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Interfacial modification of polypropylene composites filled with magnesium hydroxide

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The mechanical behaviour of polypropylene composites containing magnesium hydroxide is considered with reference to the influence on properties of filler surface modification. Compared to composites containing untreated filler, mechanical properties can be strongly affected by the chemical nature and amount of surface treatment applied. In particular, very significant improvements in toughness are obtained using sufficiently high levels of magnesium stearate to ensure complete coverage of the magnesium hydroxide surface. Results are discussed in terms of the observed deformation mechanism in the polymer matrix.

1. Introduction

Many inorganic fillers manufactured for incorporation into plastics and rubbers are surface treated with organic reagents in order to modify the characteristics of the filler–matrix interface. This may lead to improved dispersion of the inorganic phase during compound preparation, changes in the melt rheology of the resulting composite and, in particular, to improvements in the mechanical properties of filled polymer compositions.

Fillers are included into polymers simply as matrix diluents, or more commonly, in a functional role to impart some special property characteristics to the composite, such as enhanced fire retardancy. In this regard, magnesium hydroxide has been shown to be an effective halogen- and acid-free fire retardant and smoke suppressing additive for plastics, at sufficiently high levels of addition [1–3]. Under these circumstances, however, as is common with most other inorganic fillers, there is a marked deterioration in certain physical properties of the material in particular its toughness. The degree of interfacial adhesion at the boundary between polymer matrix and filler is known to have a direct bearing on the ability of a particulate composite to resist crack propagation and hence its impact behaviour.

In general, when the filler–polymer interface is extremely strong, exceeding the strength of the matrix, the failure pathway is confined to the matrix and little or no emergence of filler is observed on the fracture surface. Where the strength of the matrix is equivalent to that of the interface, a propagating crack will follow the filler–matrix boundary, unless the filler particle is weak, as for example in an agglomerate, in which case the crack will pass through the particle. With very weak interfacial bonding, the filler and matrix will separate completely and there may be very limited contribution from the filler to overall impact performance of the composite.

Other factors are also known to strongly influence the level of toughness obtained in particulate composites, including the extent of filler dispersion and the morphology of the filler particles. Poorly dispersed filler and particles with plate-like geometry can act as stress-raisers reducing the necessary crack initiation energy [4]. Certain fillers may also nucleate polymer crystallization, changing both the extent and form of morphology induced [5, 6]. In calcium carbonate-filled polypropylene, a correlation has been reported between onset crystallization temperature from the melt state and falling weight impact strength [7]. Similarly, filled polypropylene compounds with higher levels of β-spherulitic morphology have been associated with increased impact strengths [6].

From a study on the effects of average spherulite size on the mechanical properties of unfilled polypropylene, it was concluded that for optimum mechanical performance there is a requirement for small spherulites combined with a well-defined cross-hatched lamellar structure [8].

Most inorganic fillers have highly polar surfaces that are hydrophilic rather than oleophilic in character, and as such are not readily wetted by organic fluids, such as hydrocarbon solvents, oils and molten polymers, which generally have low to moderate polarity and relatively low surface energy. Mineral fillers can be rendered oleophilic by chemisorption of surface active agents, such as fatty acids, which combine within their structure similarities with the dispersing medium and polar (–COOH) functional groups which can interact with the mineral surface.

Alternatively, hydroxylic species occurring on the surface of many fillers can be used as anchor groups for attachment of covalently bound surface modifying

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agents, including silanes and metal alkoxides, notably those of titanium and aluminium. In particular, organosilanes containing halogen, alkoxide, and amino groups attached to silicon can react with surface hydroxylic species on the filler to form covalently bound surface siloxy derivatives [9–11].

A further approach to achieving greater surface interaction between inorganic fillers and organic polymers is to incorporate potentially reactive sites such as carboxylic acid or anhydride groups onto the polymer chain, either during polymerization or by subsequent reactive modification in the melt state.

This investigation considers the application of these methods for enhancing the mechanical properties of polypropylene containing high levels of magnesium hydroxide filler, with specific emphasis on the chemical character of surface modifying agents and their effect on toughness of the resulting composite. A subsequent communication will report on the influence of this filler and surface treatment on the micromorphology induced.

2. Experimental procedure

2.1. Materials

Sea water magnesium hydroxide (Lycal 96HSE) with particle characteristics given in Table I, was used throughout this study. This was combined with a powdered grade of polypropylene homopolymer (Propathene GW 522M) with melt flow index 22 g 10 min^{-1} (2.16 kg 230 °C) at filler additions up to 60% by weight (36% by volume). The following routes were adopted for modifying the interfacial properties between filler and polymer matrix with a view to influencing mechanical properties of the resulting composite:

1. Treatment of filler with silane coupling agents.
2. Surface modification of filler using titanate coupling agents.
3. Coating filler with fatty acid derivatives.
4. Using polypropylene blends with acrylic acid functionalized polypropylene (Polybond 6001).

