

## Tailoring of interphase structure in highly filled poly(propene) block copolymer via reactive processing

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### Summary

The effect of the of the reactive modifier 1,3-phenylene dimaleimide (BMI) on the interphase structure of poly(propene) block copolymer (PPBC)/magnesium hydroxide ( $Mg(OH)_2$ ) composites has been investigated. DRIFTS and DSC studies on hot decane extracted composites confirmed preferential encapsulation of the filler particles with the ethene based elastomeric phase of the PPBC. This elastomeric interphase structure, formed efficiently via reactive processing of untreated  $Mg(OH)_2$ , PPBC and BMI, conferred excellent strength and toughness to the composites. The tensile strength and elongation of a BMI modified composite containing 60% w/w  $Mg(OH)_2$ , exceeded the yield stress and strain of the unfilled matrix.

### Introduction

1,3-Phenylene dimaleimide (also commonly called meta-phenylene **bismaleimide** (BMI)) has been studied in the literature mainly as a dynamic crosslinking agent for elastomer based blends [1][2] and a reactive compatibiliser [3]. BMI, however, has received little attention in the academic literature as a reactive interphase modifier for polymer matrix composites; though Yamamoto et al [4] have filed a Patent on BMI modified poly(ethene-co-methacrylic acid)/metal hydroxide composites. The authors, however, have observed significant mechanical property enhancements in particulate filled composites produced via reactive processing with BMI with both polypropylene homopolymer (PPH) [5][6] and polyethylene (PE) matrices [7]. Data from these studies indicated that the effect of BMI on the two polyolefins was markedly different and was a reflection of their preferred reactions with free radicals. With the PE matrix composites BMI modification resulted in branching/crosslinking of the matrix that resulted in a significant reduction in matrix crystallinity [7], however, with PPH matrix

composites the level crystallinity was only slightly reduced [8]. In both cases though, composite mechanical properties significantly improved as a result of increased filler-matrix adhesion via a flexible, crosslinked interphase. The major drawback of BMI is that the significant increases in mechanical properties are counterbalanced by an increase in melt viscosity [6][7], which is particularly marked in the case of the PE based composites. Certainly, with PPH based composites the viscosity problem can be overcome via use of a lubricant [5][6]. The BMI induced reduction of crystallinity in the PE based composites changed their fracture mechanism that resulted in a toughening effect [9], it was therefore considered that the behaviour of an ethene containing poly(propene) based block copolymer matrix (PPBC) should be investigated. These materials contain sufficiently long blocks of PE to enable formation of a separate semi-crystalline PE phase together with ethene rich poly(ethene-co-propene) sequences that form a dispersed elastomeric impact modifier phase. They therefore effectively combine the rigidity of PPH with the relatively high toughness of PE, over a wide range of temperatures. The multiphase nature of these materials is also likely to result in interesting preferential encapsulation effects that have been observed in previous work with vinyl silanes [10][11]. Such effects can lead to composites with outstanding strength together with high toughness.

In this paper we examine the effect of BMI level on the mechanical and rheological properties of PPBC/Mg(OH)<sub>2</sub> composites and investigate the interphase structure in terms of preferential encapsulation and BMI matrix interactions and BMI filler interactions.

## Experimental

### *Materials*

The matrix selected was ICI GXM216 poly(propene) block copolymer (PPBC) based on propene and ethene (12-14% w/w) and contains a general-purpose stabiliser package [measured melt flow rate (MFR) was 7.3 dg min<sup>-1</sup> (2.16 kg 230°C)]. GXM216 features a dispersed impact modifier phase that consists of ethylene rich poly(ethene-co-propene) and also sufficiently long sequences of poly(ethene) (PE) to enable formation of a crystalline PE phase. DSC analysis of GXM216 therefore yields two phase transitions; one at ca. 110°C corresponding to crystalline phase and the other at 160°C corresponding the predominantly isotactic poly(propene) continuous phase. The PP and PE crystalline contents were ca. 40% and 2%, respectively (based on the approximate masses of the respective comonomers in the PPBC and assuming values of 209 Jg<sup>-1</sup> and 277 Jg<sup>-1</sup> for the heats of fusion of perfectly crystalline PP and PE, respectively). The untreated magnesium hydroxide (Mg(OH)<sub>2</sub>) used was Duhor N, from Duslo Sala [D<sub>50</sub>, 1.0 μm, specific surface area, 7.8 m<sup>2</sup> g<sup>-1</sup>] and the 1,3-phenylene dimaleimide (BMI) was obtained in a 90% active form from VUAS (Czech Republic).

