40
PA 12/CF 20%	0.16	0.89	1.44
PA 12/WF 20%	0.16	0.84	1.58

100–3000 s^{-1}, the exponent n was found to be *c*. 0.35 for HDPE and PP at 180°C and 40% filling level. For SB, the exponent had a value of 0.45.

Mechanical properties

Influence of compounding With the exception of impact strength, no significant influence of the compounding method (Buss, extruder) on the mechanical parameters of the samples was noted. This was also true when repeating the compounding treatment. In a series of experiments, PP with 20% wood flour was allowed to pass through the Buss-machine up to 3 times at 180°C. The mechanical parameters of the stress-strain curve were hardly influenced by this treatment, while the impact strength increased with the number of passes as $35 \rightarrow 45 \rightarrow 80$ kJ/m^2. This treatment produced mainly a better dispersion, giving rise to a higher impact strength. However, if the filler content was increased to 30%, no improvement of the

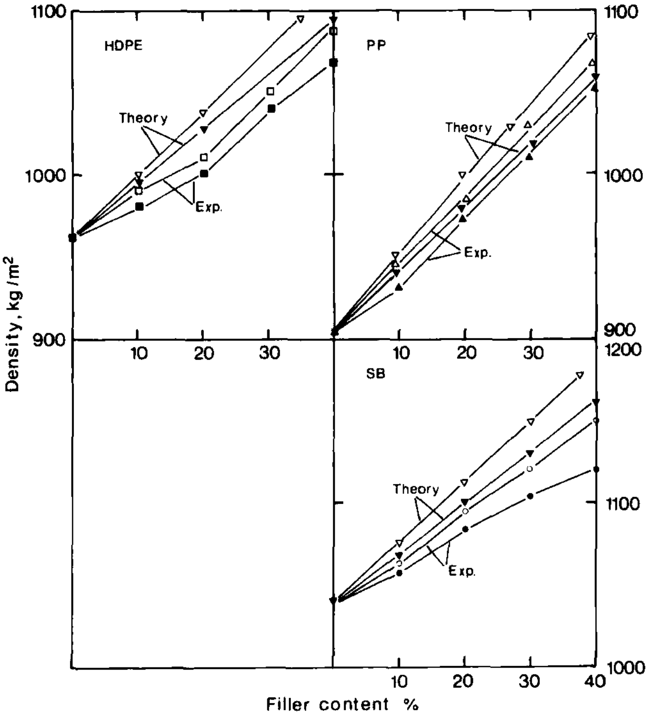

FIGURE 3 Experimental and theoretical density values for HDPE (■), PP (▲), and SB (●). Open symbols CF, filled symbols WF. The theoretical values (▼) were calculated using $\rho_{CM} = 1540\,(kg/m^3)$. Filler content in weight percent in all figures except Figure 8.

impact behaviour was recorded even for compounds Buss-mixed four times.

Modulus vs. filler content Young's modulus, E, of the injection-moulded samples is given in Figure 4 (material compounded twice on the Buss-machine) and in Figure 5 (compounding by a single extruder passage). In the latter case only the 20% and 40% filling levels were measured. Despite the differences in the visual appearance of the samples, reflecting among other things a better dispersion in the Buss-machine, the variation of E with the filler content is approximately the same for both compounding methods.

With extruder compounding (Figure 5), no major differences

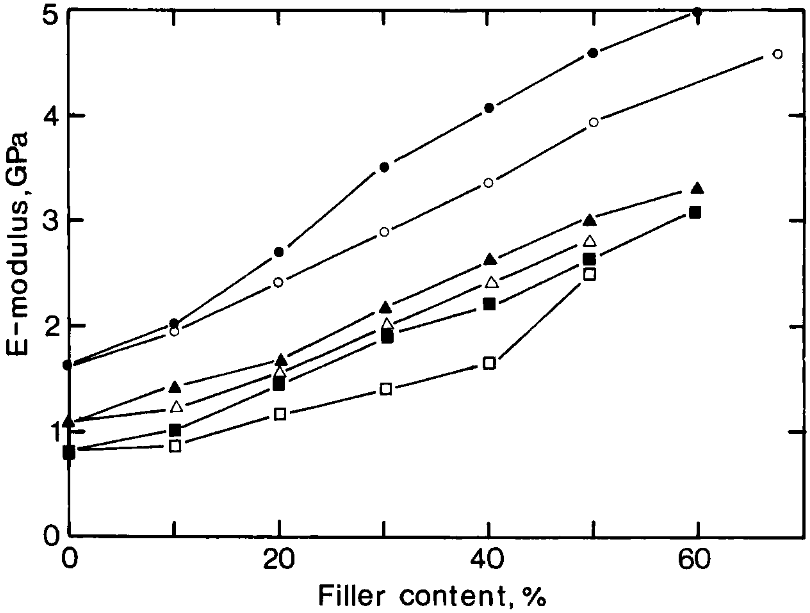

FIGURE 4 Modulus vs. filler content (mixed in Buss-Kneader) for HDPE (■), PP (▲), and SB (●). Open symbols, CF; filled symbols, WF.

