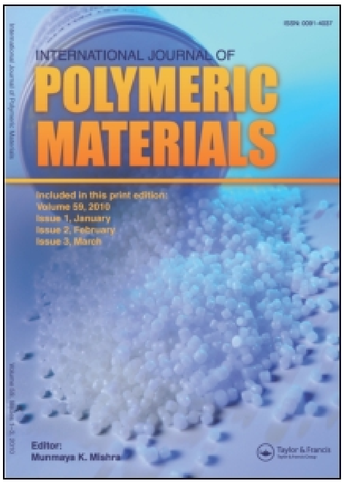

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H. Dalväg[a]; C. Klason[a]; H. -E. Strömvall[a]
[a] Dept. of Polymeric Materials, Chalmers University of Technology, Gothenburg, Sweden

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The Efficiency of Cellulosic Fillers in Common Thermoplastics. Part II. Filling with Processing Aids and Coupling Agents

H. DALVÄG, C. KLASON and H.-E. STRÖMVALL

Chalmers University of Technology, Dept. of Polymeric Materials, S-412 96 Gothenburg, Sweden

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This paper reports on the effect of additives on the properties of injection moulded composites based on polypropylene (PP) and high density polyethylene (HDPE) filled with wood and cellulose flour. Three types of additives were studied: dispersion aids, elastomeric additives, and adhesion promoting agents. Some of the dispersion aids were found to improve the filler dispersion and the impact strength. The modulus remained relatively unaffected while the strength was lowered. The high molecular weight elastomeric additives increased the impact strength and ductility, while the stiffness was reduced. An adhesion promotor based on a maleic anhydride modified polypropylene was found to behave as a true coupling agent, i.e. the strength and ductility increased, the melt strength was improved, and also the hot water resistance was raised. The experimentally determined composite moduli are found to agree relatively well with theoretical predictions. The effect of processing on the shape and size of the filler particles is evaluated using automatic image analysis.

INTRODUCTION

Thermoplastics containing cellulosic fillers represent a comparatively new class of composite materials. Apart from being relatively inexpensive, such fillers have a significantly lower density than mineral materials. The latter factor plays an important role when comparing the efficiency of various fillings on an equal weight basis. Moreover, reduced wear of the processing machinery may be mentioned as one of the advantages of such materials.

In a previous paper[1] the properties of a number of common thermoplastics (PE, PP, PS, SB, PA6, PA12) filled with wood flour (WF), cellulose flour (CF) and cellulose fibers were the subject of a systematic study. The filler and the polymer were homogenized in either a mixing extruder or a single-screw extruder prior to injection moulding of the test specimens. In general, the modulus (stiffness) of the composites increased significantly compared to the unfilled polymer, while the tensile strength remained relatively unaffected. The elongation at rupture and the impact strength were significantly reduced. On the whole, the effect of the fillers on the property profile did not exhibit any significant anomalies, cf. Ref. 2.

As with other types of fillers and reinforcing agents, a sufficient degree of adhesion to the polymeric matrix is a necessary prerequisite in the process of property optimization. Normally, this is achieved by modifying the filler/matrix interface by the incorporation of various additives or coupling agents. Such substances can be expected to improve the strength and ductility level of the composite. The effect on the elastic parameters, however, can be expected to be less significant.

Available literature lists a large number of substances for such purposes. On the other hand, no systematic study of the effect of such adhesion modifiers appears to have been published. Furthermore, the results often show a high degree of scatter as well as being based on materials produced with appreciably different fabrication techniques. As a continuation of the work presented in Ref. 1 we report in this paper the results of a comparative study of the influence of a number of additives on the mechanical parameters of high density polyethylene (HDPE) and polypropylene (PP), both filled with 30% by weight of WF or CF. The results, obtained with injection moulded samples, relate to the following types of additives:

Dispersants preventing agglomeration of the filler particles, which is likely to have an adverse effect on the ultimate properties and the impact strength.

Impact modifiers (elastomers) improving the impact strength of the composites.

Coupling agents improving the ultimate mechanical properties through better filler/matrix adhesion (in some cases by chemical bonding).

Compared to inorganic fillers and reinforcing agents, cellulosic materials offer some additional options with regard to the possibility of modifying the adhesion to the polymer matrix. This is reflected in the numerous reactions used for such purposes. Many nonreactive modifiers have also been used such as, for instance, bivalent metal salts of fatty acids which together with MgO or ZnO produced a 20% increase in impact (to 4.7 kpcm/cm^2) of WF-filled (30%) PE.[3] No improvements of the mechanical parameters were observed with a water repellent alkylketene dimer sizing agent in injection moulded WF/PP. There was a rather insignificant reduction in strength, while impact properties remained unchanged. Varying the lignin content did not influence the results.[4] Also rosin, commonly used in papermaking to hydrophobize cellulose, produced a 10–20% higher tensile and impact level in injection moulded WF/PP.[5] No effect was found with the corresponding composite containing thermomechanical pulp (filler content 20% in both cases).

Another method of conveying a hydrophobic character to WF fillers is a simple heat treatment which also reduces the evolution of decomposition products during processing (170°C, 5 h, 3.3% weight loss other than water).[6]

Benzoyl peroxide (0.1 part) is reported to increase flexural strength, Charpy impact strength, and Rockwell hardness of 50:50 WF/PP to 450 kp/cm^2, 1.8 kpcm/cm^2, and 83 (from 330, 1.6, and 65, respectively).[7] WF gave in this case higher values than $CaCO_3$. Cf. also Ref. 8.

Acetylation of paper produced only moderate improvements with paper/PE laminates.[9] A widely studied method for modifying the properties of cellulose is grafting. For instance, Ref. 10 compares the properties of PS filled with cellulose grafted with PS or benzylated. For the former, the melt viscosity was substantially higher. With regard to mechanical properties the incorporation of numerous benzyl groups was more efficient in PS than grafting with relatively few PS-chains. PMMA composites containing PMMA-grafted bagasse are discussed in Ref. 11. Also Ref. 12 claims improvements in mechanical parameters when using PMMA-grafted WF for PMMA-based compression moulded composites. Polymerization of suitable monomers in the presence of the filler/matrix components is treated in Ref. 13; for the use of grafted cellulose as a compatibilizing agent see Ref. 14.

No comparative study of the influence of grafting on the efficiency of cellulosic fillers appears to have been published.

Maleic anhydride (MA) can be used as a coupling agent providing bonds both to a filler containing hydroxyl groups (esterification) and to the polymer matrix (through peroxide addition). This method can be applied both to cellulosic and mineral fillers.[15] Another example of bonding with MA through esterification is found in Ref. 16 viz. copolymerization of styrene with maleic anhydride in the presence of birchwood sawdust (for moulded products). MA is also known to improve the properties of mineral filled plastics. For instance,[17] increasing the $CaCO_3$ content of PE from 0 to 50% reduced the tensile strength from c. 200 to 140 kp/cm^2. With 0.5% MA added in the extruder, the strength increased from 210 to 300 kp/cm^2 (yield stress independent of filling, with 0.5% MA an increase from 230 to 360 kp/cm^2). The Izod-value dropped from 5 to 3 when going from 0 to 50% filler; with 0.5% MA the change was 7 to 4.4 kpcm/cm^2. Also with $CaCO_3$-filled PP, the addition of 0.5% MA had a beneficial effect on the properties.[18] Both with PE and PP, a substantial decrease of MFI (increase in viscosity) was noted.