### *Composite preparation*

All composites prepared contained 60% w/w Mg(OH)<sub>2</sub> which is considered to be an appropriate level for flame retardant applications [12]. Melt blending was carried at

220°C using a Brabender Plasticorder fitted with a W50 chamber and cam blades. All composite samples were compression moulded at 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 pre-heating time of 3 minutes, pressure was applied for 2 minutes and the mould was then transferred to a cooled press and pressure applied during the 10 minute cooling period.

#### *Rheological investigation*

Assessment of the melt flow behaviour of the prepared composites, at a set temperature of 230°C, was carried out using MFR apparatus with 2.16 kg and 10.0 kg loads, in accordance with ASTM D 1238. The effect of residence time at 230°C was investigated by leaving the composite melt in the barrel with zero load for set time intervals within the range 5 to 20 minutes.

#### *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<sup>-1</sup>. Unnotched impact strength was measured at -20°C using a Charpy impact testing instrument. Test piece dimensions were 3 mm x 10 mm x 70 mm and the span was set at 50 mm.

#### *Analysis of insoluble matrix fraction*

The insoluble matrix fraction of the composites was isolated by a three day Soxhlet extraction with decane (to remove the impact modified PP matrix), followed by a 1 day extraction with hexane (to remove the decane). The Soxhlet apparatus was thoroughly lagged. The resulting residues were oven dried to constant mass at 110°C and then analysed by DRIFTS [10][11] and DSC (Perkin-Elmer DSC-7, heat-hold-cool-heat-cycle, 30-230°C with 5 minute hold, heating rate 20°C min<sup>-1</sup>, N<sub>2</sub> sample atmosphere). The bound matrix content was then determined by measuring the mass loss on ignition at 1100°C (4 hours) after correcting for dehydration.