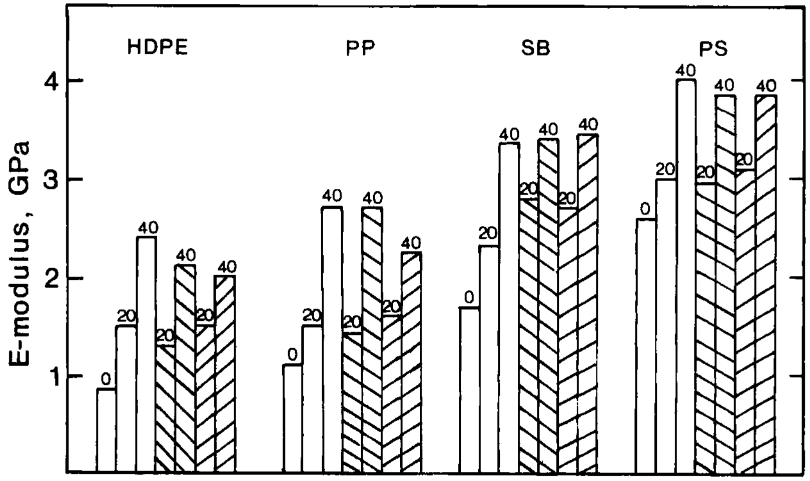

FIGURE 5 Modulus for the HDPE, PP, SB, and PS composites (single screw extruder). Numbers in Figures 5, 7 and 9–11 refer to filler concentration (%). Open areas, WF; dashed areas ▧, CF; dashed areas ▨, cellulose fibre.

between the three filler types are evident. With double Buss compounding, WF produces slightly higher *E*-values than CF. This may possibly be related to an inferior dispersion in the latter case, despite the intense homogenization involved. The CF particles tended to form aggregates about 1 mm in size.

The modulus/filler content relationship for the two polyamide plastics used, PA 6 and PA 12, is shown in Figure 6. With PA 6, the maximum filling attainable was 20% only. Higher contents produced pyrolytic degradation (melt temperature 235°C). With PA 12, such problems did not occur (processing temperature 195°C).

Figure 6 shows an appreciable stiffening effect of the three fillers on PA 12 in the as-moulded state. With WF, which could be incorporated at the 30% level, the increase in *E* was from 1 GPa to 3.0 GPa. A high stiffening effect was also found with CF. The

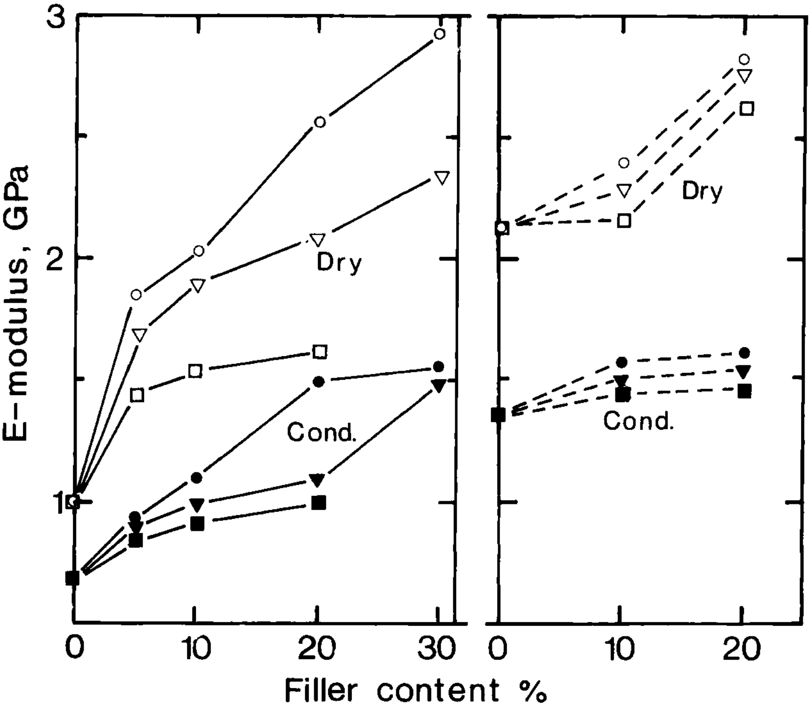

FIGURE 6 Modulus vs. filler content for PA 12 (solid lines, left) and PA 6 (dashed lines, right). ● WF, ▼ CF, ■ cellulose fibre. Open symbols = dry (as moulded), filled symbols = conditioned samples. Compounding: single-screw extruder.

behaviour of the PA 12 wood-pulp fibre composite is somewhat uncertain, as the maximum filler content attained in this case was 20% only. The same applied to PA 6. For the as-moulded samples, the fibrous filler had a lower effect than the two particulate ones.

Conditioning (15 h in water at 60°C) of the samples resulted in a marked decrease of E. This effect was especially pronounced with PA 6. There appear to be no significant differences between the fillers with regard to their stiffening effect in the conditioned samples.