TABLE I Properties of sea water magnesium hydroxide (Lycal 96HSE)

Physical	
Mean particle size (μm)	3
Oil absorption (g 100 g^{-1})	50
Surface area (by BET method) (m^2 g^{-1})	30
Packing density (kg m^{-3})	570
Specific gravity	2.4
Decomposition temperature (°C)	350–450
Endothermic heat of reaction (kJ kg^{-1}) (on decomposition)	1100
Loss on drying at 200 °C (%)	0.4–1.0
Loss on ignition at 950 °C (%)	30.0 (min–31.5)
Chemical analysis (%)	
MgO	66.5
CaO	1.5
SiO_2	0.2
Fe_2O_3	0.15
Al_2O_3	0.15
Na_2O	0.05
NaCl	0.15
Cl	0.05

2.2. Composition formulation and surface coating procedures

According to commercially available literature, the effectiveness of these additives is influenced by the method and temperature of application and/or their concentration. Of the preparation options available for surface coating of the filler, use of an aqueous slurry was expected to cause severe agglomeration of the magnesium hydroxide, whilst it was envisaged that suspension of the filler in an organic medium would entail subsequent problems from removal of flammable solvents. Dry blending techniques are dependent on temperature, molecular weight of the additive and the form of mixing adopted, all of which may influence treatment mobility onto the filler surface.

Hence, depending on the nature of the surface modification, different application methods were used. All of the silane and titanate treatments were diluted with an equal volume of solvent, generally methylethylketone for the silanes and hexane for the titanates. Known concentrations of these additives were then applied to predried magnesium hydroxide filler fluidized in a Henschel high-speed mixer operating at 3500 r.p.m. These treatments were applied at levels up to 3% by weight of filler at both 18 °C and 45 °C, the upper temperature being limited by the volatility of the solvent used.

Initially, fillers were surface modified with fatty acid variants by high speed mixing additive (generally in solid form) and filler, at room temperature. However, it was found that more effective surface coverage was obtained by first preheating the filler in an oven to 160 °C, fluidizing this in the high speed mixer and whilst still hot, introducing (cold) surface treatment at the required addition level. Concentrations of fatty acids and derivatives were, in general, higher than for previously mentioned silane and titanate treatments, ranging from 3 to 15% by weight of filler. Since it was subsequently found that significant improvements in impact strength were achievable through the use of certain fatty acids and in particular high concentration levels of magnesium stearate, some additional surface modified filler variants were prepared in the manner described above, using structurally related treatments, which differed in length of the alkyl chain and end group polarity. Furthermore, to determine the effect of surface treatment alone (in the absence of filler) on mechanical properties of the polypropylene matrix, polymer compositions were prepared containing different levels of magnesium stearate up to a maximum of 10% by weight.

Compositions were also made containing polypropylene homopolymer, modified polypropylene functionalized with 6% acrylic acid (ACPP) and predried magnesium hydroxide. Concentration levels of ACPP varied from 5 to 50% by weight of the total formulation.

In all of the compositions discussed above, including surface treated variants, the level of magnesium hydroxide present in each system was maintained at 50% by weight (27% by volume) (i.e. the weight ratio of filler/polymer (with or without modifying additives was constant at 1/1). For comparison, mixtures of polypropylene homopolymer were blended with untreated magnesium hydroxide at filler concentrations between 0 and 60% by weight.

2.3. Compound preparation

Uncoated and surface coated forms of magnesium hydroxide were predistributed with polypropylene powder in a Henschel high speed mixer. Powder blends were then dried under vacuum for at least four hours at 80 °C prior to melt compounding in a corotating intermeshing twin-screw extruder (Betol BTS40), configured in a multiple stage profile to achieve effective filler dispersion and volatile devolatilization with or without application of a vacuum [12]. Material was die-formed into strands and pelletized, using a temperature profile of 185 to 225 °C at a screw speed of 120 r.p.m.

Compositions containing a premix of powdered PP homopolymer, magnesium hydroxide and granular ACPP copolymer were hand fed into the compounder due to segregation or blockage problems using the available extruder dosing feeders. Also, with this system, two series of blends were made, one using atmospheric venting and the other with vacuum devolatilization in order to remove the expected water of reaction between the acid-functionalized polymer and basic magnesium hydroxide surface. Since mechanical properties were slightly improved using a reduced pressure during venting, only results obtained using this procedure are reported.