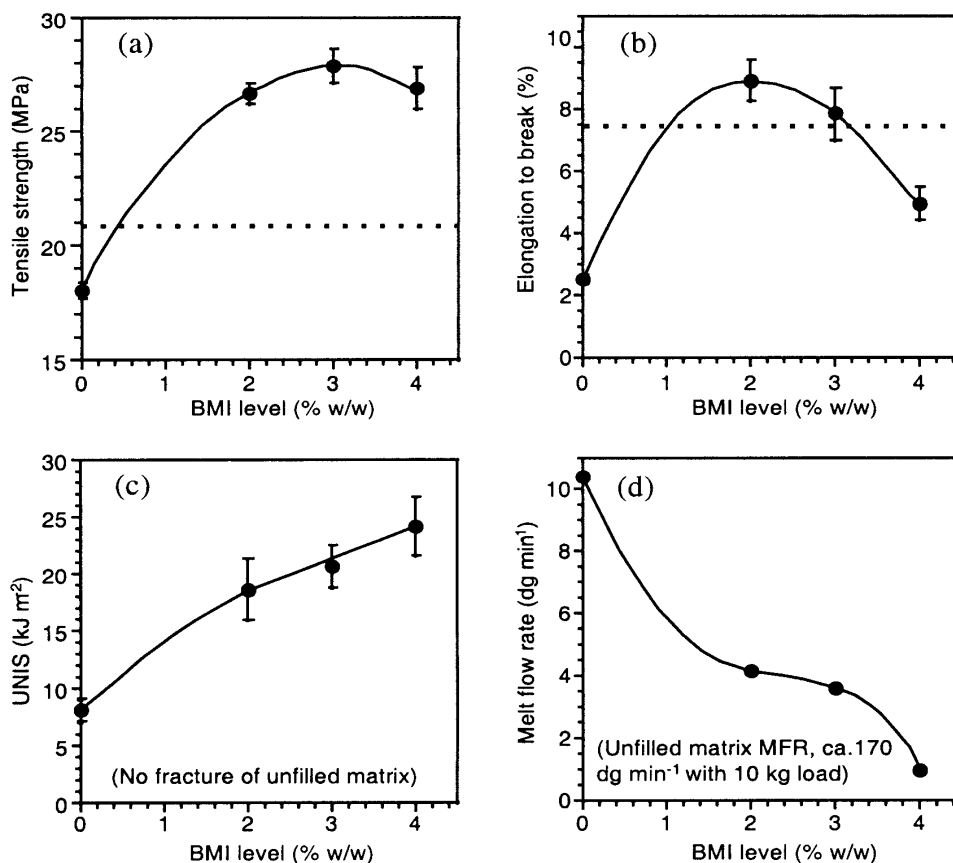
## **Results**

#### *Effect of BMI level*

The effect of increasing BMI level, keeping mixing time constant at 10 minutes, on tensile strength, elongation to break, impact strength and MFR is presented in Figures 1 (a) to (d). From this data it is evident that tensile strength reaches a limiting value between 2 and 3% w/w BMI, this value is almost 60% greater than the unmodified composite and even exceeds the yield stress of the unfilled matrix. A maximum in elongation, 250% higher than the unmodified composite and greater than the yield strain (7.4%) of the unfilled matrix, is observed over the same BMI range. Impact strength was shown to increase with BMI level within the range investigated; at 4% BMI impact strength was increased by 200% relative to the unmodified composite.

This increase in strength together with increase in toughness is likely to be associated with formation of an interphase that is elastomeric in nature but strongly bound to both the filler surface and the bulk matrix.

At this juncture it is worthwhile comparing these results with those obtained in a previous study [11] on similar composites that had been modified by using a range of filler pre-treatments, including a proprietary vinylsilane based combination.

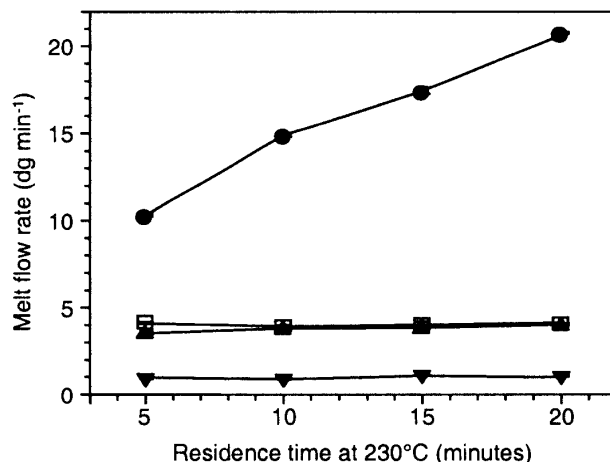


**Figure 1** Composite properties as a function of BMI level; (a) tensile strength, (b) elongation to break, (c) unnotched impact strength (UNIS), and (d) melt flow rate (with 10 kg load). Dashed line corresponds to tensile yield data for unfilled matrix.

In the latter study the best tensile results, at a filler loading of 60% w/w, were obtained using a vinylsilane based filler pre-treatment; tensile strength was 24 MPa and tensile elongation was 2.8 %, a figure well below that afforded by BMI modification. Mg(OH)<sub>2</sub> based composites modified with maleanised PP prepared by Jančář et al [13] also showed inferior relative tensile properties to those afforded by BMI modification. The latter two types of surface treatment are considered to be the most significant from a commercial standpoint; the results obtained in this study therefore highlight the superiority of BMI as an interphase modifier and the commercial potential of BMI and similar derivatives.

The MFR data (Figure 1(d)) shows that these noteworthy improvements in properties are counterbalanced by rapidly increasing melt viscosity. However, within the BMI

range (2 to 3% w/w) at which the optimum mechanical properties were observed, the reduction in MFR had reached a plateau. Increasing BMI level to 4% w/w significantly reduces MFR from  $10.6 \text{ dg min}^{-1}$  (for the unmodified composite) down to the unacceptable level of  $0.96 \text{ dg min}^{-1}$ . This data shows that from both rheological and mechanical property standpoints, it is evident that 3% w/w BMI is the optimum practical level in these composites.



