Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibres - Part 2 : Analysis of composite microstructure and mechanical properties

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Abstract

The microstructure and mechanical properties of polypropylene composites containing flax and wheat straw fibres are discussed. Particular emphasis has been given to determining the nature and consequences of fibre damage induced during melt-processing operations, fibre orientation occurring in mouldings, and possible interfacial adhesion between the matrix and fibres. Compared to unfilled polypropylene, addition of flax and wheat straw caused a significant increase in tensile modulus, particularly, in the case of flax fibres which also gave higher tensile yield strength and Charpy toughness, despite a lack of interfacial bonding. Tensile strength was increased further through inclusion of 5% by weight of maleic anhydride-modified polypropylene, which was shown to promote adhesion between fibres and matrix.

1. Introduction

Part I of this paper reported the characterization of flax and wheat straw fibres with a view to their use as reinforcing additives in thermoplastics, in particular polypropylene [1]. Of crucial importance in this regard is the manner by which their inherent mechanical properties alter on exposure to elevated temperatures, which are encountered during melt processing of the polymer. Some insight into these changes was sought through micromechanical tests, and model thermal analysis studies employing thermogravimetry. The microstructure of the fibres was also examined, because this is likely to change from its natural form, resulting from exposure to extreme conditions of temperature and shear.

This paper, Part II, examines the mechanical properties of flax and wheat straw-reinforced polypropylene composites through an analysis of their microstructure, in particular the property controlling factors of fibre-matrix bonding, fibre-length distribution and fibre orientation. Specific attention has been paid towards developing methods for enhancing inter-facial shear strength of the composites and to identifying structural damage imparted to the reinforcing phase.

2. Experimental Procedure

2.1 Materials

Polypropylene homopolymer (VS 6100K Shell Chemicals) was used as the matrix material for reinforcement by linseed flax and wheat straw fibres. This had a melt flow index of 25g $10mm^{-1}$ (2.16 kg, 230°C).The composition, structural characteristics and properties of these fibres were described in Part I. For comparison, some experiments were also carried out using 3mm long chopped E-glass fibres.

The flax fibres were pulped prior to use by passing through a co-rotating twin-screw extruder. This had the effect of reducing their length, but facilitated blending with surface treatment and subsequent incorporation into the polypropylene during melt compounding.

2.2 Formulations, fibre treatment and compounding procedures

Various means were used in an attempt to promote surface interaction between the natural fibres and host polymer matrix, in particular through the use of silane coupling agents (gamma-amino-propyl-tri-ethoxy-silane, OSI Specialities Ltd; 3-glycidoxy-propyl-trimethoxy-silane and vinyl-trimethoxy-silane, Aldrich Chemical Co. Ltd). Compositions were also prepared containing stearic acid (BDH Chemicals Ltd) and maleic anhydride modified polypropylene (MA-PP) (Polybond 3150, Uniroyal Chemical Co. Inc.).

A Henschel high-speed mixer was used to apply surface treatments to flax and wheat straw fibres using the lowest available impeller speed (1600 r.p.m.) and a jacket temperature of 70°C. Mixing times were approximately 3 min. It was necessary first to breakdown the flax fibres to approximately 5cm lengths in the pulping extruder to discourage longer fibres from wrapping around the mixer shaft. However, it was inevitable that some additional fibre damage occurred during this treatment process.

Silane treatments were added from solution during the first minute of mixing to give a 2% by weight coating on the fibres. The same addition level of stearic acid was used, but this was included with the fibres in powder form prior to blending. Some compositions were also made where MAH-PP was combined with the PP pellets at a 5% by weight addition level (based on the fibres), then mixed with the fibres prior to compounding.

Treated and untreated fibres were dried in an air-circulating oven at 85°C for up to 4h. Mixtures of PP and 25% by weight of reinforcing glass, flax and wheat straw were pre-distributed by shaking in a plastic bag. Melt compounding was undertaken in a Betol BTS40 co-rotating intermeshing twin-screw extruder using a barrel to die temperature profile between 155 and 185°C with a screw speed of 100 r.p.m. This gave a material residence time in the extruder of approximately 70s. Blends prepared in this manner were die-formed into 6mm diameter strand which was cooled by passing through a water bath, then pelletized.