2.4. Determination of mechanical properties

All mechanical tests were undertaken on injection-moulded specimens prepared using a barrel temperature profile of 195 to 225 °C and mould temperature of 50 °C. Prior to moulding, compounds were dried at 80 °C for over 8 h in an air circulating oven. All moulded samples were stored for at least 10 days at 50% relative humidity (23 °C), before testing. Tensile properties were determined at 23 °C in accordance with ASTM D638-81 using type B specimens. Flexural modulus was measured at 23 °C following ASTM D790-81 in a 3-point flexure mode. Impact strength was assessed in two ways, principally by the Gardner–Holt falling weight method (ASTM D3029-81) and in some instances using a Davenport–Rosand instrumented falling weight impact tester fitted with a 27 kg drop weight and hemispherical tup area of 10 mm^2. Both forms of impact test used 6 mm thick unclamped plaques, with measurements undertaken at 23 °C.

2.5. Structural characterization

A more detailed account of the effects on polypropylene micromorphology from introducing coated and uncoated forms of magnesium hydroxide will be reported in a subsequent communication. However, some use of scanning electron microscopy is reported here on gold-coated fracture surfaces to investigate failure modes.

Surface area of uncoated and selected treated magnesium hydroxide powders, was measured using the Haynes single point Brunauer–Emmett–Teller (BET) method and more rigorously through construction of nitrogen gas adsorption and desorption isotherms following the BET procedure, using Carlo Erba Sorptomatic 1800 gas adsorption apparatus. From these results an estimate was made of the degree of surface coverage by the applied treatment.

3. Results and discussion

3.1. Uncoated magnesium hydroxide/polypropylene composites

Mechanical properties of polypropylene containing untreated magnesium hyroxide at increasing filler levels, are shown in Table II. It is evident that relative

TABLE II The effects of magnesium hydroxide filler level on the mechanical properties of polypropylene

	Magnesium hydroxide filler concentration (% by weight)						
	0	10	20	30	40	50	60
Falling wt. impact strength J 6 mm	5.9	4.3 (1.9)	2.4 (2.3)	2.2 (3.1)	2.9 (9.5)	1.8 (10.0)	1.7 (10.2)
Flexural modulus (GPa)	1.2	1.5 (1.5)	2.2 (1.7)	2.5 (2.1)	3.1 (2.3)	3.4 (2.9)	5.0 (3.3)
Flexural strength (GPa)	35.0	26.8 (25.8)	33.6 (28.0)	35.0 (26.2)	34.4 (22.0)	30.2 (16.2)	25.0 (29.2)
Tensile strength (MPa) at yield	32.0	31.7 (28.1)	30.2 (25.6)	27.9 (22.7)	25.8 (19.8)	24.6 (17.2)	– (16.9)
Elongation (%) at yield	12.0 –	8.2 (8.2)	6.6 (7.1)	4.7 (5.0)	3.1 (3.6)	2.0 (1.4)	– (1.0)
at break	–	– (–)	– (–)	– (–)	7.7 (–)	2.3 (24.6)	1.2 (2.2)

Numbers in parentheses indicate results for magnesium hydroxide coated with 10% by weight of magnesium stearate.

to unfilled polypropylene, resistance to impact failure falls dramatically, additions of 20% of filler reducing the impact strength by 50%. This observation is consistent with results reported from many other polypropylene composites, where the presence of inorganic fillers (such as talc and mica) are frequently detrimental to toughness properties [4].

Examination of fracture surfaces obtained from impact test specimens reveals extensive cracking and lack of bonding at the filler/matix interface (Fig. 1). It is also apparent that filler particles are generally well dispersed within the polymer matrix.

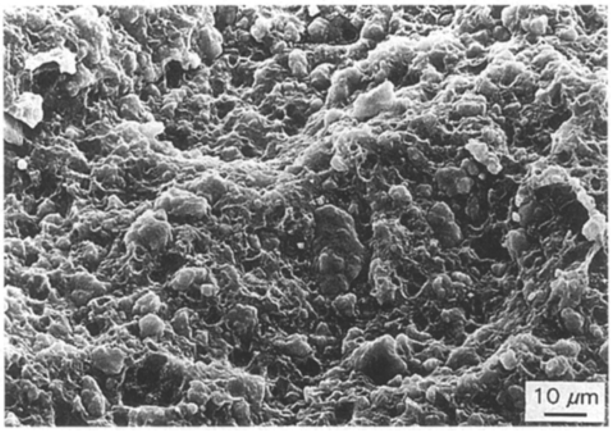

Figure 1 Microstructure of untreated magnesium hydroxide filled polypropylene composite.

