

Advances in the Reactive Processing of Polymer Composites Based on Magnesium Hydroxide*

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The presented work reports on reactive processing aimed at improving mechanical properties of polyolefine/magnesium hydroxide-based composites. Three different polymer matrix materials (polypropylene homopolymer (PP), polypropylene block copolymer (PPBC), and linear low-density polyethylene (LLDPE)) have been studied in combination with plate-like and spherical magnesium hydroxide particles (60 mass %). *m*-Phenylenedimaleimide (DMI) has been used as a reactive modifier and it became apparent that DMI is very effective in this role. In addition to the actual level of DMI used, the extent of reaction of matrix chains and filler surface with DMI, is heavily dependent on the reactive processing conditions, especially temperature. The enhancement in major mechanical properties, *i.e.* tensile strength, elongation to break and impact strength, afforded by DMI modification exceeds the improvement afforded by silane pretreatment systems. When the optimal DMI and processing temperature was applied, improvement of mechanical properties in all studied composites was higher than 100 % relative to the respective unmodified composites. This paper also affords insight into the mode of action of DMI and how the use of DMI together with a lubricant can be optimized to tailor composites to specific end-use applications.

Over the past decade fillers have moved a long way from their traditional and historical role as cheap extenders and shrinkage reduction agents for polymeric materials. It is now widely recognized that fillers can be very useful functional additives; a good example being the use of metal hydroxides to impart halogen-free flame retardancy [1, 2].

Highly flammable polymers, such as polyolefins and polystyrenes, can be made flame-retardant by addition of organo-halogen compounds combined with antimony oxide. However, the use of these flame retardants results in evolution of thick smoke together with highly acidic hydrogen halide gas. Magnesium hydroxide, along with other materials such as aluminium hydroxide and mixtures of Huntite and Hydromagnesite, is a very effective halogen-free flame retardant and smoke suppressant. As a result of these attractive properties, together with the environmental reasons, the use of these additives (known collectively as flame-retardant fillers) has been steadily increasing [3].

The most significant disadvantage of flame-retardant fillers is the amount of the additive required to

attain acceptable flame retardancy which can exceed 60 mass % (40 mass %). Such high filler levels necessitate modification of the interface region that exists between the filler particles and the bulk matrix, as this component of the composite dominates their mechanical and processing characteristics. This paper focuses on the use of *m*-phenylenedimaleimide (DMI) as a potentially cost-effective "one-step" reactive interface modifier for highly filled composites based on the magnesium hydroxide (Mg(OH)₂) and a range of polyolefins.

The resulting properties of composites based on thermoplastic matrix materials and inorganic particulate fillers are influenced by many factors. Whilst the physical and chemical nature of the filler will determine its effectiveness in a functional role, the presence of solid additives in the matrix melt will inevitably have an impact on their processability. The extent to which this occurs depends on many factors including the amount of filler present, possible interactive effects between the filler and polymer, or between the filler particles themselves [1]. With increasing filler content the influence of the above-mentioned factors is intensi-

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fied and results in deterioration of composite mechanical properties and rapidly increasing composite melt viscosity.

Use of magnesium hydroxide as a halogen-free flame-retardant and smoke-suppressant additive is a notably important example where a high-filler volume fraction (≥ 0.40) (corresponding to ≥ 60 mass %) is required to realize the desired composite property, *i.e.* flame retardancy to UL94 V0 or V1 specifications. The environmentally attractive feature of halogen-free flame retardancy is therefore offset somewhat by the high filler loadings required, which cause a significant reduction in toughness-related mechanical properties and an enormous increase in composite melt viscosity. By interface modification *via* chemical treatment of filler surface and/or use of a specially modified matrix mentioned above disadvantages can be overcome [2].