2.3 Injection moulding of test specimens

Pelletized compound was dried in an air-circulating oven for 24h at 80°C before injection moulding into test specimens for measurement of mechanical properties. Temperatures in the barrel and nozzle ranged from 150-180°C. The mould temperature was 40°C.

2.4 Mechanical testing

Specimens were conditioned for 7 days at 23°C and 50% relative humidity prior to testing. Tensile strength was measured according to BS2782 Method 320B (1976). Elastic modulus was determined using an extensometer at a crosshead speed of 1mm min^{-1}. Flexural modulus was assessed using conditioned samples, following BS2782 Method 335A (1978) at a crosshead speed of 1.5mm min^{-1}. Charpy impact tests were undertaken on notched samples according to BS2782 Part 3 Method 359 (1984).

2.5 Microstructure of the composites

The fibre-matrix interface was studied by scanning electron microscopy on tensile fracture surfaces, coated with gold. To study fibre dispersion and orientation, two methods were employed. Because the wheat straw contained significant amounts of silica, fibres could be observed using X-ray contact microradiography, which has been used previously to determine glass fibre orientation in plastics composites [2]. For this purpose, sections were cut from the centre of tensile test bars in both the longitudinal and transverse directions. These were ground and polished to a thickness of approximately 0.5 mm and exposed to soft X-rays. However, this technique could not be applied to composites containing flax straw, which were examined by reflected light microscopy on polished sections.

Fibres were removed from the composites by adopting a Soxhlet extraction method, following previously reported procedures [2,3]. Decalin solvent was used to dissolve the polypropylene by refluxing for up to 4 days.

Fibre length measurements were undertaken using a VIDS image analyser and two-point measuring programme. Fibres were spread between a glass slide and cover plate and approximately 500 measurements taken for each fibre type. Analysis was undertaken on fibres before and after processing. Exposure to the solvent during polymer removal was found to have very little effect on fibre length.

2.6 Fibre concentration and composite density

The weight fraction of fibres in the composite was determined by thermogravimetric analysis of the composition and its constituents tested in isolation, in a nitrogen atmosphere over a temperature range from 30-730°C. Assuming there is no interaction between the components during heating of the composite, the fibre weight fraction can be calculated from these results [4].

Composite density of natural fibre composites was measured by the immersion method described in BS2782 Part 6, Method 620A (1980). Samples were sectioned from tensile test bars and the cut ends polished before immersing in methylated spirits.

From a knowledge of the weight percentage of fibres combined in the polymer, the density of the composite and, by assuming there was no air entrapped, fibre volume fraction and density, were calculated [5].

3. Results and discussion

Fibre-length measurements for wheat straw fibres before and after melt processing are shown in Table I, with an example of distribution curves for wheat straw fibres given in Fig. 1. It will be evident from Fig. 2, that wheat and flax straw fibres, examined after solvent extraction from moulded composites, undergo significant damage during processing and that whereas the flax straw remains fibrous in appearance, the wheat straw, to a large extent, loses its fibrous identity, becoming much more plate-like in character. The accuracy of fibre length measurements is clearly limited by their irregular form, hence results reported in Table I are necessarily an approximation.

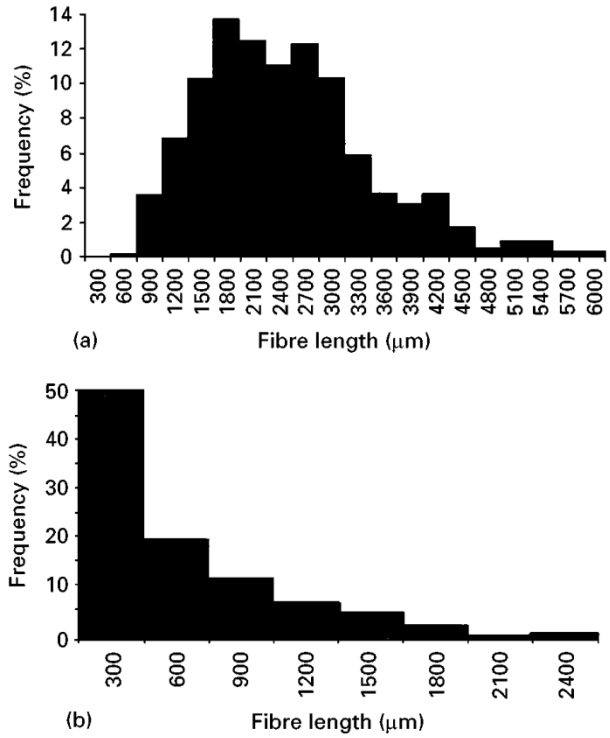

Fig. 1: Fibre length distributions for wheat straw, (a) before processing with PP, (b) after solvent extraction from PP