It is surprising to note, however, that tensile strength is little influenced by magnesium hydroxide except at very high filler additions, suggesting that there is some degree of filler–matrix interaction, capable of resisting the imposition of a tensile force. Since there is unlikely to be any chemical interaction between these phases due to large differences in surface polarity, it is conceivable that physical interaction occurs between the highly porous magnesium hydroxide particles and the polymer. Similarly, in polypropylene reinforced with wollastonite, it was suggested that the high tensile strengths observed were the result of physical adhesion between the polymer and rough filler surface [13].

3.2. Modified magnesium hydroxide/polypropylene composites – initial observations

Flexural and impact properties of filled polypropylene containing surface treated magnesium hydroxide or acid-modified polypropylene are given in Tables III to VI with a summary of results from the compositional variants shown schematically in Fig. 2.

It is apparent that the presence of silane treatments leads to a slight increase in flexural modulus, flexural

TABLE III Mechanical properties of PP composites filled with 50% by weight of magnesium hydroxide surface treated with silanes

Trade name	Chemical name	Concentration (% by wt)	Application temperature (°C)	Composite properties		
				Impact strength (J 6 mm)	Flexural modulus (GPa)	Flexural strength (MPa)
Z-6070	methyltrimethyoxysilane[a]	1	18	2.1	4.0	39.0
		1	45	1.9	4.1	31.0
		2	18	1.9	4.1	39.0
		3	18	2.3	4.0	36.0
Dynasylan	octyltriethoxysilane	1	18	2.2	3.5	39.8
		1	45	2.1	3.8	35.2
		2	18	2.1	3.8	34.7
		3	18	2.3	3.5	32.7
QC-7119	unspecified carboxy-functional silane	1	18	1.5	3.9	34.9
		1	45	2.1	3.9	35.4
		2	18	1.8	4.0	35.9
		3	18	2.1	3.7	34.2
Z-6032	(n-vinylbenzylaminoethyl)-γ-aminopropyl trimethoxysilane hydrogen chloride[b]	1	18	2.2	3.8	37.3
		1	45	1.7	4.2	36.3
		2	18	1.7	3.8	37.3
		3	18	2.2	4.4	41.4
Z-6082	vinyltris (γ-methoxyethoxy)silane[b]	1	18	2.3	3.8	36.8
		2	18	1.7	4.0	34.7
		3	18	2.1	4.5	43.1
Y-9777 (2pts) + Y-9771 (1pt)	unspecified silanes containing carboxyfunctional groups	1.5	18	1.4	4.4	42.3
		1.5	45	1.3	4.2	45.5
		3.0	18	1.6	3.3	36.3
		4.5	18	1.4	3.6	40.4
VF151	unspecified silane	1	[c]	1.5	3.6	34.9
VF152	unspecified silane	1	[c]	1.5	4.8	43.6

[a] Requires activation with addition of 0.5% water.
[b] Requires activation with 0.2% dicumylperoxide.
[c] Magnesium hydroxide supplied in coated form.

TABLE IV Effects of titanate surface treatment on the mechanical properties of polypropylene filled with 50% by weight of magnesium hydroxide

Trade name	Chemical name	Concentration (% by wt)	Application temperature (°C)	Composite properties		
				Impact strength (J 6 mm)	Flexural modulus (GPa)	Flexural strength (MPa)
KRTTS	Isopropoxytriisostearoyl titanate	1	18	1.6	3.3	37.7
		1	45	1.6	3.4	41.3
		2	45	2.8	3.5	33.0
		3	45	3.2	3.7	33.7
KR12	Isopropoxy-tris (dioctylphosphato)titanate	1	18	1.4	3.1	30.3
		1	45	1.4	3.9	34.2
		2	45	1.5	3.7	35.4
		3	45	2.9	3.7	34.9
KR38S	Isopropoxy-tris(dioctyl pyrophosphato)titanate	1	18	1.8	3.8	34.4
		1	45	2.5	3.5	32.5
		2	45	1.3	3.7	33.5
		3	45	2.3	3.6	35.6
KR41B	Tetraisopropoxy-bis(dioctyl phosphito)titanate	1	18	1.4	3.1	30.1
		1	45	1.2	3.8	35.1
		2	45	1.2	3.8	36.4
		3	45	2.6	3.8	35.4
TILCOM CA10	Isopropoxy triisostearoyl-titanate	1	18	2.5	4.1	34.7
		1	45	2.6	3.8	34.4
		2	45	2.6	3.9	35.2
		3	45	2.8	3.6	33.5
KR5512	Undisclosed composition	1	18	2.3	3.1	29.9
		1	45	1.5	4.0	36.8
		2	45	1.5	4.2	38.2
		3	45	3.0	3.7	35.8