Recent work conducted by the authors has shown the benefits of a single-step reactive processing composite formation method, where thermomechanical production of macroradicals is sufficient for creation of the required reactive intermediates. Therefore peroxides, which are often detrimental to the long-term composite stability, are not needed. Several multifunctional additives have been investigated for this role [4]; however, DMI afforded the best results by a significant margin. Unlike the majority of surface treatment systems, particularly the silanes, it was shown that DMI is equally effective with both acidic (zeolites and bentonites [5]) and basic (calcium carbonate [6]) fillers. These studies demonstrated that processing temperature is the major determinant of the efficiency of DMI.

The results obtained in these studies indicate the potential of DMI for use in highly filled systems being such as that of magnesium hydroxide-based polyolefin composites [7–10].

The objective of this work was to evaluate the effect of addition of a reactive monomer, namely, *m*-phenylenedimaleimide (DMI) on the processing and end-use properties of magnesium hydroxide-filled polyolefin composites. Three different polyolefin matrix materials (polypropylene homopolymer (PP), polypropylene block copolymer (PPBC), and linear low-density polyethylene (LLDPE)) have been studied in combination with plate-like and spherical magnesium hydroxide particles. The effect of polymer matrix structure, filler particle shape on reactive processing efficiency has been studied along with the simultaneous effects of DMI level, processing temperature, filler level, and lubricant level, on the processing characteristics and mechanical properties.

EXPERIMENTAL

Materials: Details of the polyolefin matrix materials are presented in Table 1.

Both the plate-like (Fig. 1) and spherical magnesium hydroxide particles are characterized in Table 2. Particle size and shape have been varied by careful control of the proprietary precipitation process which has been used to prepare these samples. The reactive modifier, *m*-phenylenedimaleimide (DMI), was obtained in a 90 % active form from VUAS Pardubice (Czech Republic). Structol Polydis TRO-16 (a mix-

Table 1. Details of Polymer Matrix Materials

Polymer	Designation	Producer	Commercial designation	Melt flow ratio
Linear low-density polyethylene	LLDPE	Exxon Chemicals, USA	Escorene LL 1004 YB	2.8 dg min ⁻¹ (190 °C, 2.16 kg)
Polypropylene homopolymer	PP	Slovnaft, Slovak Republic	Tatren HPF	8.6 dg min ⁻¹ (230 °C, 2.16 kg)
Polypropylene block copolymer*	PPBC	ICI Chemicals and Polymers, UK	Propathene GMX 216	10.1 dg min ⁻¹ (230 °C, 2.16 kg)

*12–14 % ethylene-rich ethylene–propylene random copolymer (EPRC) which was formed in the same polymerization as the continuous PP phase. Some of these EPRC's form a dispersed impact modifier phase.

Table 2. Particle Characteristics of Magnesium Hydroxides Used in Compound Preparation

Particle shape	Mean particle size μm	Surface area m^2	Commercial designation	Origin
Plate-like	0.8–1.0	6.9	Duhor N	Duslo, a.s. Šaľa, Slovak Republic
Spherical	20–40	–	–	Laboratory preparation

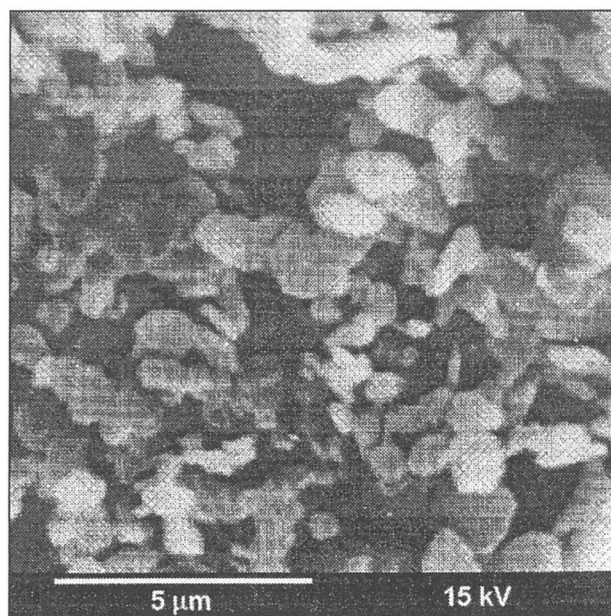


Fig. 1. Scanning electron micrographs of lamellar (plate-like) magnesium hydroxide (average particle size = 1 μm).