Improved impact properties were observed for olefin-MA-copolymers blended with rubber and WF.[19] There is a number of other examples relating to modified polymers used either as additives or matrix, e.g. the use of α-cellulose coated with a hydrocarbon/acrylate graft copolymer to increase toughness,[20,21] the addition of such polymers to the mixture,[22,23] impregnating the filler with an ethylene copolymer[24] (acetylation had same effect) or with a PF resol.[25] In the latter case, the impact value of PVC was reduced by 30% at 20% filling. The tensile strength increased with up to c. 30% filler (up to 70% filler was incorporated). By impregnating WF with a UP-resin[26] (25% and 50% of the WF-content) the modulus of PP/WF-composites increased from 4.8 GPa (100 : 100 PP/WF) to 6.2 GPa (100 : 100 : 50 PP/WF/UP). The tensile strength decreased from 37 MPa for the unfilled PP to 33.5 MPa for the PP/WF/UP-composite and to 24 MPa for the PP/WF-composition. The notched impact strength was reduced to 2.3 kJ/m^2 by adding UP (3.3 kJ/m^2 for PP/WF; 5.5 kJ/m^2 for PP/WF/UP). Polymerization of a suitable monomer in the presence of WF has also been studied. A beneficial effect obtained by coating WF with an ethylene-glycidyl methacrylate-vinyl acetate copolymer is claimed in Ref. 27.

In compression moulding of boards of poplar fibres/PE, corona treatment of the matrix powder improved the bonding.[28]

Combinations of cellulosic and inorganic fillers have been suggested in incombustible polyolefin compositions (MgOH, WF) using, among other matrices, MA-grafted PP.[29] Improved mechanical properties are claimed for PP filled with WF/$CaCO_3$ in Ref. 30. A mixture of 35% PP, 35% $CaCO_3$, and 30% WF gave a tensile strength of 33 MPa, and a modulus of 3.9 GPa (injection moulding). Using mixtures of this type, very high contents of solids can be attained.[31] Such mixtures are also useful in reducing the corrosion of the processing equipment that arises due to the acidic substances formed upon the decomposition of the cellulosic filler (MgO),[32] ($CaCO_3$).[33] Such corrosion may also be diminished by adding alkaline substances, such as urea or various amines, especially when the matrix material is PVC.[34]

The common method of increasing toughness by adding elastomers has been studied, e.g. with PP/WF,[35] or PP/$CaCO_3$/WF.[36] A similar additive is atactic PP.[37] Injection moulding of 40% PP, 37% $CaCO_3$, 20% WF, and 3% atactic PP gave a product with a tensile strength of 29 MPa, and a notched Izod value of 2.0 kpcm/cm^2. Ref. 38 gives for a 35/35/20/10 composition of these components 27 MPa and 4.5 kpcm/cm^2. Extrusion of WF with atactic PP as binder has also been reported to give useful products.[39]

Impregnation of WF with chloroparaffin is claimed to reduce humidity uptake and plasticizer consumption in calendered PVC floorings etc.[40]

Conventional coupling agents of the silane or titanate type appear to have attracted only little attention. The results reported in Ref. 41 for injection moulded PP filled with 30 or 40% WF (reed) show no significant improvement in the mechanical parameters when using 1% of a methacryloxysilane; *m*-phenylendimaleimide gave similar results. In the latter case, a c. 20% improvement in tensile strength was obtained when mixing the additive with the polymer prior to compounding of the components. Titanates are claimed to improve the efficiency of WF fillers (no data given).[42] The oligomer of poly(ethylene oxide) (PEO) used in the present investigation has been found to improve toughness in LDPE/$CaCO_3$. In 60/40 compounds, adding 10% PEO decreased the modulus from 135 to 72 MPa, while the strength fell from 8 to 7 MPa. Ultimate elongation increased from 70 to 190%, impact strength from c. 8 to 22 kJ/m^2, see Ref. 43.

For the sake of completeness, we also mention a recent paper not included in Ref. 1 (cellulosic fillers without additives). In Ref. 44 the behaviour of WF-filled PVC is reported for various filling contents (0–60%). Up to 40% the strength of the matrix is not affected by the presence of WF, but the elongation at break and the impact value decrease rapidly above 15% filling.

MATERIALS

The polymers used were injection moulding grades of high density polyethylene, HDPE (DMDS 7006, Unifos Kemi, density 960 kg/m^4, MFI 190/2.16 7.0), polypropylene, PP (copolymer GYM 121, ICI, density 905 kg/m^3, MFI 230/2.16 13.0) and an ionomeric polymer (ethylene/sodium methacrylate copolymer, Surlyn 1605, Du Pont, density 940 kg/m^3, MFI ASTM D-1238 2.8).

The properties of the fillers, i.e. wood flour (white spruce) and cellulose flour (bleached pine sulphate) have been specified in Ref. 1.

The property modifiers are listed in Table I. Stearic acid (SA) was used as a hydrophobic surface modifier as well as a dispersion promoter. Common dispersion aids like stearic acid (SA), paraffin wax (PW), polyethylene wax (PEW), and mineral oil (MO) were tested. The elastomeric additives were ethylene/vinyl acetate (EVA), chlorinated polyethylene (CPE), polyisobutylene (PIB), ethylene/propylene thermoplastic elastomer (TPO), ionomer modified PE (Surlyn) and a liquid acrylonitrile/butadiene elastomer (NBR). Also a low molecular weight poly(ethylene glycol) (PEG) was used.

A titanate compound and a maleic anhydride modified PP (Hercoprime) were used as coupling agents.

TABLE I
Additives used

Stearic acid
Solid paraffin wax (melting range 52/54°C)
Polyethylene wax, (AC-PE 6A, T_m 106°, Allied Chemical)
Mineral oil (low aromatic oil, Nypar 20, Nynas)
Polyethylene glycol (molecular weight 200)
Ethylene/vinyl acetate copolymer (Elvax 40-P, c. 40% VA, Du Pont)
Chlorinated polyethylene (CPE 4213, 42% chlorine, DOW)
Polyisobutylene (Oppanol 100, BASF)
Ethylene/propylene thermoplastic elastomer (Vistaflex 714, Esso)
Ionomer modified PE (Surlyn 1605, Du Pont)
Acrylonitrile/butadiene elastomer (liquid, Hycar 1312, Goodrich)
Titanium di(dioctylpyrophosphate)oxyacetate (KR 138S, Kenrich PI)
Maleic anhydride modified polypropylene (Hercoprime A-35, Hercules)

EXPERIMENTAL

Compounding and injection moulding

The compounds were homogenized in a mixing extruder (Buss Kneader PR46). After granulating, the mixes were injection moulded with a conventional injection moulding machine (Arburg 221E/17OR) into tensile test bars (DIN 53455, effective length 75 mm, cross section $10 \times 3.4\,\mathrm{mm}^2$). The fillers and additives were added to the polymer in the compounding step.