TABLE V Mechanical properties of polypropylene composites filled with 50% by weight of magnesium hydroxide surface treated with fatty acids and their derivatives

Trade name	Chemical name	Concentration (% by wt)	Application temperature (°C)	Composite properties		
				Impact strength (J 6 mm)	Flexural modulus (GPa)	Flexural strength (MPa)
Hycar HM10	Calcium oxidate soap (C_{18} to C_{44}) oxidate acids and esters	5	160	3.2	3.1	27.7
		10	45	3.8	2.9	28.4
		10	160	6.2	3.4	30.8
		15	160	5.2	3.1	35.4
	Magnesium stearate	3	160	3.8	3.4	32.5
		6	160	8.0	3.0	25.8
		10	45	6.1	3.4	28.2
		10	160	10.3	3.2	26.2
	Zinc stearate	3	160	3.7	3.2	29.4
		6	160	7.9	3.3	28.2
		10	45	9.5	3.6	28.7
		10	160	10.7	3.6	28.2
	Stearic acid	3	160	3.2	3.6	32.2
		6	160	3.3	3.6	30.6
		10	45	5.9	–	–
		10	160	3.4	3.6	36.3
	Glycerolmonostearate	3	160	4.2	3.3	33.0
		6	160	5.9	3.3	33.1
		10	45	3.8	3.3	39.2
		10	160	4.1	3.5	25.4
	Azeleic acid (dicarboxylic acid)	10	45	1.6	4.0	34.2
		10	160	1.5	4.2	34.6
	Oleic acid (unsaturated carboxylic acid)	6	160	1.7	3.0	29.9

TABLE VI The effect of acid-modified polypropylene on the mechanical properties of polypropylene composites containing 50% by weight of magnesium hydroxide filler

Composition % by weight			Composite properties		
Polypropylene	Functionalized polypropylene[a]	Magnesium hydroxide	Impact strength (J 6 mm)	Flexural modulus (GPa)	Flexural strength (MPa)
50	–	50	1.8	3.9	37.3
45	5	50	1.9	3.5	34.9
40	10	50	2.0	3.3	38.2
30	20	50	1.7	3.5	39.2
20	30	50	1.9	4.6	49.6
0	50	50	2.6	4.9	51.7

[a] 6% acrylic acid grafted polypropylene.

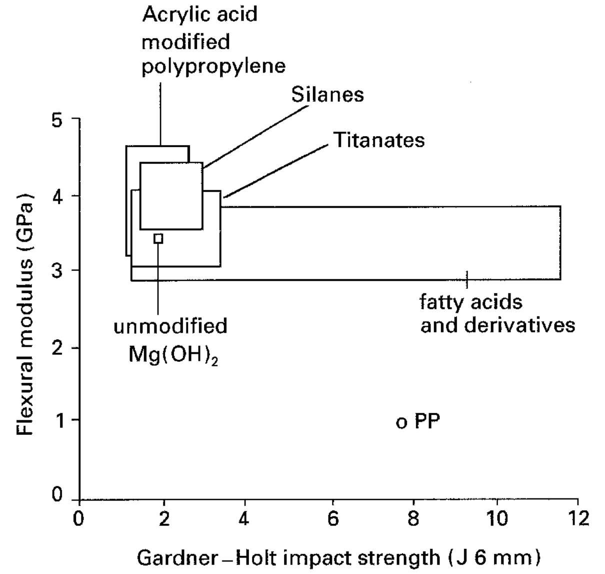

Figure 2 The effects of filler surface treatments on the mechanical properties of polypropylene composites containing 50% by weight of magnesium hydroxide filler.

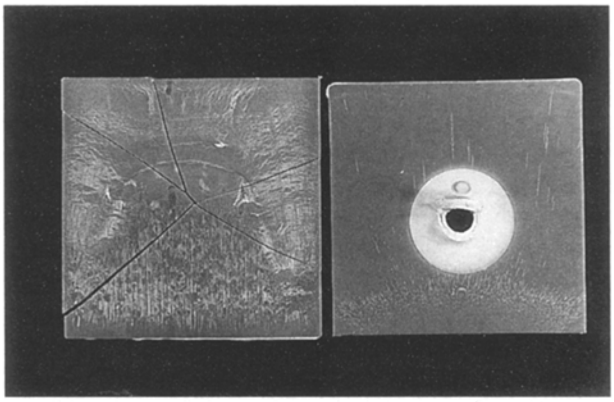

Figure 3 Impact failure modes in polypropylene filled with surface treated (left) and unmodified (right) magnesium hydroxides.

strength and falling weight impact strength, relative to untreated magnesium hydroxide compounds. It is possible that these additives assist in removal of traces of residual water from the filler facilitating dispersion. However, there does not appear to be strong chemical interaction with the filler surface regardless of the silane functionality.

