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Influence of surface treatment on hybrid wollastonite-polyethylene composite resins for rotational moulding

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Abstract The purpose of this research was to develop a reinforcing material for polyethylene-based composite manufacture by rotational moulding. Wollastonite, sisal fibres and PE are premixed by blending and compounding with a single screw extruder and then granulated to particles with diameter about 0.5 mm prior to rotational moulding, for which the mixture is placed in a mould that is heated from the outside to 250 °C for a period of about 10 min. Aminosilane was used as a surface treatment for wollastonite. It was found that incorporating wollastonite microfibres improved the tensile properties of the system. When wollastonite fibres were coated with aminosilane, the impact strength and processability were enhanced greatly. Sisal fibres were added to improve the impact properties. Scanning electron microscopy revealed good adhesion between the coated fibre reinforcement and the polyethylene matrix at the fracture surface. The mechanism of this phenomenon is discussed.

Introduction

Rotational moulding (also referred to as rotomoulding, rotational casting or co-rotational moulding) is used to make hollow thermoplastic one-piece products. Typical rotational moulded products are toys, balls, storage tanks, receptacles and surf boards [1]. The heating, melting, shaping and cooling stages all occur after the polymer is placed in the mould, providing many advantages that include comparatively low mould costs, minimum design constraints, the ability to produce complex and large parts with undercuts and intricate contours, almost zero residual stress and little material waste. However, rotomoulding has some limitations, such as high mould design cost for complex product geometry, long processing time and limited mouldable material selection (polyethylene accounts for approximately 85% of the material being rotationally moulded worldwide). To improve manufacturing efficiency and product quality, attempts have been made to incorporate reinforcements into the rotationally moulded components. The process involves reinforcement tumbling in a rotating mould in which there are few factors to promote good mixing and adhesion of the reinforcement to the polymer, which results in segregation of the reinforcement. Crawford has noted that successful fibre reinforcement of rotomoulded polyethylene parts is a challenge of great industrial significance [2].

Wollastonite is a naturally occurring calcium silicate mineral with the molecular formula $CaSiO_3$, usually formed from the reaction of calcium carbonate and silica under intense heat and pressure. The calcium silicate structure grows naturally as a chain, resulting in needle-like crystals [3]. The high aspect ratio (typically ~15) needles in wollastonite are retained by appropriate milling or broken into lower aspect ratio fragments as required for particular applications. For the reinforcement of plastics, smaller and higher aspect ratio particles expose greater surface area to better intercept stress propagation [4, 5]. The addition of micro- to nano-size fillers to polymeric materials has been observed to significantly influence

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mechanical properties such as modulus, yield stress and strain to failure, which have a strong bearing on resistance to mechanical deformation [6–8]. As a natural mineral fibre, wollastonite is readily available in the market for commercial applications and is considerably less expensive than other fibres, e.g. glass fibre. High aspect ratio fibrous wollastonites are used as reinforcements to increase mechanical properties, improve thermal and dimensional stability and provide resistance to chemical and moisture absorption. Polymer composites containing micron scale minerals reinforcing elements constitute an attractive set of organic–inorganic materials, which not only have obvious potential as technological materials but also provide a convenient macroscopic system to study fundamental scientific issues concerning confined and tethered polymers at the micro- and nano-scale. Reinforcement with wollastonite increases the starting crystallisation temperature and induces a shorter processing time in injection moulding, and consequently affects the extent of crystallinity of the composite [9]. For these reasons, reinforcement of rotational moulded articles with wollastonite is an interesting possibility.

Hybrid composites consisting of two or more different reinforcements in a single matrix possess advantages over conventional composites for tailoring the material to the requirements of designed structures and often to reduce the cost [10]. The mechanical properties of short-fibre/inorganic-filler/polymer composites may be affected by the amount of polymer matrix, the ratio of short fibre to inorganic filler and the adhesion between the fibre and the matrix. In addition, fibre orientation and length distribution play an important role in determining the mechanical properties of hybrid composites. Sisal fibres, derived from the agave plant, are one of the most widely used natural fibres [11]. Composite materials made of cellulose-based fibres, such as sisal fibres, demonstrate remarkable environmental and economical advantages [12, 13]. Earlier studies [14, 15] have shown that acicular wollastonite may be used as a co-reinforcer in short fibre composites. The use of a high volume fraction of wollastonite not only reduces the cost by replacing resin content, but also improves the tensile and impact properties of the composites [16]. Incorporation of wollastonite improves the dimensional stability, while the addition of natural fibres has the advantage of reducing the density [16, 17]. However, use of wollastonite mineral fibres together with natural fibres in rotational moulding has not been reported.