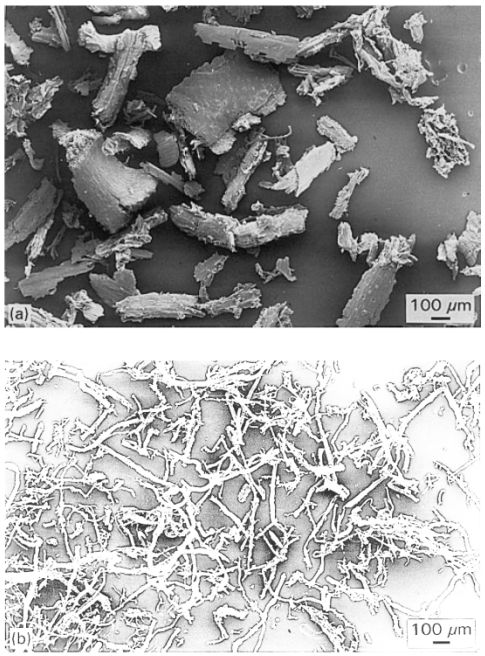

Fig. 2: Structure of natural fibres after extraction from moulded polypropylene composites: (a) wheat straw and (b) flax straw

Table I: Fibre length measurements on wheat and flax straw fibres

	Fibre length (μm)		
		Before processing	After processing
Flax straw[a]	Max.	2093	1150
	Min.	53	14
	Mean	307	258
Wheat straw[b]	Max.	5816	3567
	Min.	545	6
	Mean	2300	493

a Pulped in twin-screw extruder prior to use
b As-received, but sieved to remove fines

Nevertheless, it is apparent that wheat straw fibres are significantly more susceptible to breakage than flax during processing. Wheat straw fibres surface treated in a high-speed mixer prior to extrusion compounding also undergo substantial breakage during this pre-processing step, which was far less apparent with the flax material. Fracture surfaces of polypropylene containing untreated wheat and flax straw fibres are shown in Fig. 3. In both cases, there is no evidence of interfacial bonding between fibre and matrix phases. Indeed, as Fig. 4 shows, there is a clear imprint of the surface texture of the wheat straw remaining on the polymer after fibre pull-out. It is likely that the gaps appearing at the interface arise as a consequence of the large volumetric contraction during melt cooling and solidification of the polymer. Processing of the composite has also resulted in extensive fibre damage, particularly in the case of the wheat straw, which undergoes structural collapse and significant fracture along its length.

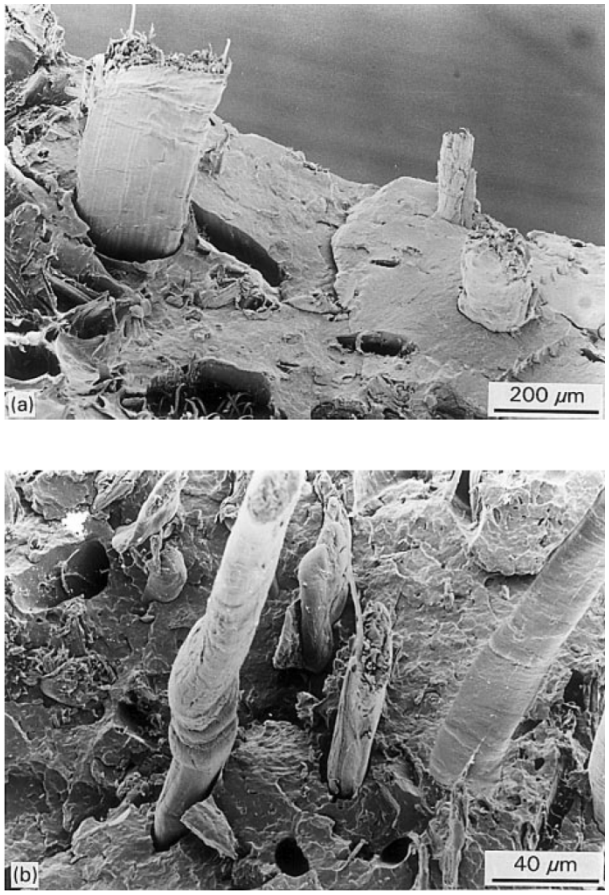

Fig. 3: Fracture surfaces of polypropylene composites containing (a) wheat straw and (b) flax straw fibres