The titanate coupling agent was dissolved in methylene chloride (1% solution) at RT, and the fillers were impregnated with the solution. After drying, the filler containing 3% of the titanate was mixed with the polymer in the Buss Kneader.

Mechanical testing

The mechanical properties of the samples (tensile modulus, tensile strength at yield and rupture, and the corresponding elongations) were measured with an Instron tensile tester (Model 1193). The strain rate was 4.2×10^{-3} and the temperature 23 ± 0.5°C. The impact strength was tested with a pendulum device (Zwick model 565K) according to the Charpy method (unnotched BS 2782). The samples were tested after conditioning at 23°C and 50% RH for 24 h; for the influence of conditioning, see Ref. 1.

Melt behaviour

The rheological behaviour of the melts was studied in a capillary viscometer (Instron Model 3211) at 180°C and 200°C. Rabinowitsch corrections and correction for entrance losses (Bagley plots) were applied. The melt strength and elongation at rupture were measured at 180°C for some of the compounds with a melt tensile apparatus (Göttfert Rheotens).

Differential thermal analysis (DTA)

The crystallinity, and the melting (T_m) and crystallisation (T_c) temperatures were determined using a Mettler TC 2000 DTA device. The heating and cooling rates were 5 K/min.

Scanning electron microscopy

After impact testing some of the fracture surfaces were studied in a scanning electron microscope (Jeol JSM 35).

Light microscopy

The influence on filler size and shape due to compounding of the cellulosic fillers used was studied by light microscopy.

Preparation for light microscopy and image analysis

Samples of injection moulded test bars of HDPE and PP containing 30% WF or CF were dissolved in hot o-dichlorobenzene. The solutions were filtered and the filler particles retained on the filter were rinsed with hot xylene and dried at 108°C for 24 h.

Image analysis

Image analysis providing information about filler size and shape was performed on microphotographs using a Kontron device.

RESULTS

Effect of dispersants and elastomeric additives

The results obtained with the property modifiers listed in Table I are reproduced in Figures 1 and 2. Figure 1 shows the impact strength for HDPE and PP filled with 30% WF and CF, respectively. Stearic acid, paraffin wax, PE-wax or mineral oil did not have any marked effect on the impact strength of the WF-filled composites, although the degree of dispersion was visibly improved especially with stearic

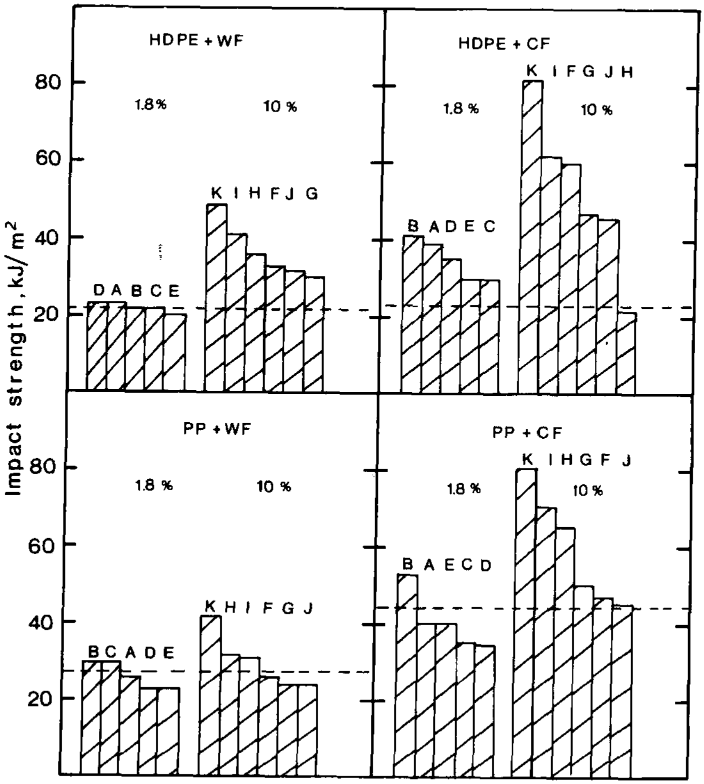

FIGURE 1 Impact strength (Charpy, unnotched) for HDPE and PP filled with 30% by weight of WF and CF and with different additives. Keys for the additives are given in Figure 2. The dashed line indicates the properties of the unmodified compound. Additive content 1.8% for A–E and 10% for F–K (in percent of total amount).

acid and paraffin wax. These additives also have a beneficial influence on the impact strength of the CF-filled samples. This was especially pronounced with HDPE, where stearic acid, paraffin wax and mineral oil were effective as dispersants, improving the impact strength from 24 kJ/m^2 for the unmodified grade to 40 kJ/m^2 with paraffin wax addition. With PP, the improvement was moderate only, although paraffin wax increased the impact strength to some extent.

The elastomeric additives raised the impact level in most of the samples. Here, also, there was a difference between WF and CF, CF giving better results. This was true for both HDPE and PP. The best result was obtained with NBR which raised the impact value of CF-filled HDPE from 24 kJ/m^2 to 83 kJ/m^2. Relatively high impact values were also obtained with Surlyn and EVA in HDPE, and with Surlyn and PIB in PP. On the other hand, the elastomeric additives did not appear to act as dispersants. In some cases, for instance with Surlyn, the dispersion was even poorer than in the unmodified samples.

As already mentioned, the impact values obtained with WF were lower than with CF. This may possibly be associated with the more irregular shape of the WF particles, resulting in local stress concentrations in the matrix.

In Figure 2 the elongation at break, ε_b, the tensile strength, σ_b, and the modulus E, are shown for DHPE filled with 30% CF. The other matrix/filler combinations followed a largely similar pattern. The ε_b-value increased with all additives, except with PIB. For example, NBR increased the ε_b-value of HDPE/CF from 4.5 to 45%. The reduction in strength, σ_b, when incorporating the dispersant, e.g. PE wax, is difficult to explain. Normally, improved dispersion results in higher strength values.[2] Probably, these additives have an adverse effect on the strength of the matrix material; they may also affect the interface between filler and matrix. A similar reduction in σ_b when using liquid oligomers has been reported.[43]

The modulus was not affected by the dispersion aids except for PEG. This is in agreement with the idea that agglomerates may be strong enough to increase the modulus.[2] As expected, elastomeric additives lowered the stiffness. For example, with NBR the stiffness fell to a value comparable to that of the unfilled matrix materials (both PE and PP).