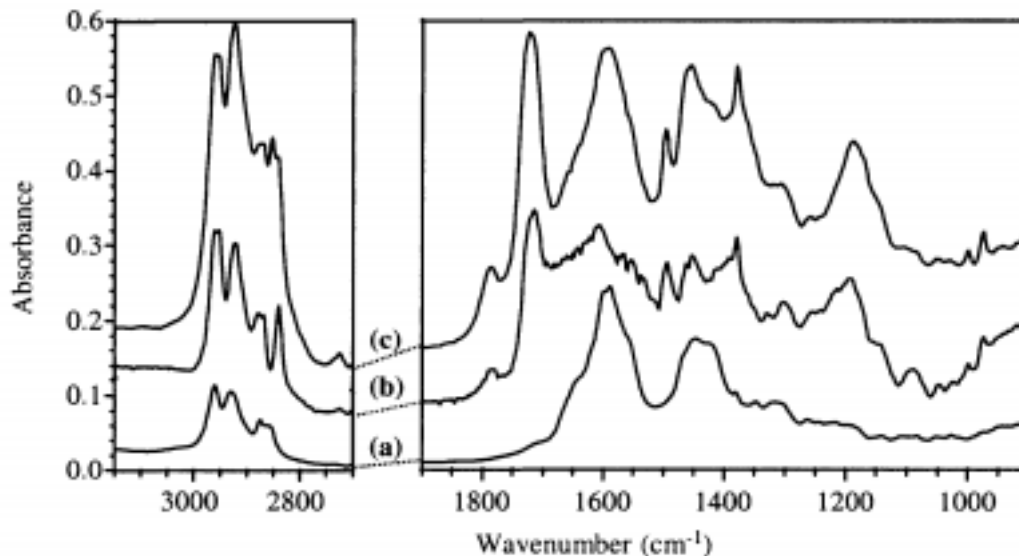
**Figure 2** Effect of residence time under zero shear in MFR apparatus (with 10 kg load) as a function of mixing time, showing effect of BMI level; ●, unmodified composite; ▼, 2.0% w/w BMI; ■, 3.0% w/w BMI; ▲, 4.0% w/w BMI.

Further work has shown that the increase in melt viscosity can be partially overcome via addition of low levels of a fatty acid amide/ester based lubricant to the formulation. However, excessive lubricant dosage can lead to preferential adsorption of the lubricant on the filler and therefore an inability to form the required elastomeric interphase via reaction of BMI with the filler and preferential crosslinking of ethene rich elastomeric sequences. The effect of the complex interplay between BMI level, processing temperature and lubricant level on the mechanical and rheological properties of such composites, and their interphase structure, has been reported elsewhere [14][15][16].

Further insight into the reactivity of BMI was gained from examination of data relating to the effect of residence time at 230°C, under zero shear conditions, on composite MFR. Relevant data is presented in Figure 2 where degradation of the unmodified composite is clearly manifested as a noticeable increase in MFR. It is likely that this degradation is associated with the initially high viscosity of the composite melt and the correspondingly high level of thermo-mechanical degradation, and rapid consumption of the stabiliser, occurring during mixing. In contrast, no increase in MFR was observed with equivalent composites modified with BMI. In these cases it is highly likely that chain scission reactions associated with degradation of PP were effectively cancelled out by the addition reactions between PP macro-radicals and the maleimide alkene of BMI [7][8].

*Investigations on insoluble matrix*

The insoluble matrix levels for the unmodified composite and a modified composite (3% BMI) are 6.1% and 19.5% (both by mass of filler), respectively (Table 1). These values are also reflected the relative intensities of the C-H stretching bands in DRIFTS spectra of the composite residues (Figure 3(a) and (c)). The level of bound matrix for the unmodified composite was higher than expected due to adsorption of matrix degradation products via carboxylate linkages that give rise to the carbonyl absorption at  $1580\text{ cm}^{-1}$  (Figure 3(a)).