ture of fatty acid amides and esters) was selected as the lubricant. In the previous work [9] TRO-16 has been shown to improve composite rheological properties without excessively compromising the positive effect of DMI on composite mechanical properties.

Composite preparation: Melt blending was carried out using a Brabender Plasticorder fitted with a W50 chamber and cam blades. Mixing time was varied from 4 to 14 min, mixing torque data were reported after the first minute of mixing after stabilization of the torque response. Mixing temperature was varied from 160 to 240°C. All composite samples were compression-moulded at 180°C and 200°C into plaques of 0.8 mm and 3 mm thickness for tensile and impact testing, respectively. The moulding (using frame moulds) was carried out using a preheating time of 3 min, pressure was applied for 2 min and the mould was then transferred to a cooled press and pressure was applied during cooling for 10 min.

Melt flow rate (MFR): Assessment of the melt flow behaviour of the composites, prepared as above, was carried out using a Chemoprojekt U. A. (Czech Republic) MFR apparatus with a set barrel temperature of 190°C and 230°C and 2.16 kg load. Otherwise the conditions were identical to ASTM D 1238.

Mechanical testing: ASTM D 638M Type M-III tensile dumbbell test pieces were cut from the compression-moulded sheets and tensile strength was measured at ambient temperature using a crosshead speed of 50 mm min^{-1} . Unnotched impact strength was measured at ambient temperature using a Charpy impact testing instrument. Test piece dimensions were 3 mm \times 10 mm \times 70 mm and the span was set at 50 mm.

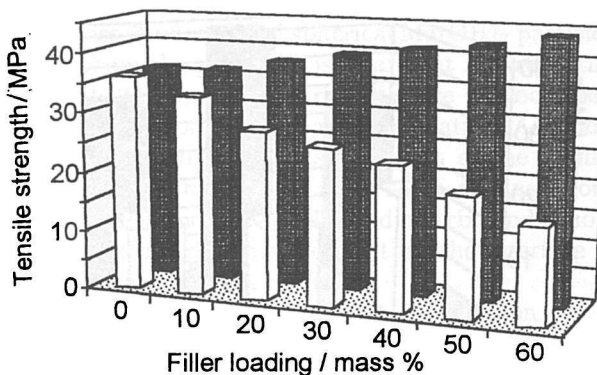


Fig. 2. Effect of plate-like $\text{Mg}(\text{OH})_2$ content on unmodified (□) and modified (■) polypropylene homopolymer-based composites.

Scanning electron microscopy: Fracture surfaces were examined using a Tesla BS-300 SEM. Prior to analysis the impact fracture surfaces were sputter-coated with a gold layer of 40–50 nm thickness using a Balzers SCD050 coating machine.

RESULTS AND DISCUSSION

Fig. 2 shows the decrease in tensile strength of PP/ $\text{Mg}(\text{OH})_2$ composites with increasing level of unmodified filler. This decrease is partly due to poor dispersion of the filler but the other reason for this effect is poor filler-matrix adhesion. Increasing the aspect ratio of the filler beyond that normally encountered with particulate fillers may increase the strength slightly but will not usually completely overcome the decreasing trend observed in Fig. 2 where despite perfect dispersion, tensile strength is reduced by 50 % (relative to the unfilled matrix) at 60 mass % $\text{Mg}(\text{OH})_2$.