Modulus vs. temperature Figure 7 shows the temperature dependence of the dynamic modulus for HDPE, PP, and SB containing 0, 20, 40, and 60% WF. The modulus was determined by the vibrating reed method (Bruel & Kjaer, Model 3930, heating rate 1°C/min, sample dimensions $10 \times 3.5 \times 75$ mm). Increasing the filler content allows an extension of the temperature range upwards. CF produced similar results.

Relative modulus A far reaching similarity with regard to the dependence of E on filler content for the various composites is evident from Figure 8 showing the variation of the ratio E_f/E_u at 23°C with the filling level expressed as the volume fraction of the filler (f, u—filled, unfilled) for HDPE, PP, and SB filled with WF and CF. The WF-curves have a higher slope, showing the higher stiffening power of this filler. The differences between the three matrix materials are relatively small; partly they may be due to experimental scatter.

The curves for the PA 6 and PA 12-based materials form two well-separated families; there is no significant difference between CF and WF. While the relative modulus of PA 12 changes with volume fraction filler in about the same way as that of PE, PP, and SB, that of PA 6 shows a small increase only.

Stress and deformation at yield and rupture The variation of the stress at yield (σ_y) and at rupture (σ_B) with the filler content was practically insignificant, and in many cases equal to the scatter in the results. This is illustrated in Figure 9, showing the relative value of σ_y filled/unfilled and ε_y for the Buss-mixed materials. It is evident that WF gives higher σ_y than CF. Cellulose fibres perform well in

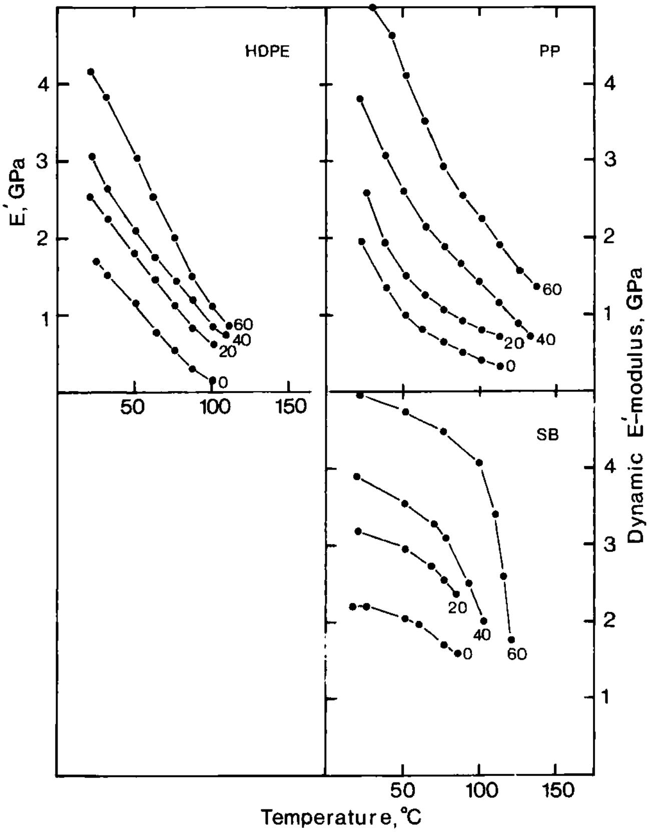

FIGURE 7 Dynamic modulus vs. temperature for HDPE, PP, and SB at different WF contents. Compounding: Buss-Kneader.

PE, while in PP and PS, due to uneven dispersion, σ_y decreases with increasing filler content.

The relative values of σ_B and ε_B for the WF-filled composite are shown in Figure 10. Again, the σ_B-values vary only slightly with the filler content, while there is a sharp drop in ε_B already at the 10% level. A comparison between the Buss- and extruder-compounded samples (Figure 10) shows the better performance of the former method. Similar results were found for CF. The large increase in the relative strength with increasing filler content for HDPE is due to the low nominal σ_B-value for this polymer.