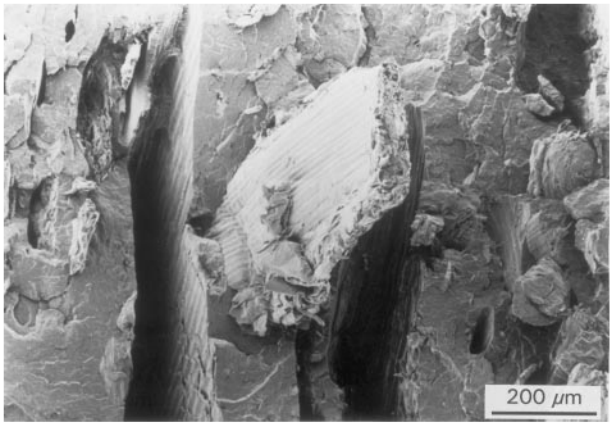

Fig. 4: Fracture surface showing lack of adhesion between polypropylene and wheat straw

In this work, composites contained nominally 25% by weight of each of the fibre types. With wheat straw fibres, amounts near to this value were measured in the polypropylene, using both solvent extraction and thermal analysis procedures (Table II). However, with flax fibres, around 21% by weight was obtained by each method. Potential sources of error in the determination of natural fibre content which might lead to lower than expected fibre content include the possibility of volatile release due to loss of tightly bound water (not removed by drying before processing) or low molecular mass products evolved as a consequence of fibre degradation during melt processing.

Table II: Fibre loading and density in polypropylene composites (standard deviations are given in parentheses)

	Nominal fibre loading (% by weight)	Actual fibre loading (% by weight)	Actual fibre loading (% by volume)	Measured material density ($kg\,m^{-3}$)	Calculated fibre density ($kg\,m^{-3}$)
Polypropylene	–	–	–	900.2	–
PP + wheat straw	25	25.0[a] 23.6[b]	16.8 (0.1)	998.8 (1.18)	1490 (11)
PP + flax straw	25	21.1[a] 21.2[b]	13.5 (0.1)	986.8 (0.54)	1540 (6)
PP + glass fibres	25	25.3[a] –	10.7 (0.1)	1076.0 (0.75)	–

a Determined by TGA

b Determined by solvent extraction

Composite density results obtained by pyknometry showed good reproducibility. Calculated density values for the natural fibres in the composite are broadly similar, and at the upper end of the density range reported in the literature [6]. These fibre types have a naturally occurring cellular structure which, as mentioned earlier, is unable to withstand the high pressures and shear forces experienced during polymer processing. Collapse of the cell walls is most distinct with wheat straw fibres (Fig. 5), leading to a marked increase in fibre density. Flax fibres, however, tend to have thicker cell walls with a smaller, or even no distinct central lumen.