Silane coupling agents have the ability to form a durable bond between organic and inorganic materials. Interfaces involving such materials are a dynamic area of chemistry research in which surfaces can be modified to provide compatibility or to incorporate the bulk properties of different phases into a uniform composite structure [18].

In this research, the primary purpose is to rotomould fibre-reinforced polyethylene composite parts. Aminosilane surface coupling agent is used to change the wollastonite reinforcement from having a relatively high energy surface to having a low energy surface, producing better adhesion with the polymer matrix. The tensile strength and impact strength of the composites were measured, and SEM analysis was used to characterise the surface modification.

Materials and methods

Materials

The matrix polymer used was rotational moulding grade medium density polyethylene (LMDPE), Cotene 9042 (supplied by Courtenay JR (NZ) Ltd), with a relatively low melting point (115 °C) and low melt flow index (4.0 g per 10 min at 190 °C). A maleated polyethylene (PE), Exxelor VA 1840 with melt flow index of 8.0, manufactured by ExxonMobil Chemical (USA), was used as coupling agent. Aminopropyl trimethoxysilane (APTMS), product code SIA0591.0, was purchased from Gelest Inc. (USA). Wollastonite (calcium silicate) was produced by Wolkem's mines (Rajasthan, India). The composition of the wollastonite was determined by X-ray fluorescence (XRF) with the results listed in Table 1. The particle size distribution and mean particle size were determined using a Malvern Mastersizer 2000 instrument. The median particle size for wollastonite was 16.6 µm. X-ray Diffraction (XRD) analysis showed (Fig. 1) that the wollastonite was highly crystalline. Sisal fibre was supplied by EC Attwood Ltd, NZ. The density of the sisal fibre was not determined experimentally. Typical values from the literature are in the range 1.35–1.5 g cm^{-3}, and we assumed the value 1.5 g cm^{-3} to calculate the volume fraction of sisal in the composites.

Table 1 Composition (wt%) of wollastonite as determined by XRF analysis

Element as oxide	SiO_2	CaO	Al_2O_3	Fe_2O_3	TiO_2	MnO_2	SO_3	K_2O
Wollastonite	49.790	49.390	0.023	0.443	–	0.264	0.018	0.014
Loss on ignition (combustibles)	0.046							
Total	99.988							

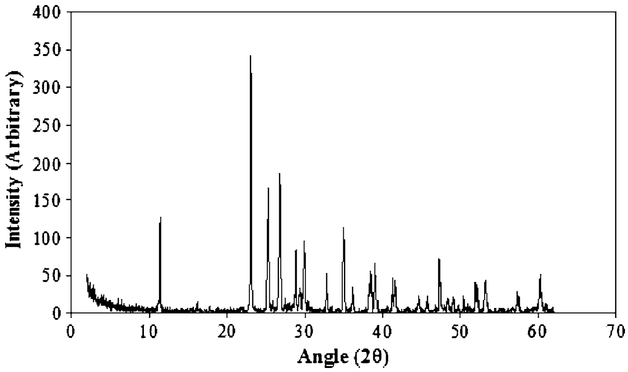


Fig. 1 XRD analysis of wollastonite

Surface modification

A 95% ethanol–5% water solution was adjusted to pH 4.5–5.5 with acetic acid, and silane was added to yield a 5% final concentration. The wollastonite crystals were silylated by stirring in the solution for 5 min and then decanting. The crystals were rinsed twice with ethanol and dried for 10 min at 110 °C. Details of this method are given in Arkles [18].

