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Reactively Processed High Performance Impact Modified Polypropylene/Magnesium Hydroxide Composites: Interfacial Studies

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Summary: The interphase structure development in impact modified PP (IMPP)/magnesium hydroxide ($Mg(OH)_2$) composites reactively processed with 1,3-phenylene dimaleimide (BMI), in conjunction with a fatty acid amide/ester based lubricant, has been investigated using a three factorial experimental design. Insoluble matrix content, DSC and IR spectroscopic responses indicated that the lubricant preferentially adsorbed on the filler and thus shifted the locus of BMI addition reactions away from the filler surface, towards the bulk matrix. This prevented formation of an effective interphase structure in which the impact modifier phase encapsulating the filler was strongly bonded to the surrounding, chain extended and branched, polypropylene phase.

Introduction

The use of metal hydroxide fillers as halogen free flame retardant fillers in polyolefins is becoming increasingly widespread due to reduction in the cost of the filler, improved composite formulations and improved methods of production. Pirelli[1] have excelled in this area and have managed to optimise cable covering formulations to the extent that far cheaper ground natural magnesium hydroxide ($Mg(OH)_2$) can be used. Despite this increase in commercial use there is still much scope for the development of novel interphase modifier systems that can promote simultaneous improvements in composite strength and toughness. It is relatively easy to bring about an improvement in just one of these properties (that is usually accompanied by a decrease in the other), but rather more difficult to improve both simultaneously. Composite strength is usually increased via use of coupling agents such as some types of silane and functionalised polymer. Composite

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toughness can be improved via use of fatty acid pre-treatment of the filler. A simultaneous increase in strength and toughness is easier to achieve if the matrix is an impact modified polypropylene (IMPP) because encapsulation of the filler with the elastomeric phase can be promoted if the correct type of surface modifier and processing conditions are used. The authors have demonstrated such effects in IMPP/$Mg(OH)_2$ composites using both silane based treatment systems[2] and more recently 1,3 phenylene dimaleimide (BMI)[3].

BMI has been shown to chemically adsorb onto magnesium hydroxide via an amide carboxylate linkage whose highly conjugated nature gives rise to the pink colouration of these composites[4]. The reaction of BMI with the matrix is via addition of matrix macro-radical fragments (arising from mechanical degradation (or the decomposition of added peroxides) during processing) to the maleimide alkene[4]. Additionally, entrapment of matrix chains may also occur through addition polymerisation of the BMI. The effect of matrix crosslinking via addition reactions to BMI on the crystallisability of the matrix depends on the relative rate of shear and thermally induced chain scission reactions. Therefore crystallinity is much reduced in a polyethylene matrix[5] but only slightly reduced in a PP[4] matrix. Modification of impact modified PP based composites with BMI has led to very significant improvements in strength and toughness. The tensile strength of BMI modified composites (26-28 MPa) comfortably exceeded the yield stress of the unfilled matrix (22 MPa) but more significantly, the failure strain of the BMI modified composites (7-8%) was equal to the the yield strain of the unfilled matrix (7.4%)[6]. These outstanding improvements however, do not come without a price, which in this case is an increase in the viscosity of the composite melt[4,5,6]. This detrimental effect has been offset by judicious use of a fatty acid amide/ester based lubricant and the simultaneous effects of lubricant level, BMI level, and processing temperature have been examined previously using a central composite design approach[3]. As well as easing the processing of the composites, the addition of lubricant led to very interesting changes in melt and solid state property responses that implied changes in interphase morphology, perhaps caused by preferential adsorption of the lubricant on the filler and a shift in the locus of addition reactions to BMI, from the filler surface to the bulk matrix. The best balance of mechanical properties was obtained at low lubricant levels combined with high processing temperatures and a level of BMI[3].

The aim of this paper is to examine these ideas and attempt to unravel the interplay between possible adsorption of the lubricant on the filler and addition reactions to BMI within the interfacial region and the bulk matrix. This has been achieved by carrying out thermal gravimetric analysis, differential scanning calorimetry and quantitative FTIR studies on solvent treated samples of the same series of composites studied in the previous paper[3].

Experimental

In the previous paper[3] a central composite design approach (Table 1) was used to investigate the simultaneous effects of processing temperature, BMI (from VUAS) level and lubricant (Structol TRO-16) level on mechanical and rheological properties. In this study the same composite samples are examined after extraction with boiling xylene in order to gain some insight into the interphase structure. The composites were formed from ICI GXM216 IMPP (40 - (lubricant + BMI) (% w/w)) and 60% w/w untreated $Mg(OH)_2$ [7.8 $m^2 g^{-1}$] (Duhor N, Duslo Sala), via melt mixing in a Brabender W50E chamber with cam blades. Mixing temperature was in the range 180 to 230°C and rotor speed was 70 r.p.m. Reactive melt mixing was followed by compression moulding against PET lined moulds at 220°C into plaques of 0.5 mm thickness.