From Fig. 2 the effectiveness of reactive processing with DMI is strongly evident and is manifested as an increase in tensile strength beyond that of the unfilled matrix. The other significant feature is that the efficiency of the DMI increases as filler level increases. These observations are clear evidence that DMI-filler and DMP—PP interactions serve to increase the adhesion between the filler and matrix and that the interface formed, as a result of these interactions, is stronger than the unfilled matrix. The latter feature is very beneficial, as already mentioned, the filler content required to afford flame retardancy to UL94 V0 in polyolefins must be in excess of 60 mass %.

Fig. 3 presents the maximum level of tensile strength received from optimization of DMI content and reactive processing conditions for composites containing 60 mass % magnesium hydroxide; the composite strengths obtained were higher than those of the respective unfilled matrix materials.

It is important to note, however, that the optimum DMI levels and processing conditions are highly matrix-dependent and principally reflect the differing

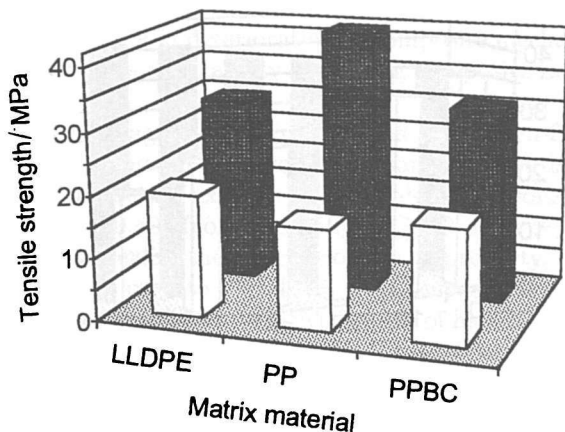


Fig. 3. Maximum tensile strength obtained for unmodified (□) and modified (■) composites containing 60 mass % of plate-like magnesium hydroxide.

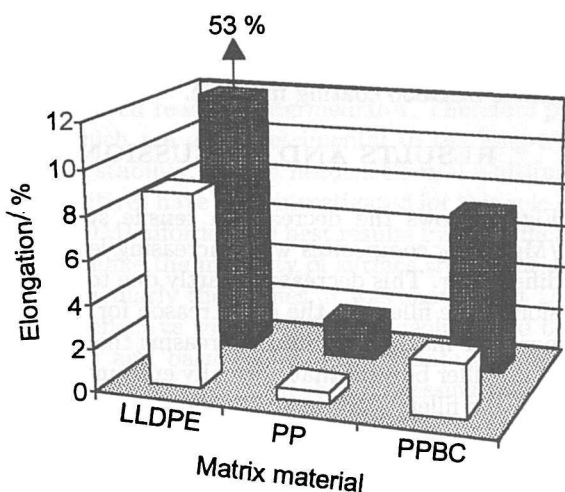


Fig. 4. Maximum elongation obtained for unmodified (□) and modified (■) composites containing 60 mass % of plate-like magnesium hydroxide.

chemistry of the matrix materials, particularly with regard to their thermomechanical degradation characteristics: PE tends to undergo crosslinking and PP tends to undergo chain scission. In the former matrix the crosslinking effect was so pronounced that the crystalline content was significantly reduced [8], however, in PP-based composites the crystalline content is only slightly reduced. The latter observations will be reported in more detail soon [8–10].

From Fig. 4 it is evident that the improvement in elongation, relative to the respective unmodified composites, afforded by reactive processing with DMI is particularly significant for the PE-based composite, though the improvements in elongation of PP-based composites can still be considered commendable. With the former composite, the reduction in PE crystalline content that occurs due to crosslinking, is the most likely explanation for the significant