Manufacturing of composite samples

Wollastonite samples (treated and untreated) were dried overnight in an oven at 90 °C prior to use. The wollastonite and PE powders were compounded using an Axon BX-18 single screw extruder The six heating zones were set to 150, 160, 180, 180, 160 and 160 °C. The extrudates were pelletised into 2 mm long granules, which were then injection-moulded into dog bone tensile specimens with size 165 × 12.7 × 3.2 mm^3 and impact samples with size 125 × 12.7 × 3.2 mm^3. The composite pellets were granulated (SM100 Retsch Mill, Retsch GmbH & Co. KG, Germany) into finer particles of 0.5 mm average size before rotational moulding. Moulding was carried out on a laboratory scale rock-and-roll machine with a 100 × 100 × 220 mm^3 aluminium mould to produce composite boxes of 3.2 mm wall thickness. The two axes ran at a rotational speed ratio of 5 to 1 with the main rolling axis rotating at 25 rpm. The rotomoulded specimens were cut into rectangular shape with dimensions 165 × 12.7 × 3.2 mm^3. During the rotational moulding process, the oven temperature was set at 250 °C and forced-air cooling started when the internal air temperature reached 180 °C.

Testing

The tensile strengths and moduli of the composite samples were measured according to ASTM standard D638 using an Instron 5567 universal testing machine with a gauge length of 50 mm and a test speed of 50 mm min^{-1} for tensile strength, and 5 mm min^{-1} for tensile modulus. Charpy impact tests were carried out with a CEAST (Italia) impact tester according to ASTM D6110-97. At least five specimens for each sample were tested to confirm repeatability. The variation was within ±5%.

Scanning electron microscopy (SEM) analyses

Impact-fractured surfaces of composite samples were vacuum coated by evaporation with platinum, then analysed using a Philips XL 30 FEG scanning electron microscope, operated at 5 KV.

Results and discussion

Tensile strength and impact strength

The first part of this work was intended to elucidate the effect of wollastonite microfibre volume fraction on the tensile and impact strength of fibre-reinforced polyethylene composites. The effect of wollastonite loading on the tensile strength and modulus, and impact strength of wollastonite-reinforced polyethylene composites (injection moulded specimens) is shown in Fig. 2. Tensile strength increases monotonically with the addition of wollastonite fibres and shows a 40% improvement at 40 vol% wollastonite. Tensile modulus increases dramatically with the addition of wollastonite. At 40 vol% wollastonite, it increases by 500%. However, impact strength decreases with increasing proportion of wollastonite. In addition, the processability also decreases after the addition of more than 12 vol%

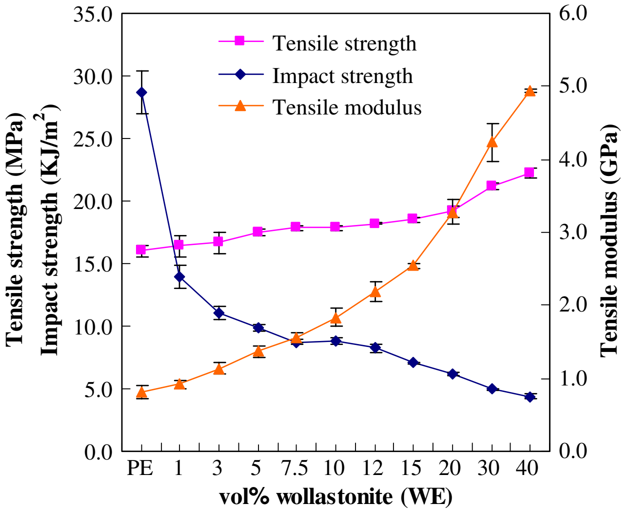


Fig. 2 Effect of wollastonite content on tensile strength, tensile modulus and impact strength of injection moulded specimens

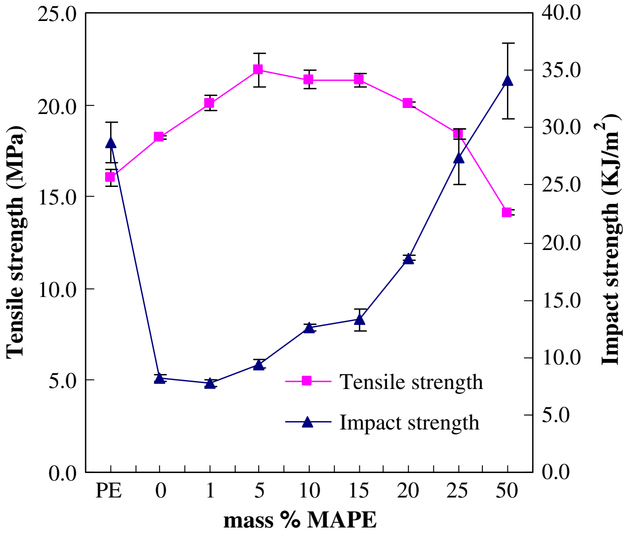


Fig. 3 Effect of MAPE content on tensile and impact strength of injection moulded specimens whether the primary requirement is tensile or impact strength