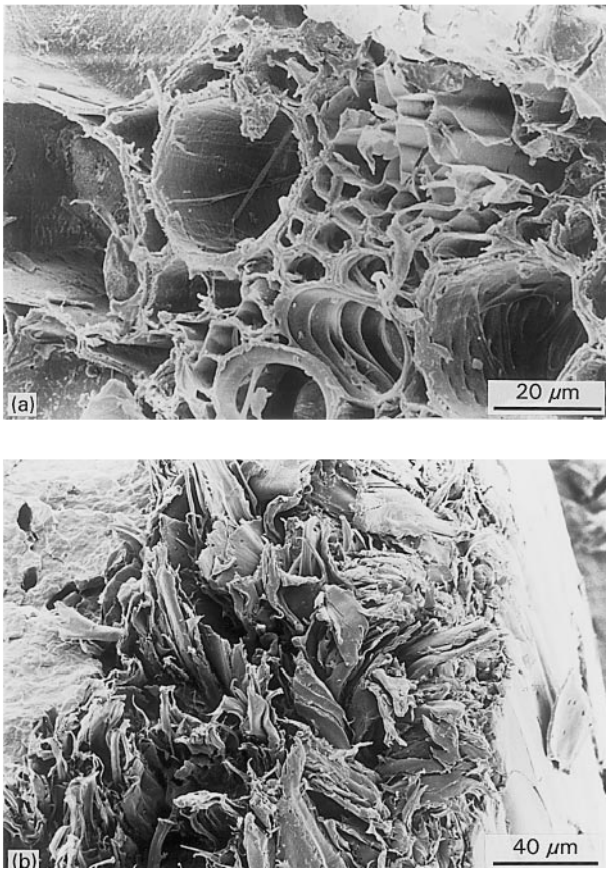

Fig. 5: Collapse in cellular structure of wheat straw (a) before and (b) after melt processing with polypropylene

Fibre dispersion and orientation throughout injection-moulded test specimens was determined by reflected light microscopy and in the case of polypropylene containing wheat straw fibres, also by contact microradiography. It is again evident that the wheat straw fibres have a much greater plate-like morphology than the flax reinforcement (Fig. 6), although both fibre types show a preferential orientation in the direction of polymer flow along the specimen length. This observation is in accordance with known orientation effects occurring in polymer melts

containing glass fibre reinforcements, being influenced by the prevailing flow fields and velocity profiles present during mould filling [7].

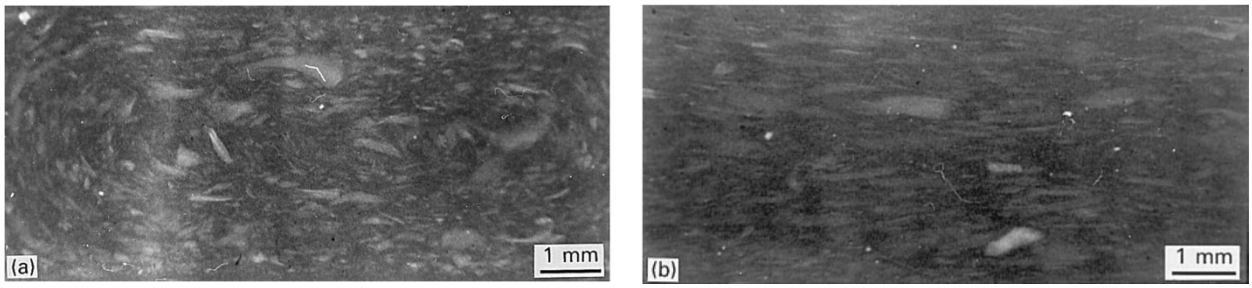

Fig. 6: Contact microradiographs of injection-moulded polypropylene containing wheat straw fibres (a) normal to the flow direction and (b) parallel to the flow direction

Fig. 7 shows transverse sections of PP/flax composites taken from the skin and core regions of the mouldings. The fibre ends in view indicate a high level of fibre alignment along the specimen length. The lines and dots at the centre of the fibre cross-section are thought to result from collapsed lumen. These micrographs also provide evidence that the fibres are well dispersed throughout the polymer matrix. Small holes present in some of the materials suggest the presence of porosity induced by release of bound water or volatile products of fibre decomposition. The degree of voiding appeared greatest in the wheat straw-filled composites.