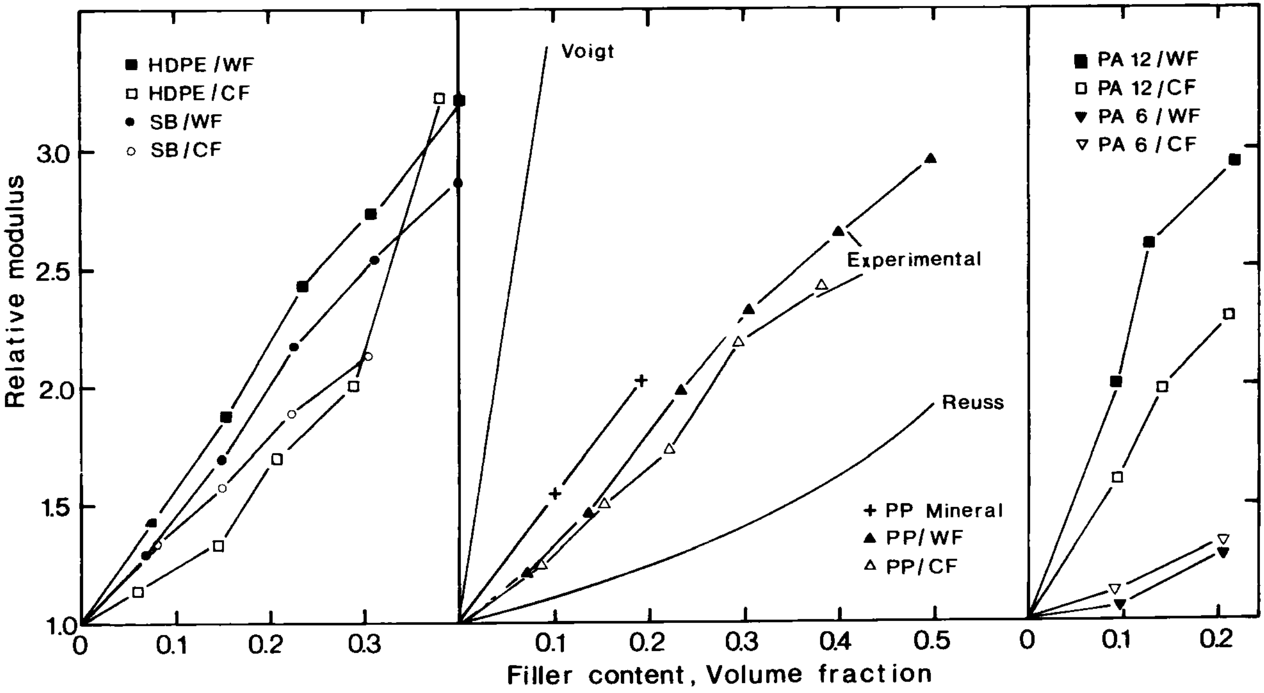

FIGURE 8 Relative modulus vs. volume fraction filler for HDPE, SB, PP, PA 6, and PA 12. Open symbols, CF; filled symbols, WF. PA 6 and PA 12 dry (as moulded). Values from Figures 4 and 6. Theoretical values, equations of Voigt[58] and Reuss,[58] shown for PP. Experimental values for mineral-filled PP also shown (+).

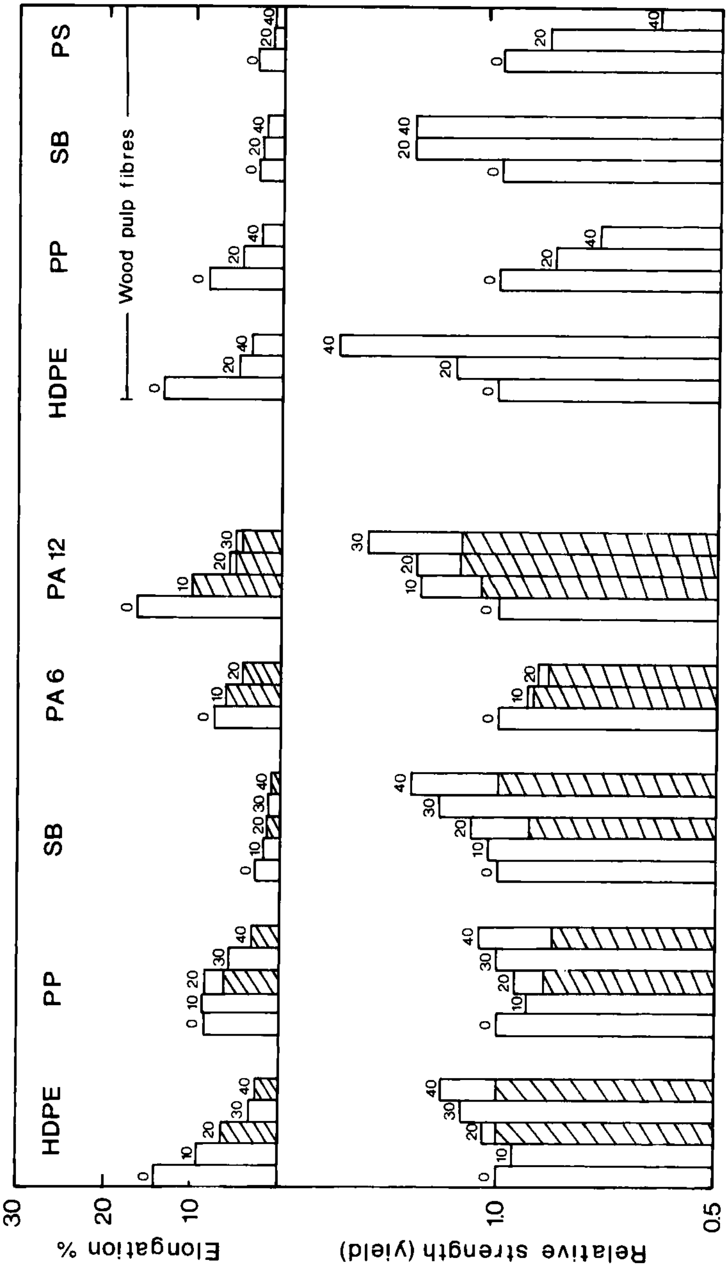

FIGURE 9 Stress and elongation at yield for HDPE, PP, SB, PA 6, and PA 12 filled with WF (undashed areas) and CF (dashed). Results for cellulose fibres in HDPE, PP, SB, and PS shown to the right. Extruder compounding.