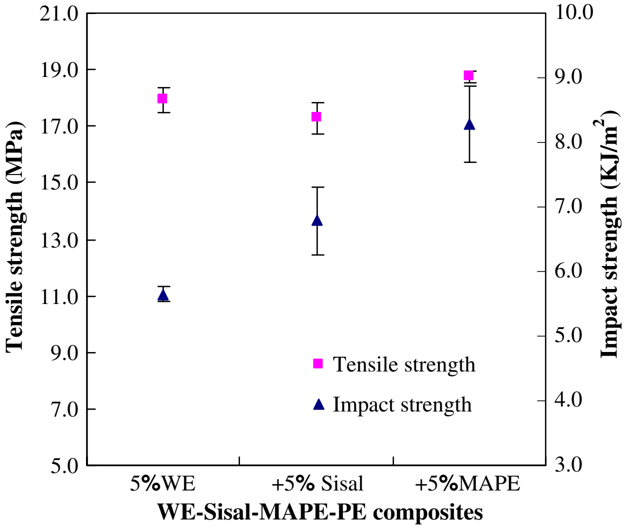


Fig. 4 Effect of incorporating sisal fibres and MAPE on tensile and impact strength of compounded rotomoulding specimens

wollastonite because of increased viscosity. It was extremely difficult to manage the extrusion of the composites when wollastonite content was higher than 40 vol% due to the poor wetting of wollastonite by polyethylene.

The effect of the coupling agent, maleated polyethylene (MAPE) VA1840, was investigated with the wollastonite fibre volume fraction fixed at 12 vol% (Fig. 3). The tests showed that the tensile strength increases with the addition of MAPE (up to 15 mass% MAPE) and reaches the highest value between 5 and 15 mass% MAPE. MAPE improves the tensile strength by 37% at 5 mass% addition with 12 vol% addition of wollastonite fibres. The processability is also improved because of the lower viscosity of MAPE. Impact strength increases steadily with addition of MAPE and is improved dramatically at 50 mass% MAPE to a level higher than that of pure PE. These results indicate that partial replacement of the matrix by cheap wollastonite mineral fibres not only reduces the cost but also increases the tensile strength of the composites. With the effect of the coupling agent, MAPE, the properties of the composite resin can be “tuned” to specific applications, depending on whether the primary requirement is tensile or impact strength.

The tensile and impact strength for 5 vol% wollastonite, 5% wollastonite + 5% sisal and 5 vol% (wollastonite + sisal) + 5 mass% MAPE under compounded rotomoulding are shown in Fig. 4, in which the samples are designated as 5% WE,+5% Sisal and +5% MAPE, respectively. The total loading of fibre reinforcement is kept at 5 vol%. Adding equal volumes of wollastonite and short sisal fibres (6 mm in length) to the composite has little effect on tensile strength but increases the impact strength by 20%. Further improvement is seen after adding 5 mass% MAPE where the impact strength is improved by 46%; with injection moulding, the impact strength is further improved by 79% (Fig. 5). It is believed that rotomoulding could further improve impact strength if all aspects (such as granulating, heating, cooling and product wall thickness) of the rotational moulding process are well controlled. This indicates the potential for developing rotational moulded hybrid polyethylene composites reinforced with wollastonite and sisal fibres.

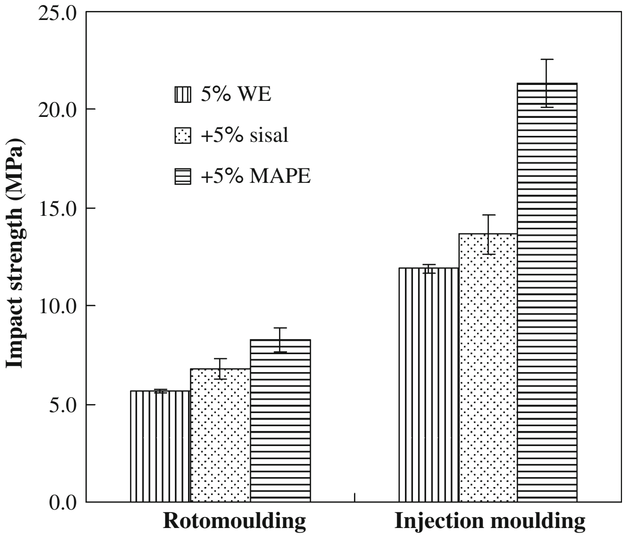


Fig. 5 Comparison of impact strength under different processing methods

Silane can be used as a coupling agent to modify the interfaces to generate desired heterogeneous environments,

