# Property Tailoring of Particulate Polymer Composites by Reactive Processing

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**Summary:** This study explores reactive processing aimed at improving the mechanical properties of polyolefin/inorganic particulate filler based composites. Three different polymer matrix materials have been studied in combination with the nine inorganic particulate fillers with different particle size and of varying pH. The reactive modifier 1,3-phenylene dimaleimide (BMI) has been shown in all cases to be very effective in terms of improving composite properties beyond those of the respective unmodified composites and in some cases beyond those of the unfilled matrix materials. The detrimental effect of BMI on melt viscosity can be overcome via judicious use of a suitable lubricant, and together with response surface methods, followed by optimization procedures, composite properties can be tailored for specific end use applications.

## Introduction

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, and possible interactive effects between the filler and polymer, or between the filler particles themselves. As filler content increases, the influence of the above mentioned factors is intensified, resulting in deterioration of composite mechanical properties that is accompanied by rapidly increasing composite melt viscosity.

In our earlier papers[1-4)] the reactive modifier 1,3-phenylene dimaleimide (BMI) has been shown to be the best of several reactive modifiers investigated in terms of enhancement of composite mechanical properties. In these published studies BMI has been shown to be a very effective one step (in situ added) interphase modifier for magnesium hydroxide based polyolefin composites.

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This paper aims to acquire further insight in to the combined effects of polymer matrix and filler surface chemistry, as well as filler particle size, on enhancement of composite performance arising from BMI modification. The optimization of reactive processing conditions and composite formulation, for attainment of the required optimum balance of melt processability and mechanical properties, has been also studied.

## Experimental

**Materials:** Three different polyolefin matrix materials (polypropylene homopolymer (PP), polypropylene block copolymer (PPBC) and linear low-density polyethylene (LLDPE)) have been studied in combination with magnesium hydroxide, aluminium hydroxide, talc, bentonite, calcium carbonate, kaolin, zeolite, barium sulphate and dolomite. Details of the polyolefin matrix materials and fillers investigated are presented in Tables 1 and 2.

Table 1. Details of polymer matrix materials

| Polymer | Producer | Commercial designation |
|---|---|---|
| Linear low density polyethylene (LLDPE) | Exxon Chemicals, USA | Escorene LL 1004 YB |
| Polypropylene homopolymer (PPH) | Slovnaft, SK | Tatren HPF |
| Polypropylene block copolymer* (PPBC) | ICI Chemicals and Polymers, UK | Propathene GMX 216 |

* Contains 12-14% ethylene rich poly(ethene-co-propene) impact modifier

**Composite preparation:** All composites prepared via reactive melt mixing contained 60% w/w filler. Parallel studies were conducted using both batch (Brabender Plasticorder W50) and continuous (twin screw extrusion (Betol BTS 30)) compounding process. Processing temperatures between 180 and 230 °C were used for both the batch and continuous blending procedures. Despite use of different processing methods similar trends in overall performance were observed. Composite test pieces were formed by compression moulding for Brabender blended composites, and injection moulding for twin screw extrusion blended composites.

Table 2. Particle characteristics of inorganic fillers.

| Filler | Particle shape and production method | Mean particle size (μm) | Producer* |
|---|---|---|---|
| magnesium hydroxide | lamellar, precipitated | 1 | Duslo, a.s. Sala, SK |
| aluminium hydroxide | lamellar, precipitated | 2 | Laboratory prepared |
| talc | anisotropic, ground | 5 | Hnúšťa, SK |
| bentonite | anisotropic, ground | 7 | Jelšový Potok, SK |
| calcium carbonate | anisotropic, ground | 10 | CZV Rohožník, SK |
| kaolin | anisotropic, ground | 12 | Synthesia, Kolin, CZ |
| zeolite | anisotropic, ground | 15 | Nižný Hrabovec, SK |
| barium sulphate | anisotropic, precipitated | 20 | MCHZ, Hrusov, CZ |
| dolomite | anisotropic, ground | 60 | Dolkam Rajec, SK |

*All listed fillers are from local Slovak Republic and Czech Republic sources.