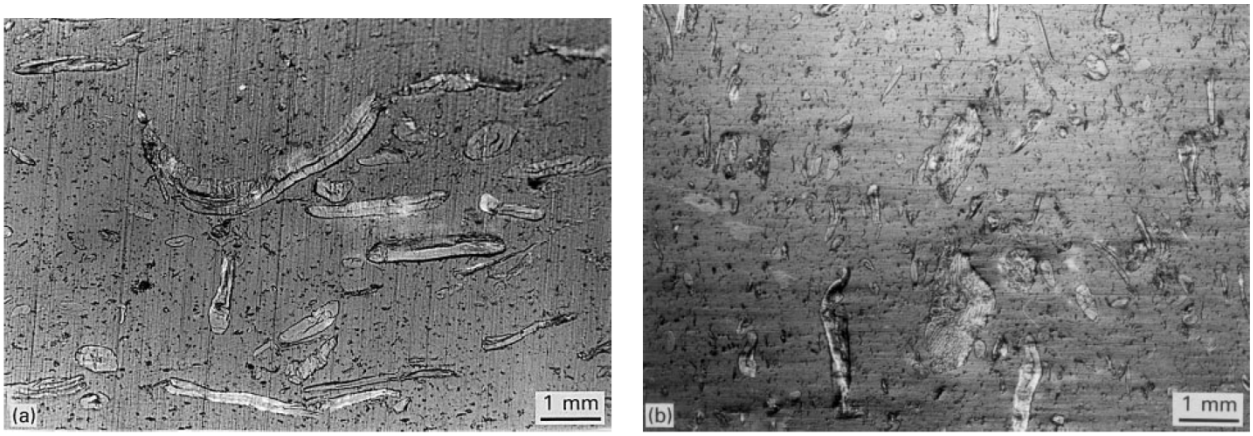

Fig. 7: Reflected light micrographs of injection-moulded polypropylene composites containing flax straw fibres: (a) skin region, parallel to the flow direction, and (b) core region, normal to the flow direction

Mechanical properties of the natural fibre reinforced polypropylene composites are summarized in Table III, including results for specific tensile modulus, calculated from measured values of composite density.

Scanning electron microscopy revealed that, in common with the untreated straw-reinforced composites, the glass fibre used showed no interfacial adhesion with the matrix. However, despite this lack of bonding, glass-reinforced polypropylene yielded significantly higher values of tensile and flexural modulus than the alternative reinforcements, although tensile and impact strengths were broadly similar. Differences in mechanical performance become less marked when specific properties are compared. It should be noted that in the systems studied, the calculated volume fraction of glass fibres is only 10.7%, whereas this increases to 13.5% and 16.8% for flax and wheat straw fibres, respectively. Hence a comparison at equal volume fractions would further favour the PP/glass composite in terms of actual mechanical properties, although specific properties would be off-set by the resulting increase in composite density.

Incorporation of flax straw into polypropylene gave higher values of stiffness and strength than did wheat straw, reflecting the inherently greater mechanical properties of flax fibres. However, the presence of both natural fibres doubled composite modulus and gave very similar tensile failure and Charpy impact strengths to unmodified polypropylene. Despite the lack of interfacial bonding and the existence of some porosity, the toughness of the

natural fibre composites was higher than expected. This is attributed to energy dissipation through a fibre pull-out mechanism, although tensile strain at failure of all the composites dropped significantly relative to unfilled PP, on account of these structural defects.

As mentioned earlier, the geometry of the test bars resulted in a high level of fibre alignment along the specimen length, which was considered to be broadly similar for all the fibre variants used. Mechanical properties of polypropylene composites containing surface-treated wheat and flax straw fibres are also shown in Table III. Also included are results for compositions containing maleic anhydride-modified polypropylene. It can be seen that none of the silane treatments used offer any real effect on properties relative to the reference untreated materials, although the presence of functionalized PP yields a noticeable improvement in tensile strength with both types of straw fibre. This is attributed to some increase in fibre-matrix adhesion as can be seen in Fig. 8 for the MA-PP/PP/flax composite system. This conclusion is supported by water-immersion test results which demonstrated that, after 7 days, water pick-up in these composites is lower when MA-PP is present. This would be the case if chemical bonding existed between hydroxyl groups on the fibre surface and carboxylic acid groups formed on hydrolysis of the maleic anhydride moieties.

Table III: Mechanical properties of polypropylene compositions containing natural fibre reinforcements (standard deviations are given in parentheses and specific tensile modulus in MPa m^3kg^{-1}, in square brackets)