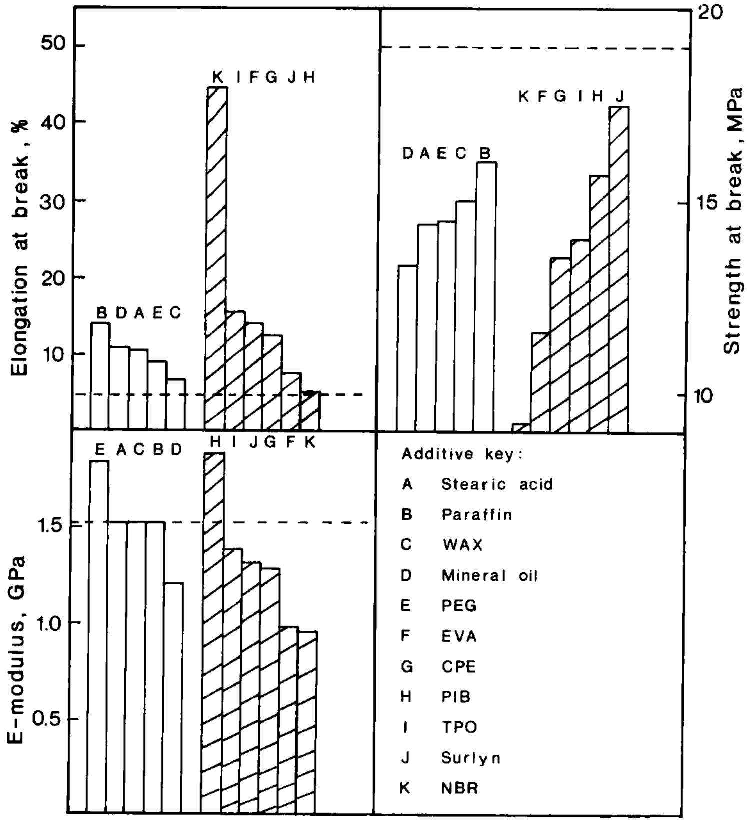

FIGURE 2 Elongation at break, strength at break and *E*-modulus of HDPE/CF-composites with different additives. Dashed line—unmodified compound. Content 1.8% for A–E; 10% for F–K.

Effect of coupling agents

In Figures 3–7 the results obtained with the coupling agents used are presented. They indicate that the maleic anhydride modified PP (MA-PP) acts as a true coupling agent, i.e. giving higher values of σ_y, σ_B, and ε_B together with increased impact strength. Figure 3 shows the yield stress for composites containing 30% filler. The amount of MA-PP was varied between 2 and 6% (based on the filler content). The strength increased c. 20% for all composites except

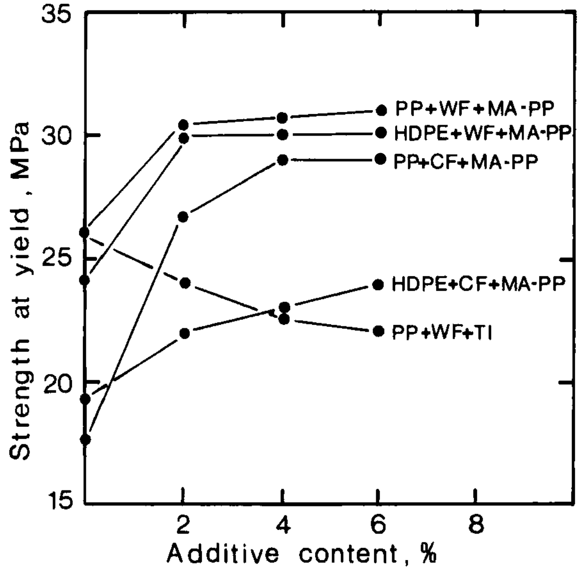

FIGURE 3 Strength at yield vs. the amount of coupling agent (maleic anhydride modified PP, titanate; calculated in per cent of filler amount) for HDPE and PP filled with 30% WF or CF.

for the PP/CF-compound, where a 70% increase was recorded (from 17 to 29 MPa). The strength reaches its maximum level at c. 3% additive concentration; further increase does not produce further improvement. In Figure 4 the results of the impact tests are reproduced. The variation of ε_b with the additive contents, as shown in Figure 5, appear to reflect the pattern found with the variation of the impact strength. Although the strength of the materials was improved with MA-PP, the modulus was influenced to a minor extent only. This is shown in Figure 6 where stress-strain curves are shown for PP/30% WF with 2 and 4% MA-PP.

Addition of the MA-PP coupling agent appears to produce a significant improvement of the wettability of the filler particles by the matrix. This is shown in Figure 7, where scanning electron micrographs of fracture surfaces of PP/30% CF-samples with and without MA-PP are reproduced. As can be seen the fracture in the modified composites occurs in the matrix material.

In case of insufficient adhesion between the phases, the interface between filler and matrix may be susceptible to attack by water

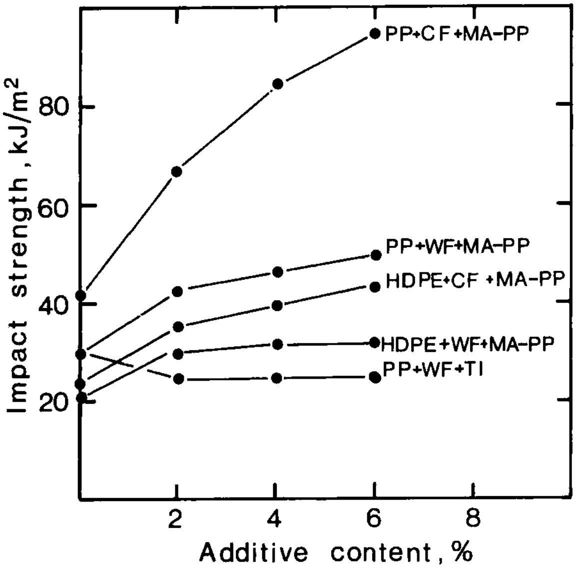

FIGURE 4. Impact strength vs. the amount of coupling agent (cf. Figure 3; in per cent of filler amount) for HDPE and PP filled with 30% WF or CF.

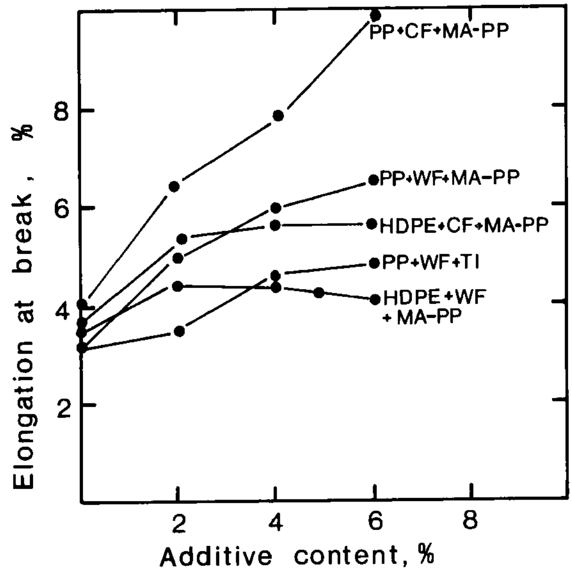

FIGURE 5. Elongation at break vs. the amount of coupling agent (cf. Figure 3; in per cent of filler amount) for HDPE and PP filled with 30% WF or CF.