Formulations containing titanate modifying agents yielded improved impact performance compared to polypropylene filled with untreated magnesium hydroxide, generally the effect being most pronounced as additive level was increased, although little difference was seen between flexural properties. Greatly improved impact strength, however, was obtained with certain fatty acid treatments and their derivatives, results being strongly dependent on the level of treatment used and the temperature of application to the filler surface. Compositions containing magnesium hydroxide treated with Hycar HM110 (a calcium oxidate soap) and various stearates, gave particularly good resistance to impact failure, with localized yielding and stress whitening occurring around the impact site, distinctly different to the brittle failure seen with untreated materials (Fig. 3). However, the calcium oxidate treatment imparted a brown colour and unpleasant odour to mouldings and was considered less acceptable, therefore, to alternative stearate modified compositions.

At treatment levels of 6% by weight and above (based on filler) stearate salts (magnesium and zinc stearates) gave markedly higher impact strengths than fatty acids (stearic acid, azelaic acid and oleic acid). In addition, it was found that pre-heating the filler to 160 °C (rather than to 45 °C) prior to coating with stearate salts improved impact performance still further, resulting in filled compositions with substantially higher falling weight impact resistance than the unfilled polypropylene homopolymer. During treatment of magnesium hydroxide with oleic acid and azelaic acid, water was observed to condense on the lid of the mixer during coating, suggesting that a reaction had occurred. This was confirmed by infra-red analysis of the treated powder which yielded evidence of organic salt formation. These results suggest that chemical coupling of fatty acid treatments is not conducive to high impact strength of the particulate composites.

Several of the fatty acid and fatty acid derivative treatments for magnesium hydroxide caused a slight decline in flexural modulus and flexural strength relative to the equivalent composition containing untreated filler, the reduction being least with azelaic and stearic acid coatings, due to the enhanced chemical interaction with the filler using these systems.

Similarly, significantly increased flexural properties were observed in compositions containing acrylic acid functionalized polypropylene, although falling weight impact strength was little affected compared to untreated magnesium hydroxide/polypropylene composites. It was apparent that the presence of acid-modified polymer improved filler wet-out and markedly enhanced bonding at the filler surface, although this offered no greater resistance to crack propagation.

3.3. Further observations on polypropylene composites containing magnesium hydroxide treated with fatty acids and fatty acid derivatives

In view of the significant improvements in impact performance observed using certain filler treatments discussed above, the use of fatty acid variants, and in particular magnesium stearate, was explored further. The influence of magnesium hydroxide filler level on flexural modulus and falling weight impact strength is shown for both surface modified (10% magnesium stearate treatment, by weight of filler) and unmodified filler, in Table II. Whereas flexural modulus increased linearly up to 50% addition levels for both modified and untreated magnesium hydroxide variants, it is only at filler additions in excess of 30% by weight, that magnesium stearate treated filler caused the substantial rise in impact strength mentioned earlier. This effect corresponded to a change from brittle to ductile failure in the material, accompanied by the appearance of stress whitening (Fig. 4). This originates from the formation of micro-voids, resulting from localized polymer deformation and dissipation of energy around the filler particles. Hence high impact resistance is obtained only when there is sufficient filler and an appropriate amount of surface treatment present [14]. However, flexural and, in particular, tensile strength falls as filler loading is raised, the decline being most evident in material made from surface treated filler.

Figue 4 Microvoiding within stress-whitened polypropylene filled with 50% by weight of magnesium stearate treated magnesium hydroxide.

Polypropylene formulations containing magnesium stearate (with no filler present) were also characterized to explore the effects of the treatment alone on the ductility and strength of the matrix. Although modulus and tensile strength (at yield) were hardly affected, even by high additions of stearate salt, falling weight impact strength fell markedly at levels above 2% by weight (Table VII). Failed specimens with poor impact properties exhibited well-defined skin-core structures comprising a softer surface region in relation to the internal core. It was also apparent that the strength of the skin-core interface deteriorated with increasing stearate concentration and that all failures, whether due to imposed impact or tensile stresses, were initiated at this skin-core boundary, i.e. the specimens delaminated under stress. Electron probe microanalysis (EPMA) and infra-red analysis of these compounds suggested that initially magnesium stearate distribution was uniform. However, after ageing for one year at room temperature, considerable amounts of treatment were found on the surface of these mouldings, which continued to delaminate under stress. By contrast, long term storage of corresponding polypropylene specimens containing magnesium hydroxide, modified with magnesium stearate coating, showed no evidence of treatment migration to the sample surface and no loss of ductility. Coating magnesium hydroxide with magnesium stearate or other fatty acid-based surface treatments leads to a marked reduction in surface area (Table VIII).