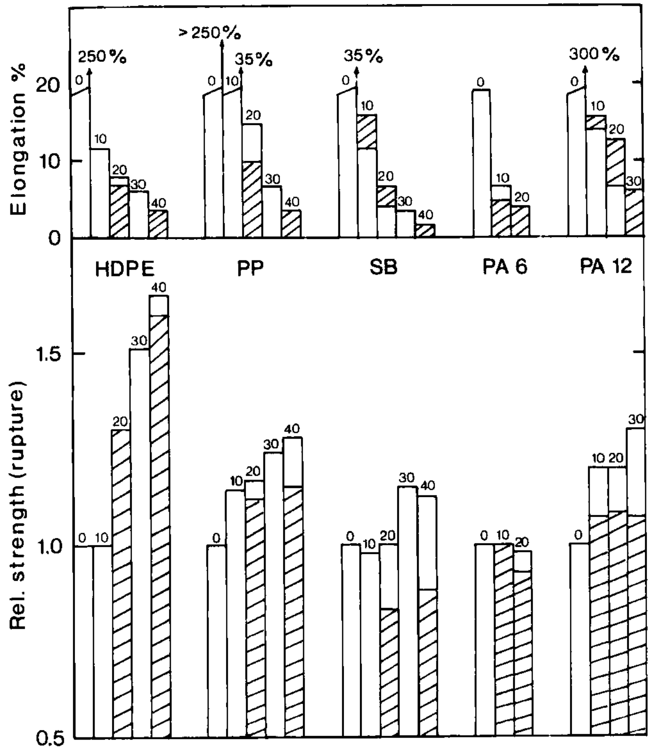

FIGURE 10 Tensile strength and elongation at rupture for HDPE, PP, SB, PA 6, and PA 12 filled with WF. Compounding: single-screw extruder (dashed areas), Buss-Kneader (open areas).

Impact strength The decrease in the elongation at rupture indicates a similar decrease in the impact strength. This is indeed verified by the results shown in Figure 11 for HDPE, PP, and SB filled with WF and CF. The data show a sharp drop in IS (Charpy, unnotched) with increasing filler content, and appreciable embrittlement is observed already at the 10% level. In absolute terms, the decrease per unit of filler added is lower the higher the filling level.

With HDPE and PP, IS at 20% filler is only slightly higher than that of clear PS (32 kJ/m^2), shown in the diagram for comparison. There appear to be no significant differences between WF and CF. The Buss-compounded materials have higher IS-values. The influence of repeated Buss-mixing has been mentioned above. Up to