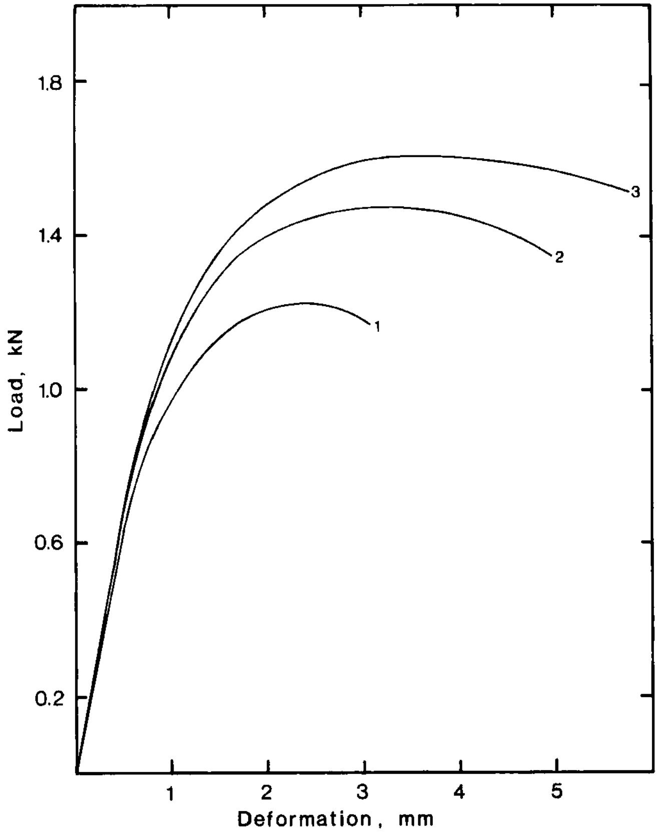

FIGURE 6 Load-deformation curves for PP/WF-composites. (1) PP+30% WF; (2) PP+30% WF with 2% MA-PP; (3) PP+30% WF with 6% MA-PP. (MA-PP: maleic anhydride modified PP). Sample length 80 mm, cross section 10×3.4 mm.

resulting in loss of strength.[2] To examine this effect, samples of HDPE and PP filled with WF and CF, with and without MA-PP coupling, were immersed in boiling water for 24 h. The samples were then inspected and mechanically tested. The results are given in Table II. They show that the MA-PP modified samples show a minor decrease in strength only, while the unmodified samples suffer a significant strength deterioration. Furthermore, visual inspection of the modified samples revealed no changes in their appearance; the unmodified test bars, on the other hand showed loss of gloss and

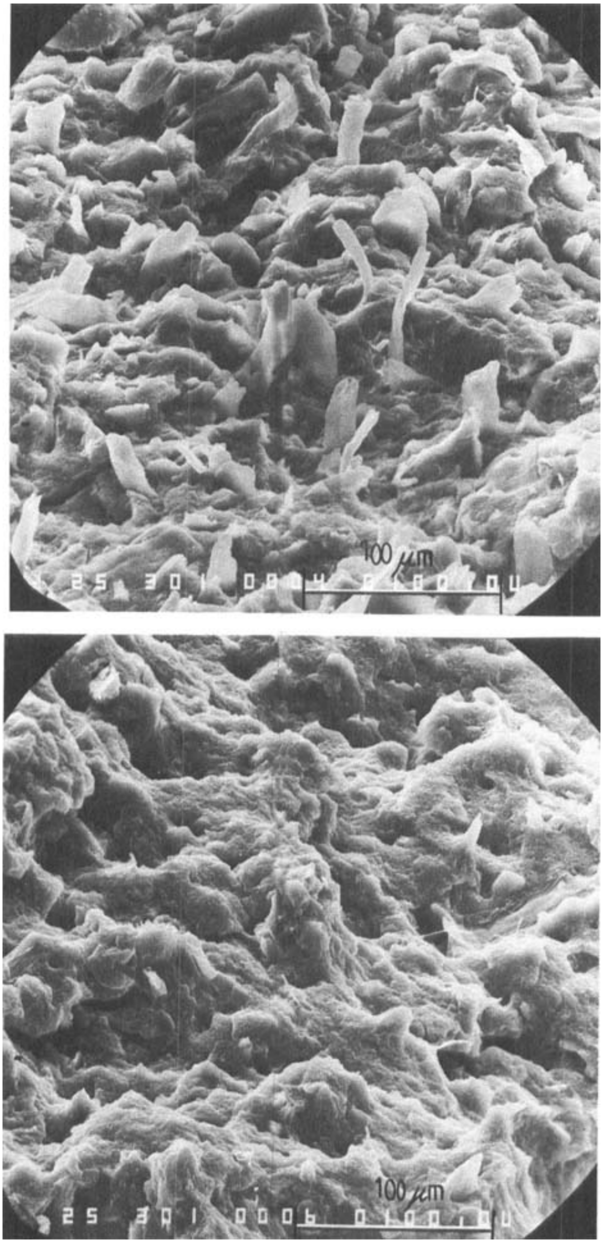

FIGURE 7 Scanning electron micrograph of a fracture surface of a PP/CF-composite without (upper photo) and with 6% MA-PP (lower photo). The lower photograph shows that the failure has occurred in the matrix.

TABLE II

Effect of immersion in boiling water for 24 hours

Composite with	Strength at break, MPa	
	Before treatment in water	After treatment in water
HDPE+CF	19	14
HEPE+CF with 6% MA-PP	24	24
HDPE+WF	20	13
HDPE+WF with 6% MA-PP	24	22
PP+CF	18	14
PP+CF with 6% MA-PP	25	24
PP+WF	19	12
PP+WF with 6% MA-PP	26	26

with, for instance, unmodified WF-filled composites, surface cracking.

The titanate coupling agent did not perform well since it caused both strength at break and impact strength to decrease, Figures 3–5. Although the ε_b-value was increased to some extent, the mechanical parameters were in general not improved by titanate coupling.

Melt rheology

The rheological behaviour of molten thermoplastics containing cellulosic fillers has only been reported for polystyrene,[45,46] the fibres used increasing the viscosity approximately in the same way as mica. The flow curve fell between those of glass fibre and glass bead filled PS melts at a volume fraction of 0.2. Appreciable fibre damage was noticed.

The flow behaviour of CF and WF-containing melts follows the general pattern found with cellulose fibres.[45,46] Figure 8 shows the influence of cellulose flour (30% level) and coupling agent addition on the flow properties of PP melts (apparent viscosity vs. shear rate). The influence of the filler is not very pronounced. More interesting is the increase in viscosity due to the addition of 1.2% MA-PP (4% on filler content). Similar effects due to improved coupling between