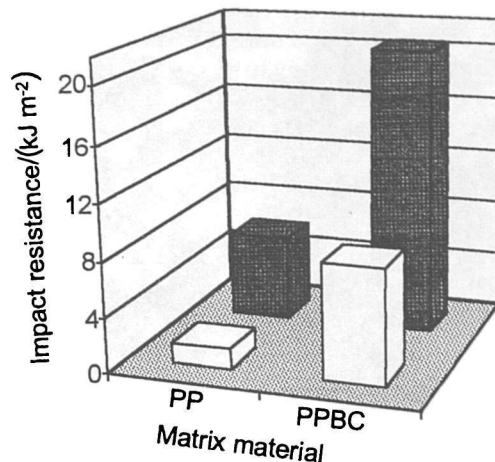


Fig. 5. Influence of reactive processing on impact resistance of polymer composites, unmodified (□) and modified (■).

improvement in elongation. It can be considered that the DMI-crosslinked PE matrix has become similar to a rubbery, largely amorphous, crosslinked polymer, such as an ethylene-propylene or ethylene-vinyl acetate random copolymer. This effect, together with strong filler-matrix adhesion, results in good strength and elongation, which occurs uninterrupted by the excessive physical crosslinking afforded by a semicrystalline structure. In the PP-based composites the improvement in elongation is hampered by retention of a semicrystalline matrix morphology, which results in the modified interface affording the principal contribution to the improvement in elongation. The greater improvement in elongation observed with the PPBC-based composite (relative to that based on PP), may be explained by encapsulation of the filler with the dispersed impact modifier phase of the PPBC. The latter is based on an ethylene-rich random copolymer of ethylene and propylene. Its ethylene-rich nature may result in more interaction with the DMI-Mg(OH)₂ adducts and hence an ethylene-rich encapsulation around the filler particles. To verify this effect further investigations are required. Similar trends to those observed in the elongation data are also apparent for impact strength (Fig. 5) and can be explained *via* the same mechanisms as for the former behaviour.

Scanning electron microscopy (SEM) of the fracture surfaces affords visual insight into the nature of the filler matrix interaction and, on a qualitative level, can provide information on interface thickness. In this paper SEM images of novel spherical particle Mg(OH)₂/PP composites are presented. It is important to emphasize that unlike plate-like magnesium hydroxide, the spherical particle shape affords clearer interpretation of interfacial characteristics in these composites. The poor filler-matrix adhesion is highly apparent from examination of Fig. 6, which presents a tensile fracture surface of a composite based

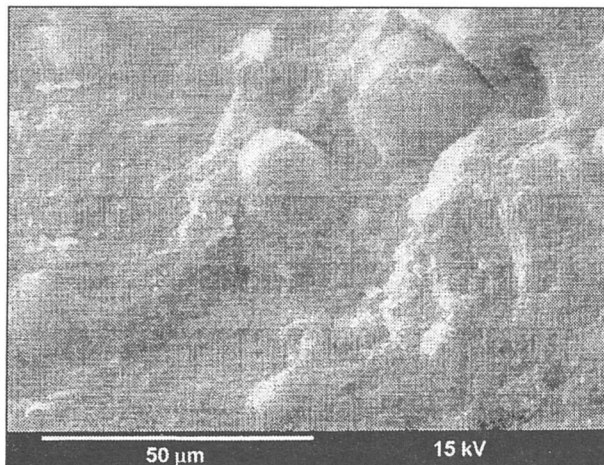


Fig. 6. Fracture surface of polypropylene composite based on 60 mass % untreated spherical magnesium hydroxide.

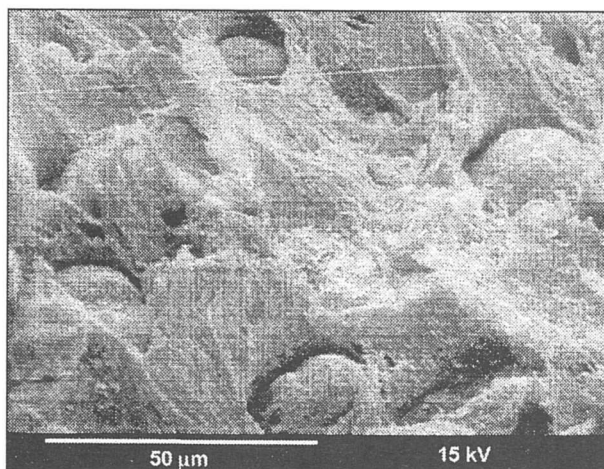


Fig. 7. Fracture surface of 2.5 mass % DMI-modified polypropylene composite based on 60 mass % spherical magnesium hydroxide.