**Evaluation of end use properties:** The influence of BMI modification was followed by measurement of mechanical and rheological properties. Composite melt flow rate (MFR) was determined at 230°C using a Chemprojekt MFR grader with a 10 kg load and the standard (2.1 mm diameter x 8.0 mm length) die. Tensile testing was carried out at ambient temperature using ISO R37 type 2 dumbells in an Instron 4301 tensometer at a crossshead speed of 10 mm $min^{-1}$. Charpy impact testing was conducted at -20°C on unnotched test pieces (thickness 3.0 mm, depth 10 mm and span 40 mm). A central composite design approach was used to investigate the simultaneous effects of reactive modifier level, lubricant level and processing temperature. From the contour plots obtained optimum formulations were determined to provide required end use property profile.

## Results and discussion

From Figs.1-2 it is evident that BMI is an effective interphase modifier for all the fillers investigated in a PP matrix, ranging from acidic clays, through to more neutral fillers and to strongly basic fillers. This is a significant advantage as, for example silane based coupling agents can only be successfully used with fillers that have reactive OH groups on their surfaces. Therefore fillers such as $CaCO_3$, and wood flour have been shown to be unresponsive to silane treatment. In the majority of cases, BMI modification resulted in an 80-100% improvement in tensile strength, relative to respective unmodified composites. With BMI modified magnesium hydroxide, aluminium hydroxide, talc and barium sulphate based composites, tensile strength exceeded that of the unfilled matrix (33.1 MPa).

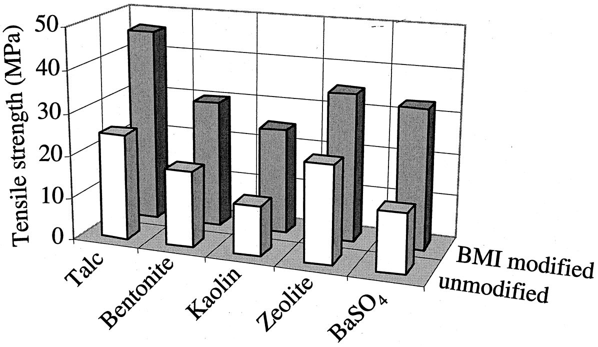

Fig. 1: Effect of talc, bentonite, kaolin, zeolite and $BaSO_4$ on efficiency of BMI modification.

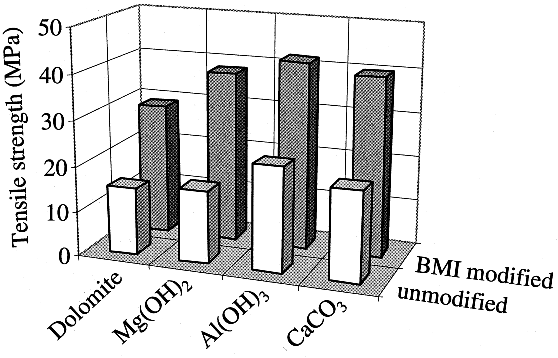

Fig. 2: Effect of dolomite, $Mg(OH)_2$, $Al(OH)_3$ and $CaCO_3$ on efficiency of BMI modification.

Although specific types of filler do not generally have a unique particle size, it is generally accepted that most fillers used in the thermoplastics industry have average diameters in the range 0.1 μm to 10 μm. The kaolin, zeolite, barium sulphate and dolomite fillers investigated (Table 2) are outside the upper limit of this range. The efficiency of BMI modification, (as measured by the ratio of improvement in tensile strength (relative to the unmodified composite), to the tensile strength of the unmodified composite) together with average particle size is presented in Fig. 3. Surprisingly, no decrease in BMI efficiency was observed as filler particle size increased. For fillers in the particle size range 1-10 μm, addition of BMI gave rise to a tensile strength improvement of ca. 80%, relative to the respective unmodified composites (i.e., BMI modification efficiency was ca. 80%).