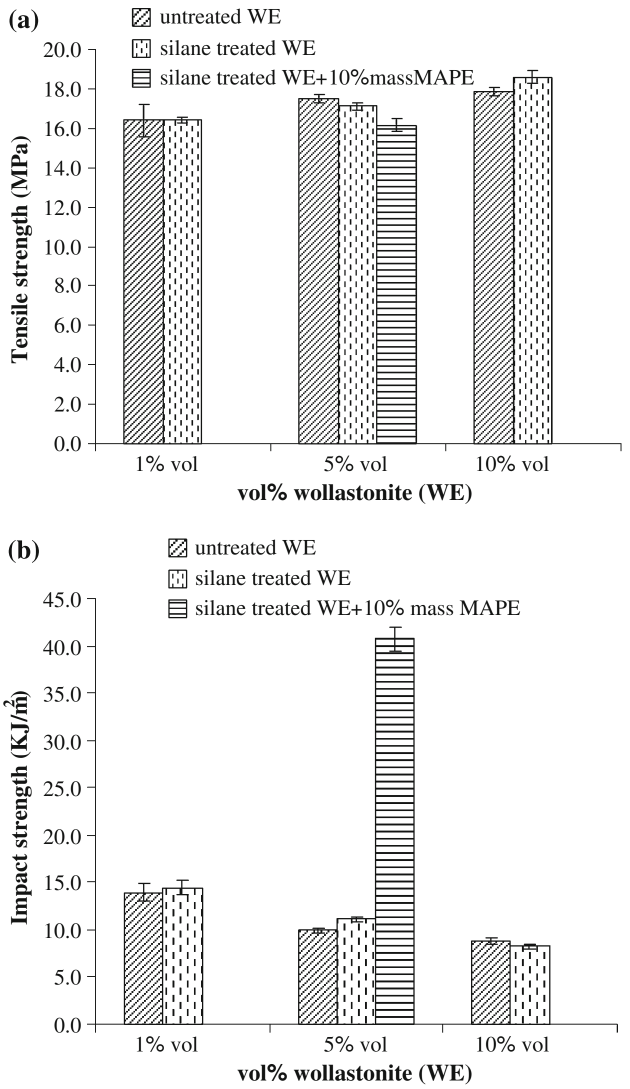


Fig. 6 Effect of silane treatment on (**a**) tensile strength and (**b**) impact strength of injection moulded specimens

or to incorporate the bulk properties of different phases into a uniform composite structure [18]. Figure 6 shows the tensile and impact strengths of composites with untreated wollastonite, aminopropyl trimethoxysilane (APTMS)-coated wollastonite and coated wollastonite with 10 vol% MAPE in the PE matrix, and wollastonite proportion varying from 1 to 10 vol%. There is little difference for the three compositions in terms of the tensile strength (Fig. 6a). However, the impact strength (Fig. 6b) is dramatically increased by silane treatment of the wollastonite, in the composite with 5% wollastonite and 10% MAPE.

Microscopic failure analysis by scanning electron microscopy (SEM)

SEM analysis clearly shows that without MAPE, there is no apparent bonding between PE and the wollastonite surface (Fig. 7a). However, after adding 5 mass% MAPE at 15 vol% wollastonite, there is good adhesion between wollastonite fibres and the polyethylene matrix on the fracture surface (Fig. 7b). The interfaces between wollastonite and PE were observed to be very well bonded in the test specimens shown in Fig. 6c, which contained 5% vol wollastonite coated with aminosilane and 10% mass MAPE. The results also reflected a significant increase of the impact strength. For hybrid wollastonite and sisal fibre-reinforced polyethylene composites, wollastonite microfibres act as small anchors around the sisal fibre surface (Fig. 8a, b) This increases the frictional shear strength and energy related to fibre pull-out when sisal fibre is pulled from the wollastonite-filled matrix, by hindering crack propagation [19]. The tensile strength of discontinuous fibre-reinforced thermoplastic bulk composites reportedly correlates well with frictional shear strength as measured in the single filament pull-out test [10, 17]. The enhancement of the tensile strength by the inclusion of a high percentage of wollastonite microfibres may be attributable to the increase in frictional stress. This possibly implies a generally improved interfacial bonding, which is corroborated by the scanning electron micrographs, Fig. 7, in good agreement with the findings of Herrera-Franco [9].