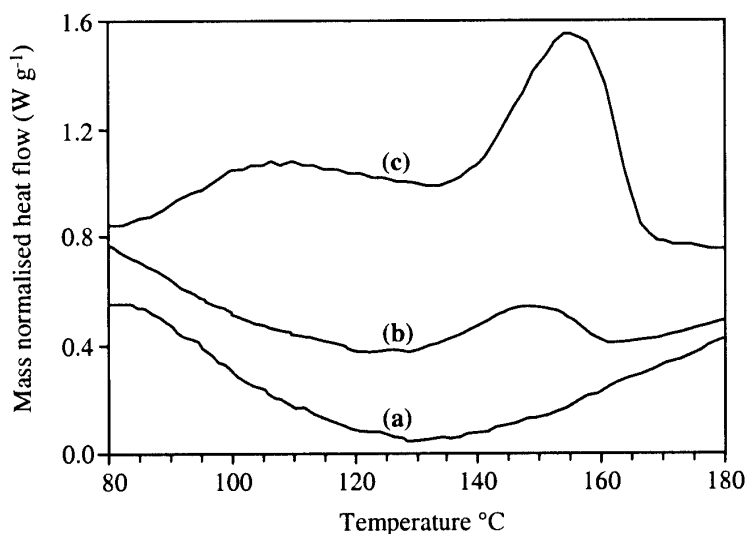


**Figure 3.** DRIFTS spectra of composite residues after decane extraction, (a) unmodified composite, (b) modified composite based on PPH, (c) modified composite based on PPBC.

The relative ethylene content of the soluble matrix residues can be determined by measuring the absorbance ratio of the methylene asymmetric C-H stretch [ $\text{Abs}_{(\text{CH}_2\text{-H})}$ ] (at ca.  $2930\text{ cm}^{-1}$ ) to the methyl asymmetric C-H stretch [ $\text{Abs}_{(\text{CH}_3\text{-H})}$ ] (at ca.  $2960\text{ cm}^{-1}$ ) (Table 1). It is evident that the filler-matrix residue for the unmodified composite is richer in degradation products derived from propene sequences due to the greater susceptibility of these sequences to oxidative attack. The level of degradation was so severe that the degraded fragments were unable to crystallise as no melting endotherm was observed in corresponding DSC data (Figure 4(a)); furthermore, a high degree of disorder is also reflected in the relatively high methylene C-H stretching frequencies (Table 1). It has to be emphasised that this result is a little unexpected on the basis of previous work where elastomeric encapsulation of untreated filler was observed [10][17]. This is likely to be due to high levels of degradation during processing (in a Brabender open to air) and the harsh extraction regime (ca.  $160^\circ\text{C}$  for three days). Under these conditions, acidic PP oxidation products may have displaced the elastomeric phase, an effect that is corroborated by the DRIFTS data.

The insoluble residue from the BMI modified composite based on PPBC has a higher

ethylene content; this data together with the very low PP crystalline content (relative to the unfilled matrix) (Table 1, Figure 4(b)), clearly indicates strongly retained encapsulation of the  $\text{Mg}(\text{OH})_2$  by the impact modifier phase. There was no melting endotherm corresponding to crystalline PE in the DSC data from the latter composite residue (Figure 4(b)). Such an endotherm, however, is apparent in the DSC data from the unfilled matrix. This discrepancy is likely to be due to the high level of crosslinking induced by addition reactions to BMI and degradation. For comparison, an equivalent composite based on a PP homopolymer (PPH) [45% crystalline,  $T_m$  163°C] was also extracted under the same conditions. In this case the crystalline content of the insoluble matrix was higher relative to the unfilled PPH matrix (Figure 4(c), Table 1). It is interesting to note, however, that the addition reactions to the adsorbed BMI and possible BMI related chain extension/crosslinking reactions have caused the PPH based insoluble matrix (mainly the filler-matrix interfacial region) to have a lower



**Figure 4.** DSC data for composite residues after decane extraction; (a) unmodified composite based on PPBC, (b) BMI modified composite based on PPBC, (c) BMI modified composite based on PPH

crystalline content, and slightly lower  $T_m$ , than the unfilled material. The simultaneous effects of processing temperature, BMI level and lubricant level on the latterly described DRIFTS and DSC responses is the subject of a conference presentation [15] and a forthcoming paper [16].

Reaction of the maleimide alkene of BMI with matrix macro-radicals resulted in disappearance of the alkenic C-H stretch ( $3110\text{ cm}^{-1}$ ). Interaction of BMI with the filler surface is most probably via an amide carboxylate, which is likely to result in the broad absorption centred at  $1600\text{ cm}^{-1}$ . Model compound studies [8] have shown that the pink-purple colouration of the BMI modified composites is associated with the high degree of conjugation in the amide carboxylate. These observations are identical to those obtained in our previous studies on PPH and PE based composites.