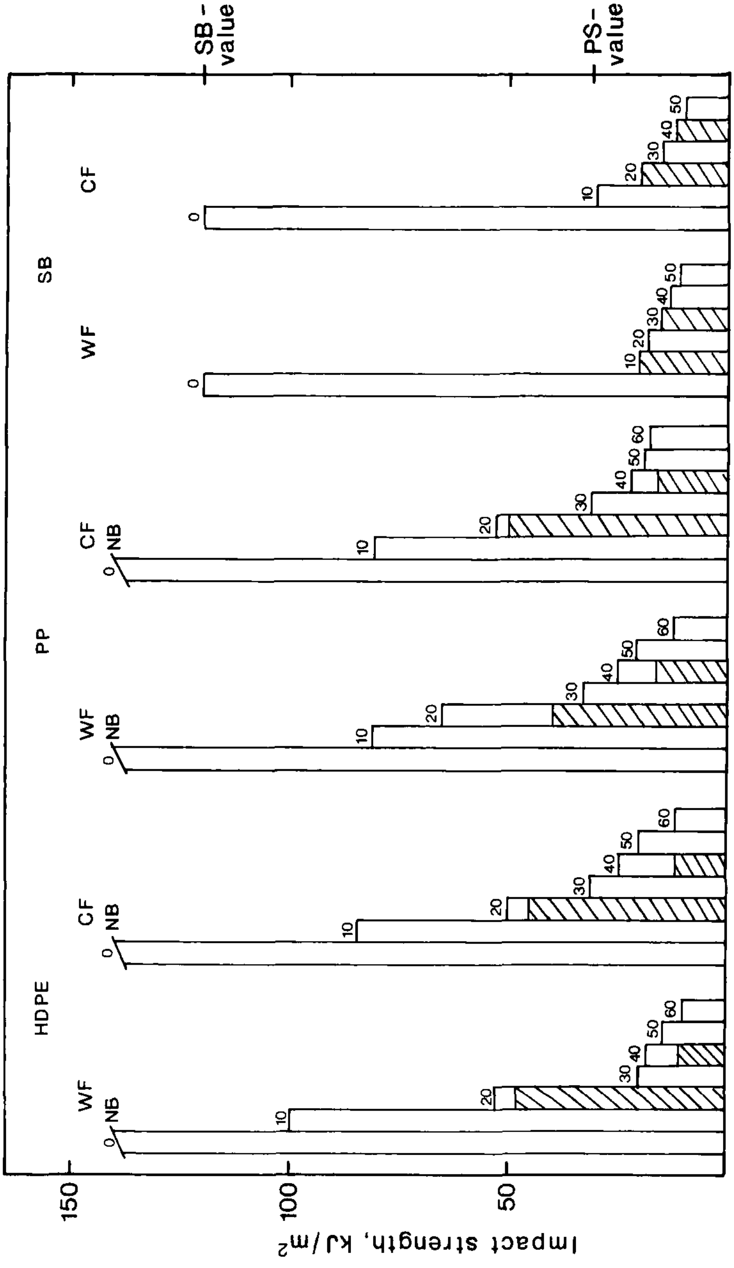

FIGURE 11 Impact strength (unnotched Charpy) for HDPE, PP and SB filled with WF and CF, respectively. Compounding as shown in Figure 10. (NB, no break).

20% filler content, impact values increase with the number of mixing stages. Above 20% filler level, no influence is recorded. For PS, a brittle material already in the unfilled state, only a limited decrease in IS was observed and is not snown in Figure 11.

On the whole, the materials discussed above show IS-values of the order of 10 kJ/m^2 at the highest filling levels. This corresponds to a brittleness higher than that of normal PS. At the normally occurring filling levels, a brittleness approximately corresponding to that of normal PS may be expected. The highest IS-values were found with conditioned PA 6 and PA 12. At 20% filling level the samples did not break, and at 30% (Pa 12) a value corresponding to that of SB was recorded.

Influence of moisture content on the impact strength At 40% filling, the HDPE, PP, and SB-composites containing WF and CF exhibited a rather limited dependence on the moisture content of the samples. As Table V shows, the decrease in the impact value upon conditioning (50% RH, 2 month) is rather insignificant. Increasing the water content to the 7–10% level by immersion in hot water produces in some cases a further, slight decrease due to surface cracks introduced by the hot-water treatment.

It is clearly demonstrated in Table V that the IS-value of dry samples is always higher than that of conditioned samples. This may be due to physical aging.[48] Such effects and the long time needed to

TABLE V

Influence of moisture on impact strength on moulded test-bars. Filler content 40%. Charpy (unnotched) values in kJ/m^2

Moisture content (conditioning)	Impact strength, kJ/m^2					
	HDPE/CF	HDPE/WF	PP/CF	PP/WF	SB/CF	SB/WF
Moisture nil (dry as-moulded)	17	20	28	25	10	12
Moisture 0.04–0.2% (1 day at 50% RH)	16	19	24	24	9	12
Moisture 0.6–1.8% (2 months at 50% RH)	16	19	24	24	9	12
Moisture 7–10% (wet[a])	14	16	24	25	8	10

[a] 1 week in hot water (90°C), resulting in surface defects (cracks, rough surface) on test bars.

reach moisture equilibrium make standardized tests of plastics containing hygroscopic fillers difficult.

Dimensional stability at elevated temperatures (thermal shrinkage)

In order to demonstrate the dimensional stability, a test was carried out where filled and unfilled samples of SB, PP, and HDPE were subjected to thermal treatment. The samples were stored for 30 minutes at temperatures exceeding the T_g and T_m-values of the polymer (SB 120°C, PP 165°C, HDPE 135°C). The resulting shrinkage of the bars was then measured. Filling with WF and CF markedly reduced the shrinkage, for example, for SB from 23% (unfilled) to *c.* 0.6% (40% WF). Filling with CF produced similar effects. The thermal shrinkage for unfilled PP and HDPE was smaller than for SB, 7 and 9%, respectively. Filling with 40% WF reduced the shrinkage to *c.* 2% for both polymers. The samples retained their shape without any warpage. Also, the cross-section remained undeformed.

FINAL REMARKS

Wood-based fillers exhibit certain appealing characteristics. Apart from a low density, normally <1500 kg/m^3, they are relatively rigid and strong. For wood fibres, modulus and strength values in the range of 25–40 GPa and 0.4–1 GPa, respectively, have been reported.[24,49–55] The extension at rupture is a few percent. Normally, various types of ground material are used (wood flour, cellulose flour), where the particle size is substantially smaller than the length of the fibres constituting the wood. Often, the particles are fractured fibre bundles. Typically, the aspect ratio is 2–15. The density of scandinavian softwood flour is *c.* 1400 kg/m^3 (*c.* 1500 for softwood fibres).