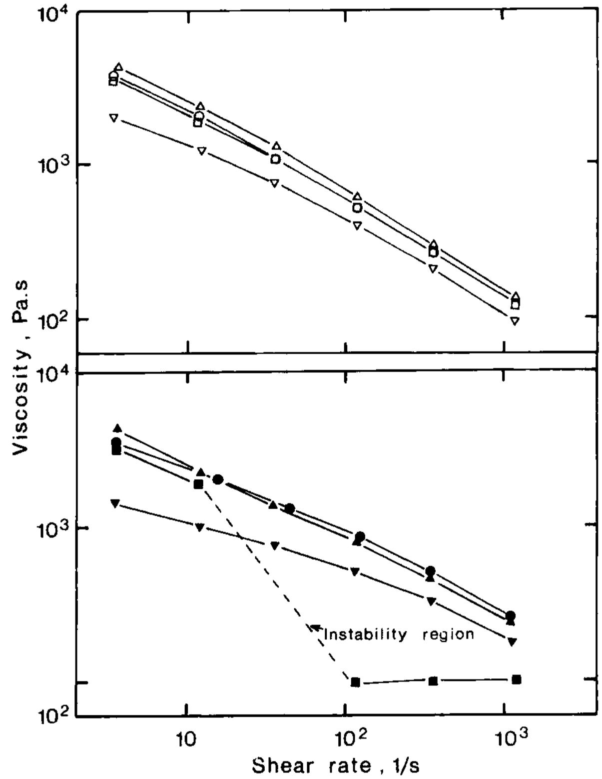

FIGURE 8 Viscosity vs. shear rate for: PP (▽), PP containing 30% CF (○), PP/30% Cf and 1.2 MA-PP (△), PP/30% CF and 1.2% titanate (□) (upper Figure); HDPE (▼), HDPE/30% CF (▲), HDPE/30% CF and 1.8% paraffin (●), HDPE/30% CF and 10% NBR (■) (lower Figure).

polymer and filler have been reported earlier.[47] The titanate coupling agent did not influence the viscosity at all.

Figure 8 also shows the viscosity vs. shear rate graphs for PE/30% CF and the influence of paraffin wax and NBR additions. The incorporation of CF resulted in a minor increase of the apparent viscosity of the PE melt, while adding 1.8% of paraffin (6% on the CF content) to the filled compound did not influence the viscosity markedly. On the other hand, the behaviour of the NBR-containing compound was unexpected. At low shear rates, the viscosity changed as with the unmodified material; at higher shear rates the decrease in viscosity was substantial. At intermediate rates an instability region appeared.

There was no significant difference in the behaviour of the WF- and CF-filled melts.

Melt strength measurements showed that adding 6% MA-PP resulted in a c. 100% increase in melt strength and elongation at break for both PP and PE.

Fibre length reduction during compounding and injection moulding

With the automatic image analyzer used in this study the area of each filler particle as well as its perimeter and longest dimension are readily obtained. In Figure 9 the distribution of the longest dimension (D_{max}) of the CF particles is shown. This figure includes data for unprocessed filler particles and particles that have passed one or four times through the mixing extruder and subsequently through the injection moulding machine. Evidently the compounding and moulding results in a significant fibre length reduction, the extent of which increases with the number of compounding steps. Similar behaviour was observed with WF. This is in agreement with the results found for glass reinforced thermoplastics.[48,49]

From the image analysis the aspect ratio (L/D) of the fillers may be estimated as

$$\frac{L}{D} \approx \frac{D_{max}^2}{\text{Area}}. \qquad (1)$$

In Table III the average values of L, D and the aspect ratio L/D are given for as-received, as well as compounded and injection moulded PE and PP samples containing CF and WF. For WF the compounding results in a significant reduction in fibre length (given by D_{max}) as well as in fibre diameter. The aspect ratio, however, remains rather unaffected by the compounding and moulding steps. For CF a somewhat different behaviour is observed. Here the aspect ratio and the fibre length are reduced as the number of compounding steps increases (from c. 4.3 to c. 2.8 for PP) while the fibre width changes relatively little. This behaviour is probably due to the more fibre-like (slender) character of the CF-particles, and possibly also to the lower strength of these particles, in the transverse direction.

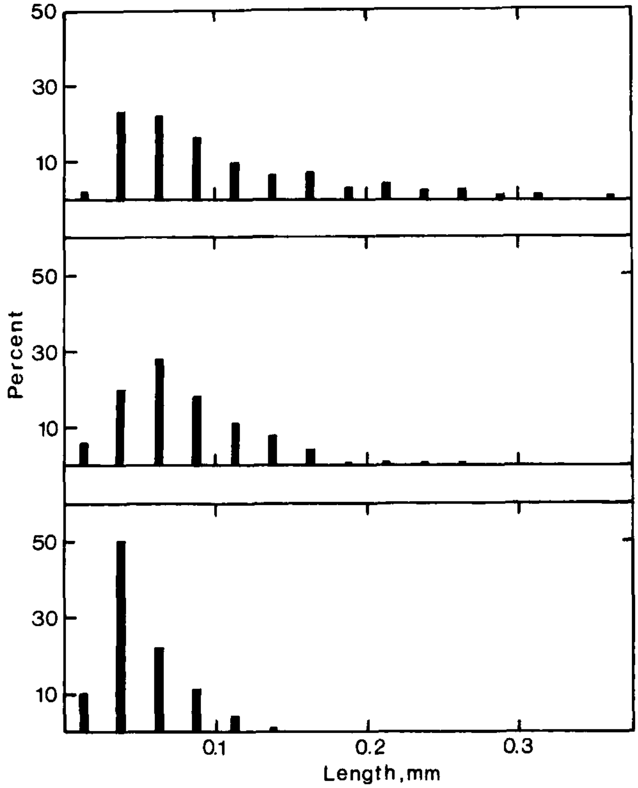

FIGURE 9 The distribution of the longest dimension (≈the fiber length) of the CF-particles for the as-received filler (upper Figure) and for particles that have passed one (middle) or four times (lower) through the mixing extruder and prior to injection moulding.

Crystallinity and thermal properties

Crystallinity measurements made using DTA show that the fillers used may, in some cases, increase the crystallinity of the matrix material. For instance, the crystallinity of unfilled HDPE was 58%; adding 30% WF did not change this figure, while adding 30% CF increased it to 65%.

The different additives used had no significant effect on the amount of crystalline material in the polymers. The figures for PP

TABLE III

Effect of processing on the average shape of the fillers as evaluated from the image analysis. Filler content 30%

Materials	*L*/*D*	*L* μm	*D* μm	Number of processing steps[a]
WF (as received)	2.5	103	40	—
PP+WF	2.6	74	28	1
HDPE+WF	2.3	68	29	1
CF (as received)	4.3	103	24	—
PP+CF	3.8	77	21	1
PP+CF	2.8	50	18	4
HDPE+CF	3.5	78	22	1

[a] In the mixing extruder.

were 72% for the unfilled polymer and 85% for both the CF- and WF-filled composites.

The melting temperature, T_m, was unaffected in both HDPE and PP, while the crystallization temperature, T_c, increased to some extent in both cases. For PP, T_c increased 5°C by adding 30% WF or CF, while the effect on HDPE was significantly smaller; (0.5 to 0.75°C).

Properties of an ionomer based composite

Figures 10 and 11 show the results obtained with an ionomeric polymer (Surlyn) as matrix material. The stiffness increased from 0.2 GPa for the unfilled material to 1.4 GPa at 60% filling; this was accompanied by a substantial increase in strength, from 17 to 29 MPa. For 30% CF filling the *E*-value was 0.6 GPa and the strength 20 MPa, see Figure 10. This shows that CF acts as a reinforcing filler in the matrix material used. As expected the filler caused a reduction in impact strength, Figure 11. However, compared to filled HDPE and PP (see also Ref. 1), the impact strength remained at a relatively high level.