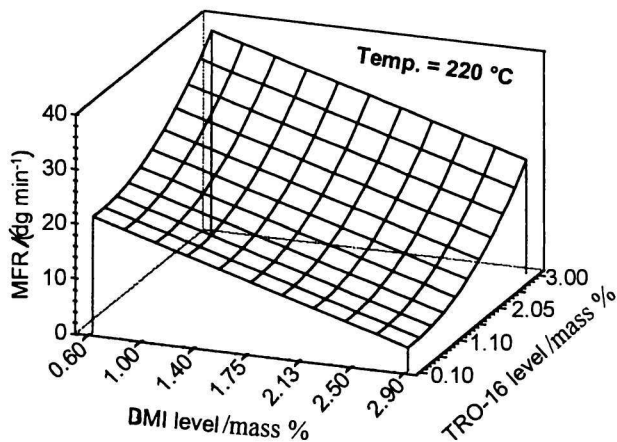


Fig. 8. Effect of reactive modifier (DMI) and lubricant (Structol TRO-16) composition on the melt flow rate (MFR).

on 60 mass % unmodified spherical $\text{Mg}(\text{OH})_2$ particles in PP. From the picture it is clear that failure of the composite at the filler-matrix interface has occurred together with some yielding of the matrix. Addition of DMI completely changes the locus of the failure (Fig. 7), which has moved away some distance from the interface between the filler and matrix and is now in the bulk matrix; this reflects that the interface is stronger than the bulk matrix.

An improvement in interfacial adhesion in a thermoplastic-based composite is virtually useless if the rheological properties of the composite melt are increased to an unacceptably high level. As it is effectively illustrated by Fig. 8 with DMI/PP/ $\text{Mg}(\text{OH})_2$ -based composites this increase in viscosity can be overcome by the use of a lubricant Structol TRO-16. It is important to appreciate that the mechanical property enhancing effect of DMI is much more significant than the slightly detrimental effect of TRO-16 on mechanical properties. This indicates that TRO-16 is likely to act in the matrix and does not adsorb onto the filler surface in preference to DMI/DMI-PP adducts. The previous work [8] has shown that this is not the case with fatty acid pretreated filler where DMI filler reactions are blocked by the adsorbed fatty acid with the result that the mechanical property enhancement effects of DMI are severely diminished.

CONCLUSION

This study highlights a novel approach for improvement of the mechanical properties of magnesium hydroxide-based polyolefin matrix composites. The following matrix materials were used: polypropylene homopolymer (PP), polypropylene block copolymer (PPBC), and linear low-density polyethylene (LLDPE) matrix.

The following major conclusions were reached:

1. Single-step reactive interface modification, using *m*-phenylenedimaleimide (DMI) as the reactive modifier, has been shown to be very successful at improving composite properties at high filler loadings.
2. The enhancement in major mechanical properties, *i.e.* tensile strength, elongation to break and impact strength, afforded by DMI modification can exceed the improvement afforded by expensive silane pretreatment systems.
3. Along with DMI content, the effectiveness of the reactive processing strongly depends on temperature.
4. When statistically determined optimal DMI levels and processing temperatures are used, improvement in mechanical properties, in all composites investigated, was greater than 100 %, relative to respective unmodified composites.
5. The detrimental effect of DMI on composite melt viscosity has been overcome by the use of a fatty acid ester/fatty acid amide-based lubricant.

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