When used as a filler in thermoplastics, cellulose fibres do not produce any significant degree of reinforcement, despite their obvious stiffness and strength potential. This is largely due to the length reduction brought about by the intense shear forces in the compounding and processing machinery. This explains the similarity between fibrous and particulate cellulose fillers as demonstrated in the present study. Another factor of importance relating to fibrous cellulose fillers is their tendency to flocculate in the plastics matrix, thereby adversely affecting the properties of the compound. This lack of dispersion, frequently encountered also with particulate material, may be largely avoided by additives improving the homogeneity of the composites. The role of such additives will be studied in a forthcoming publication, where also the particle size distribution will be subjected to a closer scrutiny. On the whole, the fillers studied act as low-reinforcing fillers, their effect on the property profile resembling that of untreated mineral fillers on an equal volume basis. Cellulosic fillers, however, have distinct advantage of a substantially lower density, an important factor in applications where weight reduction is imperative. This is also brought out in calculations of break-even costs on an equal volume basis for compounds where the filler is used as an extender for the polymer matrix. This applies, however, only to WF, as the cost of CF and the fibrous cellulose, together with the cost of compounding, is prohibitive, ruling out the use of the latter materials as simple extending fillers. In such cases, the underlying cost relations have to be based on other criteria: increased stiffness at a given volume, etc. Here it may suffice to state that the break-even point for filling with WF and an untreated mineral filler (calcium carbonate) is at *c.* 25% filler content when the cost per unit of weight is considered. When, on the other hand, one is calculating the cost per unit of volume, a filling level of 45% is found for CF, while *c.* 85% of the mineral filler has to be incorporated for the break-even point to be reached. This is a highly tangible illustration of the advantage of using low density fillers.

A crucial factor when discussing the properties of composites is the adhesion between the phases. Experimental evidence points towards a strength value practically independent of the loading when the adhesion is good;[56] lack of adhesion results in a reduction of the strength parameters with increasing filler fraction.[57] Applied to the above results, the adhesion between the phases may thus be considered as good. The modulus, on the other hand, is largely independent of these factors. With regard to the impact strength, the adhesion and the character of the interlayer between the phases are crucial.

While the strength parameters of particulate composites are not easily amenable to theoretical treatment, the variation of the modulus with the loading has been the subject of numerous studies, reviewed, e.g., in Ref. 58. For volume fractions below 0.3, the different equations do not differ significantly. We have tried to apply some of these equations to the present systems; agreement with experimental data was, however, not achieved without substantial modifications of the formulae, which are difficult to substantiate in physically reasonable terms. In view of the wide particle size distribution, a factor not taken into account in the different theories, this is hardly surprising. In Figure 8 we therefore limit ourselves to illustrating the common limits of composite behaviour as described by the equations of Voigt[58] and Reuss[58] for the parallel and series case, respectively. Figure 8 also shows an example of the variation of the modulus of PP with the volume fraction of a dolomitic filler (Myanite), compounded and injection moulded under the conditions used in the present investigation. This filler, being a typical exponent of untreated mineral fillers, influences the modulus in largely the same way as wood flour on an equal volume basis. A comparasion with literature data on the modulus of mineral-filled PP confirmed this finding.

Apart from the advantage of low density of cellulosic fillers, also their lack of significant hardness may be mentioned, an important factor when the wear of the processing machinery is considered. Also the possibility of modifying the composite in various ways by impregnating the cellulosic filler particles appears to be potentially useful.

Acknowledgements

The authors wish to express their thanks to the Swedish Board for Technical Development for supporting this project financially.

References

1. E. Galli, *Plastics Compounding*, **5:3,** 103 (1982).
2. K. Berggren, C. Klason and J. Kubát, *Kunststoffe*, **12,** 69 (1975).
3. G. R. Lightsey, P. H. Short and V. K. K. Sinha, *Polym. Eng. Sci.*, **17,** 305 (1977).
4. Anon., *Mod. Plastics Int.*, **12:7,** 52 (1982).