THEORETICAL ESTIMATES OF THE COMPOSITE MODULUS

There exist a number of relations for calculating the modulus of composite materials in terms of its constituents, cf. Ref. 2. In this

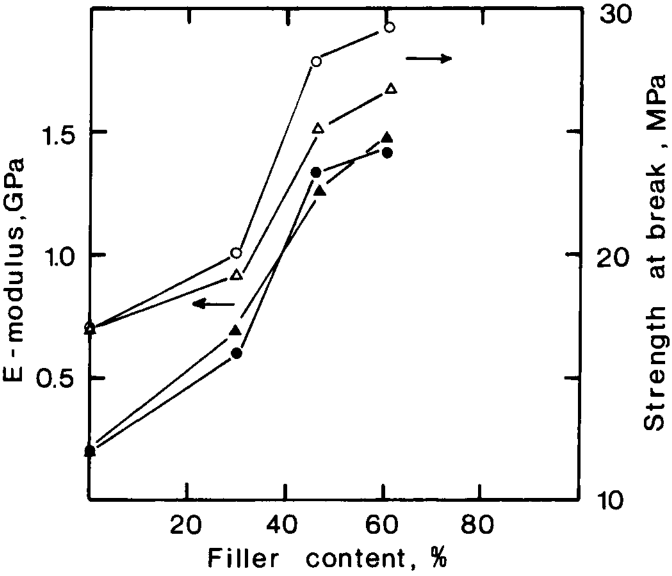

FIGURE 10 The tensile modulus (filled symbols) and the tensile strength at break (unfilled symbols) vs. the content of (▲) WF and (●) CF in an ethylene-based ionomer (Surlyn).

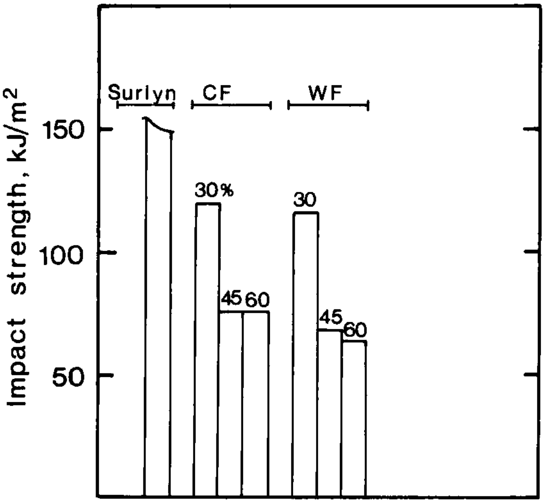

FIGURE 11 Impact strength of an ethylene-based ionomer (Surlyn) containing different amounts of WF or CF.

section, some of these equations will be applied and the results compared with experimental data.

The simplest equations for predicting the modulus of a composite material are the upper and lower bounds given by the rules of mixture,[2] i.e.

$$E_c = v_m E_m + v_f E_f \tag{2}$$

and

$$\frac{1}{E_c} = \frac{v_m}{E_m} + \frac{v_f}{E_f}, \tag{3}$$

respectively. Here E_c is the composite modulus, E_m and E_f are the moduli of the matrix and filler, respectively, and v_m and v_f are the corresponding volume fractions.

Eqs. (2) and (3) correspond to the idealized case where the constituents of the composite respond to external stresses in a parallel and series fashion. Normally, the bounds represented by these two limiting cases are too far apart to be of practical use. Comparison with our experimental data shows that they are closer to the lower modulus bound.

The parameters entering Eqs. (2,3) are, at least for the filler components, not easily specified. The approximate values used in the present case are as follows:

$E_{\mathrm{CF}} = E_{\mathrm{WF}} = 20$ GPa, cf. Ref. 50

density of CF 1540 kg/m^3, and

density of WF 1420 kg/m^3, cf. Ref. 1.

The corresponding values for the matrix materials are:

HDPE $E = 0.9$ GPa, density 960 kg/m^3

PP $E = 1.1$ GPa, density 905 kg/m^3.

It should be noted that the E-values of the fillers are approximate only; they are not amenable to direct measurement.

For polymers containing nearly spherical particles the Kerner or the equivalent equation by Hashin and Shtrikman can be used to calculate the modulus of the composite. Tsai and Halpin have shown that the Kerner equation and similar relations can be written in a more general form, formulated by Nielsen after still further generalization[2,51,52]

$$\frac{M_c}{M_1}=\frac{1+ABv_2}{1-B\psi v_2}. \tag{4}$$

In this equation, which holds for both particulate fillers and fibre reinforcements, M_c and M_1 denote the elastic moduli (Young's, shear or bulk) of the composite and matrix, respectively, v_2 is the volume fraction of the filler, and A and B are constants. The constant A depends on the Poisson's ratio of the matrix and the aspect ratio of the filler, while B takes into account the moduli of the matrix and the filler, as it is known that a hard filler gives a higher stiffening effect with a rubbery material than with a rigid thermoplastic. The upper and lower bounds expressed by Eqs. (2) and (3) correspond to $A \rightarrow \infty$, and $A \rightarrow 0$, respectively.

The constant B is given by

$$B=\frac{(M_2/M_1)-1}{(M_2/M_1)+A} \tag{5}$$

where the subscripts 1 and 2 refer to the matrix and filler phase, respectively. The factor ψ takes into account the existence of a maximum packing fraction of the filler. The product (ψv_2) in Eq. (4) can be regarded as the reduced volume fraction of the filler phase; it is expressed as

$$\psi v_2=1-\exp\left(\frac{-v_2}{1-v_2/v_m}\right) \tag{6}$$

where v_m is the maximum volumetric packing fraction of the filler. In some cases, the v_m-value can be calculated theoretically. For spherical particles, v_m varies from 0.60 for a random loose packing to 0.74 for hexagonal close packing. For fibres, its value lies between 0.5 for random orientation to 0.9 for the parallel hexagonal packing. For the cellulosic fillers used here, it is difficult to assume a correct value of v_m due to the deformability of the particles during the injection moulding step. Therefore, the factor ψ is assumed to be equal to unity.

The value of A, which is correlated with the Einstein coefficient k_E by $A = k_E - 1$, has the value 1.5 for rigid spheres in a matrix with a Poisson's ratio of 0.5 when the material is deformed in shear. For particles of nearly spherical shape, A is given by $A = (7-5\nu_1)/(8-10\nu_1)$ giving a value of 1.17 for a Poisson's ratio of 0.35 for a PP or HDPE matrix. For parallel rodlike particles or fibres, the value of A is equal to $2(L/D)$ if the tensile stress is applied in the direction of orientation (L/D-aspect ratio). If the stress is acting perpendicular to the orientation direction of the fibres, A equals 0.5.

In the present case, the Tsai-Halpin equation (4) has been employed to obtain estimates of the modulus based on the following assumptions:

a) The filler particles are assumed to be rodlike, $A = 2(L/D)$, uniaxially oriented in the tensile direction. The factor ψ is assumed to be unity, i.e. $v_m = 1$, for the sake of simplicity. The average value of the (L/D) ratio is used (identical particles, no distribution).

b) Same as above but with the value of A being 0.5. This means that the tensile stress is applied perpendicular to the orientation direction.

c) The filler particles are assumed to be spherical. The value of A is 1.17, and the factor ψ is assumed to be unity.

d) Same as a) with particles distributed with regard to their length and width, i.e. the L/D-value.