**Table 1** Data relating to interphase structure

Composite	Bound matrix content (%) <sup>*</sup>	PP crystalline content of bound matrix (%) <sup>+</sup>	Abs <sub>(CH-H)/</sub> Abs <sub>(CH<sub>2</sub>-H)</sub>	C-H asymmetric stretching frequencies (cm <sup>-1</sup> )	
				methyl	methylene
unmodified	6.1	nd	0.94	2961	2930
modified	19.5	3.4	1.13	2956	2923
modified (PPH)	8.9	14.1	0.94	2953	2922

<sup>\*</sup>, % by mass of filler in residue; <sup>+</sup>, Crystalline content is based on crystallisable PP (there was no clear evidence of crystalline PE); nd, no peaks were resolved.

It is apparent from the DRIFTS spectra (Figure 3(b) and (c)) that not all the BMI has been converted to the amide carboxylate, as a significant amount of imide carbonyl (1720 cm<sup>-1</sup>) still remains after decane extraction. Residues of composites containing lower levels of BMI also showed evidence of unreacted imide [15][16]. This observation may be explained by reaction of only one of the imide groups with the Mg(OH)<sub>2</sub>. Once the filler surface becomes saturated with adsorbed BMI, addition reactions to BMI will continue in the bulk matrix, leaving the imide groups intact.

## Conclusions

This paper investigates the effect of level of 1,3-phenylene dimaleimide (BMI) on the melt and solid state properties of composites based on a poly(propene) block copolymer and magnesium hydroxide. The outstanding mechanical properties of the modified composites are explained by ethene rich elastomeric encapsulation of the filler particles that was promoted by the interaction of BMI with the filler surface and preferential crosslinking of ethane rich chains grafted to the maleimide alkene. Under the determined optimum conditions, tensile strength and elongation to break increased, not only beyond that of the unmodified composite but also beyond the equivalent yield values of the unfilled matrix. Such improvements in mechanical properties for a highly filled flame retardant composite are greater than can be achieved via use of organosilanes and maleanised PP and therefore broaden the application envelope for such materials.

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## References

1. Inoue T, Suzuki T (1995) *J Appl Polym Sci* 56:1113
2. White DA (1995) US Patent 5,578,682
3. Zhang HX, Hourston DJ (1999) *J Appl Polym Sci* 71:2049
4. Yamamoto K, Ikeda K, Fukuyama M, Nisahama T (1996) Japanese Patent 08283482
5. Khunová V, Liauw CM, Sain MM, Alexy P (1999) *Angew Makromol Chem* 269: 78



6. Khunová V, Liauw CM, Alexy P (1999) *Angew Makromol Chem* 269: 84
7. Khunová V, Hurst SJ, Liauw CM (1999) *Polym Bull* 42. 457
8. Liauw CM, Khunová V, Lees GC, Rothern RN, (2000) *Macromol Mater Engng* 279:34
9. Khunová V, Liauw CM (2000) *Chemical Papers* 54:177
10. Liauw CM, Lees GC, Hurst SJ, Rothern RN, Ali S (1998) *Composites Part A. Applied Science and Manufacture* 29A: 1313
11. Liauw CM, Lees GC, Hurst SJ, Rothern RN, Dobson DC (1995) *Plast Rubb Compos Process Applns* 24:249
12. Hornsby PR, Watson CL (1986) *Plast Rubb Process Applns* 6: 169
13. Jančář J, Kučera J (1990) *Polym Engng Sci* 30:714
14. Liauw CM, Khunová V, Lees GC, Rothern RN (2001) *Macromol Symp* 170:205
15. Liauw CM, Khunová V, Lees GC, Rothern RN (2001) *Proc. Eurofillers 2001*, Lodz, Poland, July 2001
16. Liauw CM, Khunová V, Lees GC, Rothern RN (2001) *Macromol Symp* (received September 2001)
17. Pukánszky B, Tüdös F, Kolarík J, Lednický F (1989) *Polym Compos* 2:491