5. E. Döring, *Chem. Ind.*, **32:5,** 314 (1980).
6. G. Gracia, *Ph. D. Thesis* (Mississippi State Univ., 1979).
7. Anon., *Reinf. Plast.*, **24:3,** 66 (1980).
8. Anon., *Plastics Eng.*, **30:2,** 15 (1974).
9. Anon., *Mod. Plastics Int.*, **4:2,** 22 (1974).
10. Anon., *Plastverarbeiter*, **28:4,** 199 (1977).
11. A. M. Usami, G. L. Ball, I. O. Salyer, D. W. Werkmeister and B. S. Bryant, *J. Elastomers Plast.*, **12,** 18 (1980).
12. S. Ishihara, H. Sasaki, I. Osada, J. Hasegawa and H. Kajiwara, *Mokuzai Kogyo*, **35:395,** 71 (1980).
13. V. K. Platonov, A. D. Zaionchkovskij, E. E. Glakhov and F. M. Seifullin, *Kozh-Obuvn. Prom-st.*, **16:10,** 50 (1974).
14. G. R. Lightsey, A. L. Hines, D. W. Arnold and V. K. K. Sinha, *Plast. Eng.*, **31:5,** 40 (1975).
15. G. R. Lightsey, L. Mann and P. H. Short, *35th Annual Tech. Conf.*, (SPE, Montreal, 1977), p. 362.
16. *idem, Plast. Rubber: Mater. Appl.*, **3:5,** 69 (1978).
17. G. R. Lightsey, B. D. Herzog, P. H. Short and L. Mann, *Plast. Des. Process.*, **19:5,** 28 (1978).
18. S. B. Driscoll, *35th Annual Tech. Conf.*, (SPE, Montreal, 1977), p. 366.
19. Anon., *Plast. Des. Process.*, **15:4,** 13 (1975).
20. Anon., *Mod. Plastics Int.*, **9:7,** 43 (1979).
21. Brit. 14, 26, 936.
22. J. A. Johnson and W. T. Nearn, *Theory and Design of Wood and Fiber Composite Materials*, edited by B. A. Jayne (Syracuse Univ. Press, Syracuse, 1972), Chap. 3, pp. 371–400.
23. A. J. Michell, J. E. Vaughan and D. Willis, *J. Polym. Sci.*:Symp. No. **55,** 143 (1976).
24. A. J. Michell and D. Willis, *Appita*, **31:5,** 347 (1978).
25. R. E. Prud'homme, *J. Appl. Polym. Sci.*, **21,** 947 (1977).
26. A. B. Moustafa, B. M. Abd El-Hady, and N. A. Ghanem, *Angew. Makromol. Chem.*, **85,** 91 (1980).
27. A. Nagaty, *J. Appl. Polym. Sci.*, **23,** 3263 (1979).
28. U.-P. Wang, *Ho Tzu K'o Hsueh*, **12:1,** 12 (1975).
29. A. J. Michell, J. E. Vaughan and D. Willis, *J. Appl. Polym. Sci.*, **22,** 2047 (1978).
30. C. Y. Kim and D. A. I. Goring, *Cellulose Chem. Technol.*, **8,** 401 (1974).
31. G. R. Lightsey, P. H. Short, K. S. Kalasinsky and L. Mann, *J. Mississipi Acad. Sci.*, **24,** 76 (1979).
32. Japan 72, 13, 304.
33. U.S. 4, 144, 304.
34. Ger. Offen. 2, 335, 844.
35. Brit. 1, 457, 015.
36. Ger. Offen. 2, 305, 150.
37. Neth. Appl. 75, 05, 138.
38. U.S. 3, 915, 910.
39. Japan 72, 40, 699.
40. Ger. Offen. 2, 658, 810.
41. J. Kubát and H.-E. Strömvall, *Plast. Rubber: Proc. Appl.*, (in press).
42. R. D. Deanin, S. B. Driscoll, R. J. Cook, M. P. Dubreuil, W. N. Hellmuth and W. A. Shaker, *36th Annual Tech. Conf.*, (SPE, Washington, 1978), p. 711.

43. V. E. Gul', M. S. Kurilo and E. G. Lyubeshkina, *Vys. Soed.*, **12A,** 1829 (1970).
44. R. D. Deanin, *ACS Organic Coatings and Plastics Chemistry*, **37:2,** 440 (1977).
45. L. Czarnecki and J. L. White, *J. Appl. Polym. Sci.*, **25,** 1217 (1980).
46. D. G. Baird and R. Pisipati, *Polymer News*, **8,** 79 (1982).
47. R. J. Crowson, M. J. Folkes and P. F. Bright, *Polym. Eng. Sci.*, **20,** 925 (1980).
48. L. C. E. Struik, *Physical Aging in Amorphous Polymers and other Materials* (Elsevier, Amsterdam, 1978).
49. H. Corte, *Composite Materials*, edited by L. Holliday (Elsevier, Amsterdam, 1966), Chap. **10,** pp. 486–489.
50. R. B. Seymour, *Pop. Plast. Rubb.*, **23:11,** 27 (1978).
51. R. B. Seymour, *Polym. Plast. Technol. Eng.*, **7:1,** 49 (1976).
52. A. H. Nissan, G. K. Hunger and S. S. Sternstein, *Encyclopedia Polym. Sci. Technol.*, edited by N. M. Bikaels (Interscience, New York, 1965), Vol. **3,** pp. 133–135.
53. B. M. Walker, *Handbook of Fillers and Reinforcements for Plastics*, edited by H. S. Katz and J. V. Milewski (Van Nostrand Reinhold, New York, 1978), Chap. **17,** pp. 292–298.
54. N. A. Waterman, R. Trubshaw and A. M. Pye, *Int. J. Mater. Eng. Appl.*, **1:2,** 74 (1978).
55. A. W. McKenzie and J. P. Yuritta, *Appita*, **32,** 460 (1979).
56. V. Dolákova-Svehlová, *J. Makromol. Sci.-Phys.*, **B21,** 231 (1982).
57. L. Nicolais and L. Nicodemo, *Intern. J. Polymeric Mater.*, **4,** 229 (1974).
58. S. McGee and R. L. McCullough, *Polym. Composites*, **2,** 149 (1981).