To account for condition d the fractions of filler particles having L/D-values within certain limits were evaluated from microphotographs. The following classes (limits) for L/D were chosen: up to 2, 2–4, 4–6, 6–8, 8–10, 10–12, and greater than 12. The corresponding fractions v; for CF were 0.28, 0.31, 0.25, 0.07, 0.06, 0.015, and 0.015, respectively. This procedure was only performed on the PP/CF composites which had been homogenized once in the mixing extruder and injection moulded. The Tsai-Halpin equation (4) was then applied to each L/D-class giving a corresponding E_c-value. These values were then weighed together using the fractions corresponding to the L/D-classes above giving an estimate of the composite's stiffness, giving E_c as

$$E_c = \sum_i v_i E_i \tag{7}$$

where $\sum_i v_i = 1$.

Table IV shows the predictions of the Tsai-Halpin equation evaluated under the different assumptions specified above. It is

TABLE IV

Predictions of the stiffness of the composites according to Eqs. (2)–(4) and comparison with experimental data. Filling level 30% by weight. E-values for PP and HDPE 1.1 GPa and 0.9 GPa, respectively. Moduli in GPa

			Nielsen-modified Tsai-Halpin equation				
			Uniaxial direction of rodlike particles			Spheres	
	Rule of mixture		Fiber direction, $A = 2$ (L/D)		Transverse direction, $A = 0.5$	$A = 1.17$[a]	
Material	Upper bound Eq. (2)	Lower bound Eq. (3)	Average (L/D)	(L/D)-classes			Experimental data
PP+CF	4.9	1.4	2.5	2.3[b]	1.5	1.6	1.9
PP+WF	4.9	1.4	2.1	—	1.5	1.6	2.0
HDPE+CF	4.7	1.1	2.1	—	1.2	1.4	1.5
HDPE+WF	4.7	1.1	2.9	—	1.2	1.4	1.8

[a] $A = \frac{7 - 5\nu_1}{8 - 10\nu_1}$ where ν_1 is Poisson's ratio of the polymer matrix, assumed to be 0.35.

[b] Only performed for PP/CF-samples. Due to the low aspect ratio very little is achieved using this approach.

clearly seen that the experimental data falls within the upper and lower bounds given by this equation for the two main directions of orientation (rodlike particles). The assumption of a spherical shape of the filler particles gives an E-value which is somewhat too low.

The analysis using the superposition of various L/D-fractions gives an E_c-value which is close to the composite modulus calculated using the average value of the aspect ratio, cf. Table IV. This is to be expected since the aspect ratio of the fillers in this case is rather low.

On the whole, it may be concluded that the cellulosic fillers act as short rodlike or ellipsoid shaped particles.

If the average aspect ratio could be kept high, i.e. above 20, the stiffness of the cellulosic fillers could certainly be utilized more efficiently. A uniaxial orientation of the fibres would thus give an E_c-value of c. 10 GPa. In the more realistic case of random orientation, E_c would fall somewhere between this upper limit and the lower bound corresponding to $A = 0.5$ in Eq. (4).

DISCUSSION

The additives used in the present study to improve the mechanical property profile of PP and HDPE containing wood-based fillers appear to produce results not easily classified according to their anticipated effect. In view of the complexity of the systems studied and their sensitivity to different kinds of surface effects, this is hardly surpising. Furthermore, cellulosic fillers, contrary to mineral materials, may absorb various amounts of a substance added as a surface coating. Such phenomena may also be complicated by the presence of minute quantities of water, or by chemical changes of, in the first hand, the cellulosic fractions of such materials during processing. The latter effect is particularly difficult to control in conventional processing equipment, as it is the result of a complicated interplay between factors like temperature, humidity, and the presence of air. The latter factor, not encountered with normal fillers, must be considered as especially difficult to control.

The dispersion aids used here did in some cases (stearic acid and paraffin) prevent agglomeration of filler particles, thereby improving the impact strength and elongation at rupture. Such additives were most effective for the HDPE/CF-compounds. As expected an improvement in dispersion did not affect the tensile modulus appreciably. The decrease in strength due to the incorporation of dispersion aids is however difficult to explain. It cannot be excluded that these additives can have a plasticizing effect on the matrix material.

As anticipated, elastomeric additives improved impact strength and elongation to break, significant effects being obtained already at a 10% level. The improvement in ductility was, rather naturally, parallelled by a reduction in stiffness and strength. The addition of elastomers to HDPE- and PP-composites changed the character of these materials, making them resemble thermoplastic elastomers.

The MA-PP additive used as an adhesion promotor exhibited the characteristics of a true coupling agent. Impact, strength, and elongation values increased significantly, while the modulus remained practically unchanged. This is a typical example of what can be expected from an improved adhesion between matrix and filler. In this case, immersion in boiling water did not significantly affect the strength or the visual appearance of the composite. Also SEM-pictures revealed that the failure did not occur in the interface but in the matrix material. The increase in melt viscosity and melt strength when adding MA–PP was another indication of an improved adhesion between polymer and filler.

Surprisingly enough the titanate-based coupling agent, did not have any positive effect on the performance of the composites. The reasons for this were not investigated.

On the whole, the values of the mechanical parameters appear to agree with literature data. However, the improvement in impact obtained with the MA–PP coupling agent is remarkable.

The use of coupling agents is only one of the ways to improve the adhesion between the two phases. Other methods are, for example, graft polymerization on the filler or the use of polymers containing suitable functional groups attached to the main chain, cf. our results with the ethylene-based ionomer.

From the processing point of view, CF- and WF-filled PE and PP melts did not present any particular problems. The increase in viscosity was similar to what could be expected for mineral fillers at the same volume fraction. As a rule the additives used improved the surface appearance of the mouldings.

The aspect ratio of the fillers was relatively low, i.e. 2–5 from image analysis. For both CF and WF the processing steps resulted in a further decrease of this ratio. In general, CF is potentially more effective due to its higher *L/D* value. This appears to be true also when the adhesion between filler and matrix is improved.

The theoretical estimates of the modulus values of the various composites show a relatively high degree of agreement with experimental facts. Further refinement of the theoretical models is hardly appropriate, since there are additional factors difficult to include in such a theoretical framework. In the first place, one may refer to the laminate structure of injection moulded parts, consisting of layers of widely differing structure (skin, shear zone, core). Not only is the crystallinity and crystallite size and habit different in the various strata but also the orientation. Considering such complicating features, the agreement between predicted and experimentally found modulus values must be considered highly satisfactory.

Apart from the advantages of wood-based fillers already mentioned, one may also note their sensitivity to hydrolytic attack. It is well-known that exposure of such materials to the action of, for instance, dilute inorganic acids at elevated temperatures results in a high degree of embrittlement. Wood-based fillers treated in such a way can be comminuted into much smaller particles than the untreated material. Especially interesting is the possibility of conducting such comminution during compounding. Also the utilization of this self-comminuting property of the filler to reduce the lateral dimensions of the particles, thereby increasing their aspect ratio, is a promising approach. The fibrils produced in this way may be anticipated to have a reinforcing effect far in excess of what has been reported in the present paper.

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