To understand the effects of aminosilane on the interfacial bonding (shown in Figs. 6b and 7c), the following mechanism is proposed.

Aminopropyl trimethoxysilane (APTMS) (Fig. 9) is initially hydrolysed when it comes into contact with water, so that some or all of the methoxy groups are converted to hydroxy groups. The silicate surface of wollastonite, like other silicates and oxides, is a high energy surface that is strongly hydrophilic and would normally have at least a monolayer of strongly adsorbed water. If the adsorption energy is sufficiently large the silicate surface may be partially hydroxylated, and condensation reactions can occur spontaneously with hydroxy groups of the hydrolysed silane molecules. The remaining silane hydroxy groups may condense with neighbouring silane hydroxyl groups as depicted in the idealised schematic representation in Fig. 10. The amino groups in the silane 'tails' can interact via hydrogen bonding (and/or acid–base reaction) with the carboxyl groups of the MAPE units (Fig. 11) as indicated in Fig. 12. Those interactions promote compatibility between the coated wollastonite fibres and the polymer matrix.

Conclusions

In this research, a pretreatment procedure has been developed for the incorporation of wollastonite microfibre/sisal

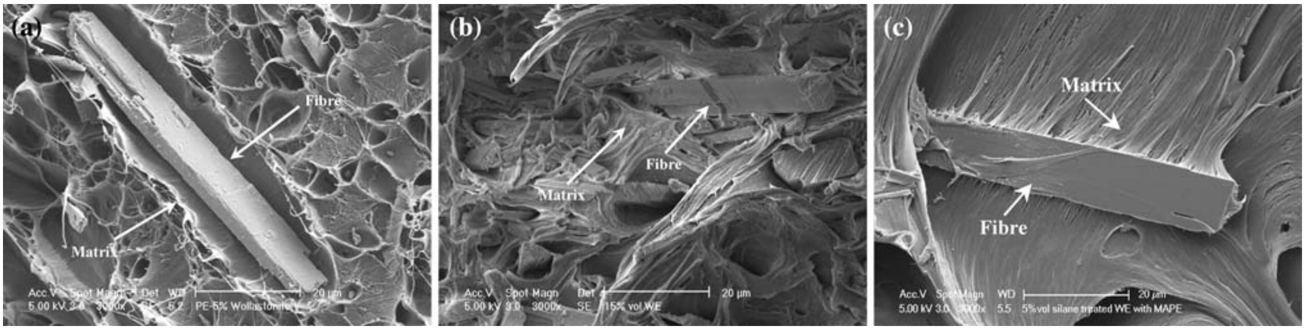
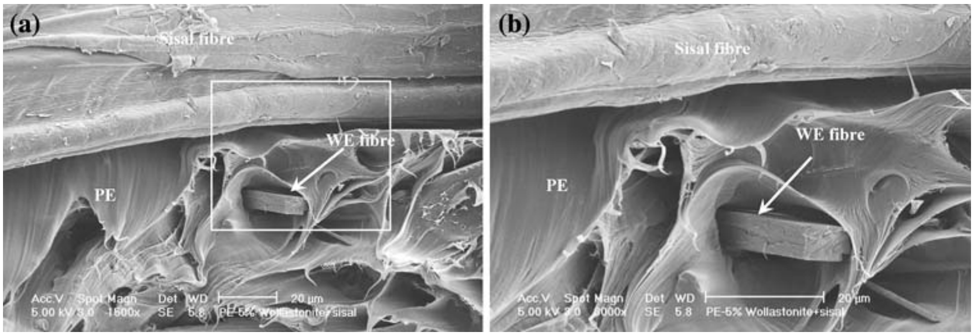


Fig. 7 SEM micrographs of the fracture surface of wollastonite—PE composites (**a**) at 5% vol wollastonite with no MAPE; (**b**) at 15% vol wollastonite with 5 mass% addition of MAPE; and (**c**) at 5% vol wollastonite coated with aminosilane with 10% mass MAPE