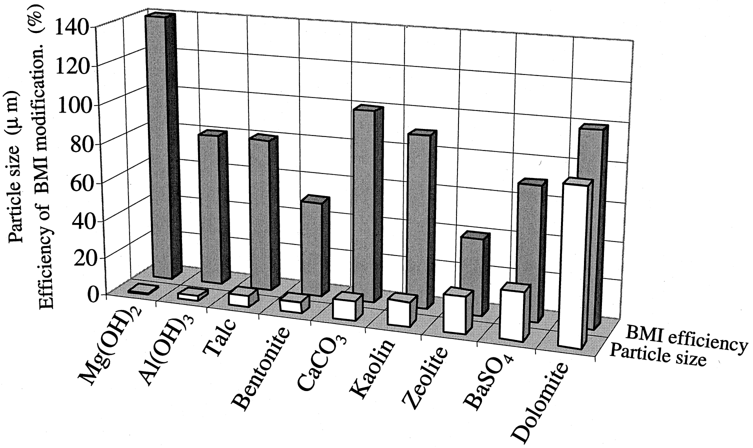

Fig. 3: Influence of filler particle size on efficiency of BMI.

Furthermore BMI modification efficiencies greater than 100 % (i.e., tensile strength was more than double that of the respective unmodified composites) have been achieved using fillers with particle size of 1µm (magnesium hydroxide), 10 µm (calcium carbonate) and 60 µm (dolomite) as a result of reactive interphase modification with BMI.

Figures 4-6 illustrate the effect of polyolefin matrix chemistry and structure on the tensile properties of BMI modified composites containing 60% w/w magnesium hydroxide. These response surfaces show the simultaneous effect of BMI level, processing temperature and lubricant level for PPH, PPBC and LLDPE based composites. It is clearly evident that the matrix chemistry plays a vital role in influencing the nature of BMI modification. For example, in polypropylene homopolymer based composites (Fig. 4), even the lowest level of BMI investigated resulted in mechanical properties that were well in excess of those attained by the unmodified composite. Surprisingly, similar improvements were also observed in toughness related properties (Fig. 5). The highest improvement in impact strength was observed with PPBC based composites, as this matrix contains an ethylene rich dispersed impact modifier phase. These aspects are discussed in the partnering paper and are related to the differences in the degradation mechanisms of polyethylene and polypropylene and the concomitant effects on matrix crystallization and interplay between chain scission and crosslinking reactions.

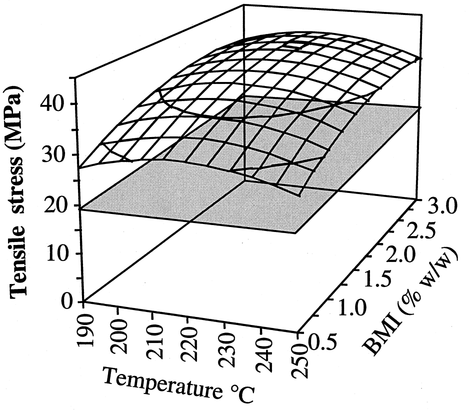

Fig. 4: Contour plot showing the influence of BMI level and processing temperature on the tensile strength of $Mg(OH)_2$/PPH composites (lubricant level 0.5 % w/w)