Plots of volume of nitrogen adsorbed against partial pressure (Fig. 5) are indicative of Type IV isotherms with hysteresis loop suggesting that a large proportion of the area measured by nitrogen adsorption is internal, indicative of extensive porosity. This fact is confirmed by transmission electron microscopy (Fig. 6). It is evident from Fig. 5 that although surface coating the filler yields a significantly reduced surface area, extensive internal porosity remains even after the treatment is applied.

TABLE VII Mechanical properties of polypropylene containing magnesium stearate (at 23 °C)

Properties	Concentration of magnesium stearate (% by weight)					
	0	2	4	6	8	10
Falling weight impact strength[a]						
peak force (N)	3723	4116	1434	1047	922	828
failure energy (Nm)	14.4	18.3	7.2	4.5	4.4	3.7
Tensile modulus (GPa)	1.3	1.3	1.0	1.3	1.1	1.1
Tensile strength at yield (MPa)	42.3	42.4	42.6	42.5	41.7	41.5

[a] Determined using an instrumented impact tester.

TABLE VIII Surface area of treated and untreated magnesium hydroxide variants

Treatment	Haynes $m^2 g^{-1}$	BET $m^2 g^{-1}$	Degree of surface coverage (%)[a]
None	21.9	25.8	–
None (H)	–	27.6	–
3% MS	17.8	19.6	44
6% MS	17.8	20.3	87
10% MS	17.0	18.9	150
15% MS	16.0	17.2	217

(H) magnesium hyroxide pre-heated to 160 °C before outgassing.
MS magnesium stearate.

[a] Calculated assuming a terminally oriented surface treatment molecule, occupying a surface area of 2.05 nm^2 and based on the surface area of preheated filler (H).

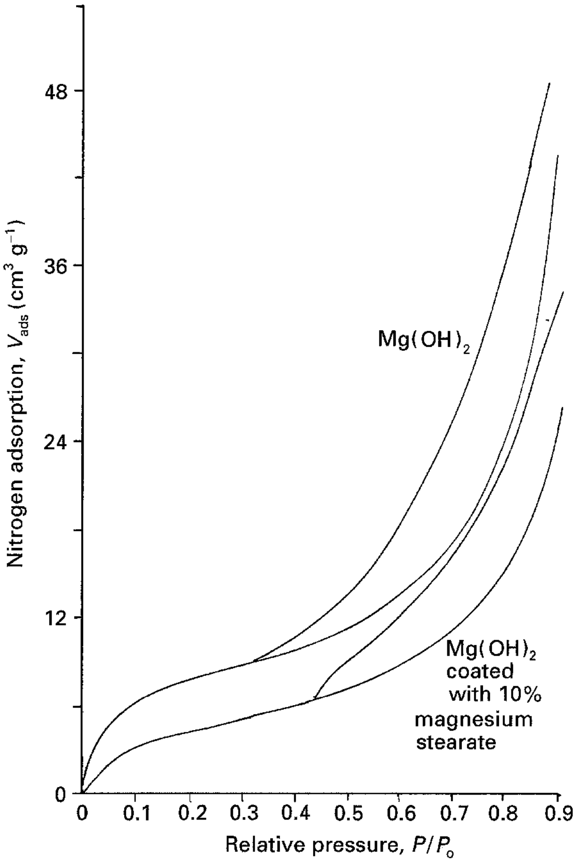

Figure 5 Nitrogen gas adsorption (BET) isotherms for unmodified and surface treated magnesium hydroxide.

Based on these results, an estimate of the degree of surface coverage by magnesium stearate was made assuming that the surface treatment molecule is terminally oriented, occupying a surface area of 2.05 nm^2 (Table VIII). From these calculations about 7% by weight of treatment is required to acheive monolayer coverage. This value is in broad agreement with measurements reported for a porous grade of magnesium hydroxide (surface area 13 $m^2 g^{-1}$) requiring between 7–8% of stearic acid to obtain a complete monolayer [15] and for calcium carbonate (surface area 32 $m^2 g^{-1}$) needing 8% of stearic acid to effect full surface coverage [16].