Material	Fibre/ composition treatment	Tensile modulus (GPa)	Tensile yield stress (MPa)	Strain at break (%)	Flexural modulus (GPa)	Charpy impact strength ($kJ\,m^{-2}$)
PP	–	1.18 [1.31] (0.08)	32.91 (0.09)	125.6 (31.0)	1.2 (0.01)	2.46 (0.26)
PP + 25 wt% flax straw	None	3.41 [3.46] (0.33)	36.44 (0.18)	4.9 (0.1)	3.01 (0.03)	3.63 (0.22)
	VMS[a]	3.46 (0.32)	36.68 (0.63)	4.5 (0.1)	3.0 (0.04)	3.35 (0.20)
	APES[b]	2.77 (0.36)	36.13 (0.17)	4.9 (0.3)	2.73 (0.06)	3.53 (0.16)
	GPMS[c]	3.12 (0.4)	35.69 (0.37)	4.5 (0.1)	2.93 (0.05)	3.27 (0.09)
	SA[d]	2.83 (0.62)	35.7 (0.27)	4.8 (0.3)	2.82 (0.04)	3.51 (0.1)
	MA-PP[e]	3.42 [3.47] (0.74)	39.1 (0.23)	3.8 (0.2)	3.01 (0.06)	3.03 (0.39)
PP + 25 wt% wheat straw	None	2.63 [2.67] (1.03)	29.68 (0.17)	3.6 (0.1)	2.35 (0.04)	2.22 (0.17)
	VMS	2.17 (0.31)	29.75 (0.15)	3.6 (0.2)	2.34 (0.03)	2.19 (0.04)
	APES	2.25 (0.43)	29.48 (0.16)	3.7 (0.2)	2.32 (0.02)	2.20 (0.09)
	GPMS	3.0 (0.27)	29.36 (0.15)	3.8 (0.2)	2.3 (0.11)	2.28 (0.21)
	SA	2.43 (0.37)	28.72 (0.16)	3.5 (0.2)	2.33 (0.02)	2.24 (0.09)
	MA-PP	2.39 [2.22] (0.29)	32.33 (0.12)	3.1 (0.2)	2.34 (0.03)	2.21 (0.13)
PP + 25 wt% glass fibres	None	4.15 [3.85] (0.64)	35.23 (0.16)	9.5 (1.0)	4.09 (0.18)	2.63 (0.16)

a VMS, Vinyltrimethoxy-silane
b APES, γ-aminopropyl-triethoxy-silane
c GPMS, glycidoxy-proyl-trimethoxy-silane
d SA, stearic acid
e MA-PP, maleic anhydride polypropylene

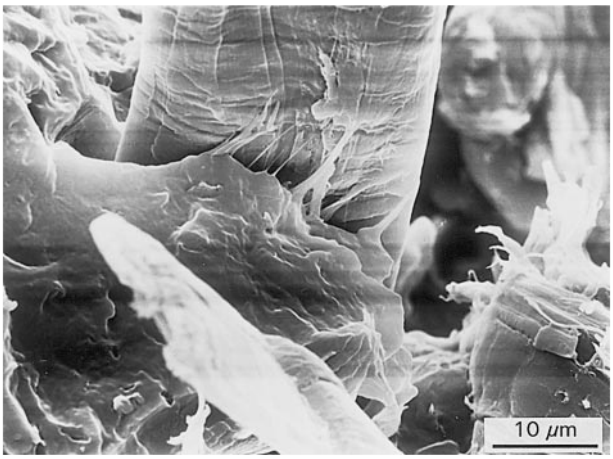

Fig. 8: Fibre-matrix bonding in polypropylene/flax straw composite containing MA-PP

4. Conclusions

The presence of up to 25% by weight of wheat or flax straw fibres in polypropylene caused a significant increase in tensile modulus relative to unfilled polymer. With flax, this was accompanied by a corresponding improvement in tensile yield stress and impact strength, although a slight decline in these properties was observed using wheat straw. Because neither fibre type showed any adhesion to the polypropylene matrix, the irrelative performance is attributed to differences in inherent stiffness and strength, and the presence of longer flax fibres preserved after compounding and moulding operations. Melt processing caused much greater damage to wheat straw by reducing the fibre length and compacting the cellular structure, causing some densification.

Silane treatments applied to these fibres had little or no effect on mechanical properties; however, inclusion of 5% by weight of polypropylene, functionalized with maleic anhydride, increased tensile yield strength significantly by promoting fibre-matrix interaction.

The fibre content of these composites was successfully determined by solvent extraction and thermogravimetric analysis procedures, whereas fibre orientation in mouldings was assessed by reflected light microscopy and X-ray microradiography in the case of wheat straw fibres, owing to the residual silica content in this material. These results also revealed that the additives were predominantly aligned along the long axis of the mouldings, the wheat straw appearing more plate-like than fibrous in form.

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