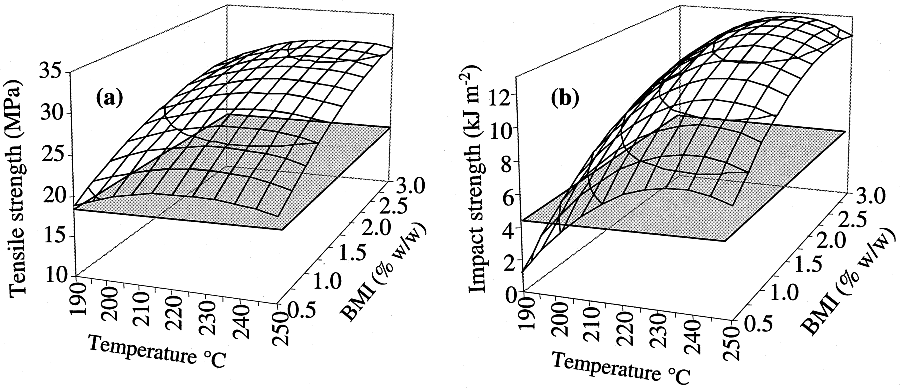

Fig. 5: Influence of BMI on; (a) tensile and (b) impact strength of polypropylene block copolymer/magnesium hydroxide composites. ▨, unmodified composite data plane.

The disadvantage of BMI, when used alone, is that in ethylene-rich polyolefins, in particular, melt viscosity can reach unacceptably high levels, due to the predominance of crosslinking reactions occurring together with interphase structure development (Fig. 6b). We have found that fatty acid pre-treated filler cannot be used to counteract this problem as the coupling effect of BMI is significantly impaired due to the BMI adsorption sites on the filler surface being blocked by the adsorbed fatty acid molecules.

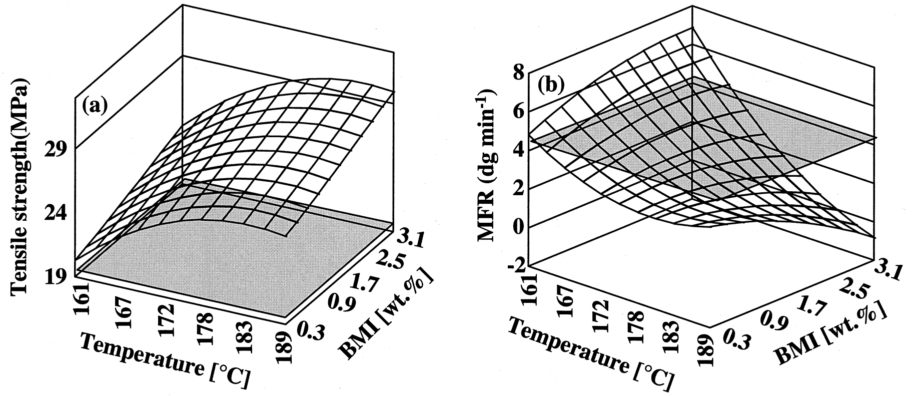

Fig. 6: Influence of BMI on; (a) tensile strength and (b) MFR of LLDPE/magnesium hydroxide composites. ▨, unmodified composite data plane.

However, use of a lubricant (consisting of a blend of fatty acid amides and esters) added directly to the pre-mix of filler, matrix (PPH, PPBC) and BMI, has been found to offset the problem of unacceptably high melt viscosity whilst allowing excellent mechanical properties to be retained. We have found that optimal formulations determined from response surface equations, enables tailoring of end-use properties; for example achievement of maximum strength together with maximum MFR. Application of the three factorial experimental design followed by optimization procedures therefore allows tailoring of composite properties for specific end use applications. Optimization of polypropylene homopolymer based composites is the topic of one of our more recent papers$^{3)}$. Optimization of polypropylene block copolymer based composites will be explored in a forthcoming paper.

## Conclusion

The enhancement of major mechanical properties, i.e., tensile strength, elongation to break and impact strength, afforded by BMI modification exceeds the improvement afforded by current organic coupling agent pre-treatment systems (including those based on silanes). However, unlike these modifiers, BMI is an effective interphase modifier for all fillers in current use, whether they are acidic, neutral or basic. The interphase structure development associated with BMI modification was even effective with fillers of particle size greater than that usually encountered in thermoplastics applications. The performance of BMI was found to be dependent on the ethylene content of the polyolefin matrix used. Potential problems with excessive melt viscosity can be surmounted via use of a lubricant based on a fatty acid amide/ester blend.

## References

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