Additional filled polypropylene compositions were prepared containing magnesium hydroxide coated with surface treatments structurally related to magnesium stearate, but differing in the length of the alkyl chain and the nature of the polar end group. In all cases, the treatment level was maintained at 6% by weight of filler. Mechanical properties of these composites are compared in Table IX. There is little difference between their tensile and flexural properties, although impact behaviour showed considerable variation. In this respect, with fatty acid treatments it would appear that impact strength is sensitive to the length of the alkyl chain, since highest values for this property were obtained with lauric and stearic acids. As indicated earlier, however, sodium and magnesium salts of stearic acid yield significantly higher impact values than the more reactive acid forms.

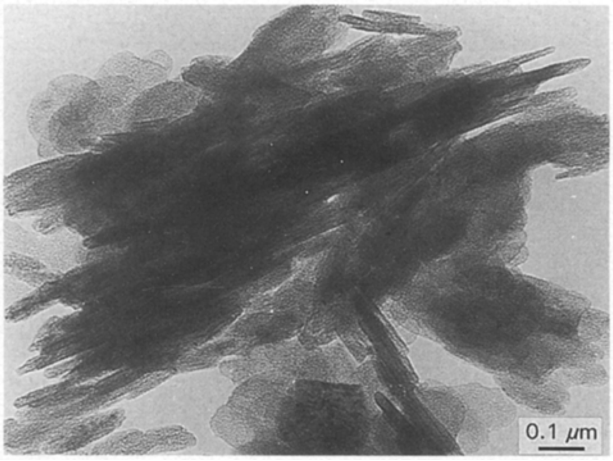

Figure 6 Transmission electron micrograph of magnesium hydroxide particles.

Impact properties of surface treatments with amide end groups were broadly similar to those obtained from stearic acid, although there appears to be a noticeable increase in ductility in the formulation modified with oleamide, which contains a double bond in the structure. Metal stearate salts, however, were significantly more effective in raising impact strength than stearate esters (glycerol monostearate), stearamide, and stearyl alcohol.

4. Conclusions

The mechanical properties of polypropylene containing magnesium hydroxide filler have been considered, with specific reference to the effects of surface treatment on the additive surface. Whereas silane coupling agents gave some improvements in impact and tensile strength of the composite, fatty acid derivatives were found to be by far the most effective surface treatments for improving toughness, although with some accompanying decline in flexural and tensile properties. This significant improvement in impact performance is attributed to a modification of the polymer deformation mechanism in the vicinity of the filler particles resulting in localized voiding, manifested as stress whitening. To be most effective it was found that the fatty acid derivative should be a carboxylate salt, preferably with an alkyl chain of at least 10 carbon atoms to increase interaction with the polymeric phase.

TABLE IX Mechanical properties of polypropylene composites filled with 50% by weight magnesium hydroxide surface treated with selected fatty acids and derivatives

Surface modifying agent	Falling weight impact strength (J 6 mm)	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile yield strength (MPa)	Functional group	No. of carbon atoms in R group
Hexanoic acid	2.7	3.3	32	20.0	–COOH	6
Decanoic acid	1.9	3.4	30.9	18.4	–COOH	10
Lauric acid	5.1	3.2	30.6	17.7	–COOH	11
Stearic acid	4.3	3.5	30.6	18.9	–COOH	17
Oleamide[a]	7.2	2.7	33.4	17.7	$-CONH_2$	17
Lauramide	4.3	2.7	34.1	17.2	$-CONH_2$	11
Stearamide	4.8	2.9	33.4	17.2	$-CONH_2$	17
Erucamide	5.0	2.5	32.0	16.9	$-CONH_2$	21
Sodium stearate	7.3	3.2	37.0	19.4	$-COO^-Na^+$	17
Magnesium stearate	8.0	3.2	36.6	19.2	$-COO^-Mg^+$	17
Stearyl alcohol	3.8	3.2	35.0	17.0	–OH	17

All compositions contain 50% by weight of magnesium hydroxide filler coated with 6% by wt. of surface treatment.

[a] Contains unsaturated group i.e. $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$.

The level of surface treatment applied to the magnesium hydroxide also has a significant effect on the composite properties obtained. For the filler used in this study, monolayer coverage was achieved by coating with approximately 7% by weight of fatty acid salt (magnesium stearate), causing a reduction in the effective surface area of the filler. Using an appropriate application procedure magnesium stearate treatment remained bound to the filler surface, even after prolonged storage, unlike polypropylene compositions containing only surface modifier (without filler), where additives migration was evident and a marked deterioration in physical properties resulted.

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