Fig. 8 SEM micrographs of the fracture surface of wollastonite and sisal-reinforced PE composites at 5 vol% fibres loading: (**a**) overall fracture surface, (**b**) magnified view of identified area



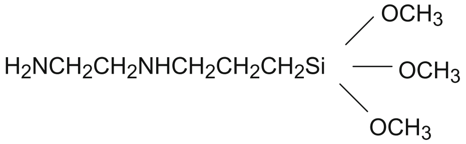


Fig. 9 The structure of aminopropyl trimethoxy silane (APTMS)

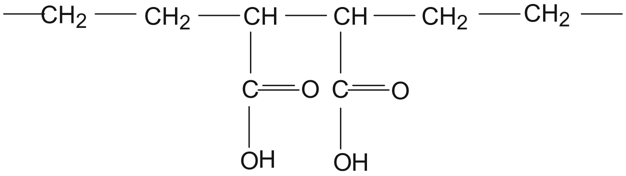


Fig. 11 Idealised structure of MAPE

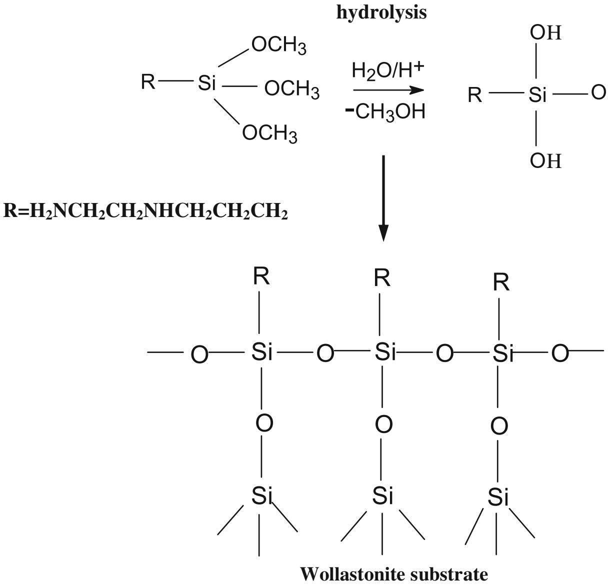


Fig. 10 Silane coupling to mineral surface

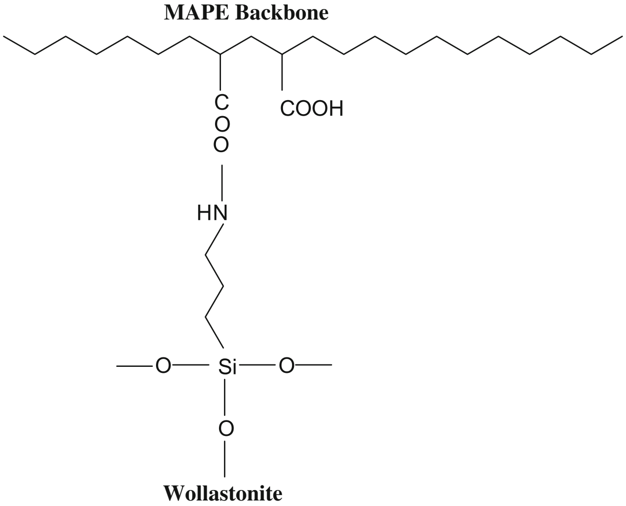


Fig. 12 Acid–base bonding of aminosilane treated wollastonite to MAPE

fibre into polyethylene composites, utilising a coupling agent that can also alter the rheological properties of the composite system. Surface treatment with aminopropyl trimethoxysilane (APTMS) was performed on the wollastonite fibres. The tensile strength of injection moulded specimens increases monotonically with the proportion of wollastonite microfibres. The tensile modulus increases dramatically with the addition of wollastonite, but impact strength is reduced. In addition, the processability is decreased by the addition of more than 12 vol% wollastonite because of the increased viscosity. Incorporation of MAPE provides a better overall balance of stiffness and impact strength for both injection and rotational moulded products, and improved processability. Incorporation of sisal fibres increases the impact strength while maintaining the same (or slightly higher) level of tensile strength. SEM analysis shows extremely good adhesion between wollastonite fibres and the polyethylene matrix with added MAPE, particularly when coated with aminopropyl trimethoxysilane (APTMS).

This technology allows the material properties of the composites to be ‘tuned’ to specific applications, depending on whether the primary requirement is tensile strength or impact strength.

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