The interphase region and level of PP crosslinking was examined by extracting the bulk of the matrix with boiling xylene for 24 hours. Prior to extraction, 0.5 mm thick compression moulded composite sheets were cut in to ca. 4 mm x 4 mm squares and ca. 1.0 g of these squares were wrapped in glass cloth bound with wire then immersed in boiling xylene. After extraction the envelopes containing the xylene insoluble fraction were dried to constant mass at 80°C.

The insoluble matrix content of the composites were then determined using a Netzch TG109 thermal gravimetric analyser (TGA) (with air purge) by first allowing the samples to equilibrate at 120°C for 5 minutes followed by heating to 900°C at 20°C min^{-1}, the samples were then allowed to equilibrate for 5 minutes at 900°C. The mass loss from the end of the 120°C equilibration period to the end of the 900°C equilibration period was used in calculation of insoluble matrix level, after taking account of mass loss associated with dehydration of pure $Mg(OH)_2$ under identical conditions. The insoluble matrix content was used for determination of crystalline content of the insoluble matrix by DSC analysis.

The heat of fusion of the crystalline component of the insoluble matrix was determined using a Perkin-Elmer DSC-7 power compensation DSC with samples contained in closed aluminium pans. The DSC head was purged with nitrogen. The samples (ca. 5 mg) were heated from 40°C to 230°C at 20°C min^{-1}. In the calculation of crystalline content, a value of 209 J g^{-1} was used for the heat of fusion of perfectly crystalline PP.

The ratio of ethylene to propylene derived repeat units in the bound matrix was then assessed by ratioing the absorbance values of the methylene and methyl asymmetric C-H stretching absorptions in the infrared spectrum. The relative level of BMI in the composite residue was assessed by ratioing of the absorbance values of the BMI carbonyl stretching absorption and the OH stretching absorption of the magnesium hydroxide. These spectra were obtained via diffuse reflectance Fourier Transform infrared spectroscopy (DRIFTS) using a Spectra-Tech cell fitted to a Nicolet 510P. The samples were ground then diluted to ca. 5% w/w with ground KBr. Spectra were made up of 150 scans and resolution was set to 4 cm^{-1}.

All contour plots were plotted using only statistically significant regression coefficients (95% confidence).

Results and Discussion

Contour plots for insoluble matrix content as a function of processing temperature and BMI level at the lowest, middle and highest lubricant levels are presented in Figure 1. In these contour plots the role of the lubricant, in terms of influencing the location of BMI reactions, is clearly evident. Such effects are manifested as interesting changes in the temperature = 181°C plane of the contour plots; in this area the level of insoluble matrix increases with lubricant level. This observation points to a shift in the locus of addition reactions to BMI from the filler surface to the bulk matrix, this is most probably caused by preferential adsorption of the lubricant on the filler surface. The unmodified composite yielded an insoluble matrix content of 2.3% w/w, a figure consistent with strongly adsorbed matrix chains that are present in all unmodified particulate filled composites[7].

Table 1. Coded values for three-factorial experimental design

	Factor	-1.681	-1	0	+1	+1.681	Step
X_1	Temperature (°C)	180	190	205	220	230	15
X_2	BMI (% w/w)	0.29	0.60	1.05	1.50	1.81	0.45
X_3	Lubricant (% w/w)	0.05	0.42	0.96	1.50	1.87	0.54

In the BMI = 0.3% w/w plane of the plots, the temperature coefficient of the insoluble matrix response (the 181-229°C secant) goes from positive (at the lowest lubricant level) through to zero at around the middle level of lubricant, and then becomes strongly negative at the highest level of lubricant. At low lubricant levels a significant proportion of the filler surface is available for reaction with BMI, therefore, as temperature increases the rate of BMI-filler and BMI-matrix coupling reactions increases, thus explaining the increase in insoluble matrix content. Once the level of lubricant exceeds monolayer coverage of the filler surface, any additional lubricant will reside in the bulk matrix. At low processing temperatures the level of insoluble matrix is high due to BMI addition reactions in the bulk matrix resulting in crosslinking, principally of the random ethylene-propylene copolymer impact modifier (EP) phase; though our earlier work has also shown that significant chain extension and branching of the PP phase can also occur[4]. As processing temperature increases the role of the lubricant as a pro-degradant becomes clear. Degradation of polyolefins associated with fatty acids and fatty acid salts/derivatives is an effect that has been observed by the authors in ethylene vinyl acetate/fatty acid treated magnesium hydroxide composites[8], the purity of the fatty acid was found to affect composite thermal stability with the acid of greater purity having a

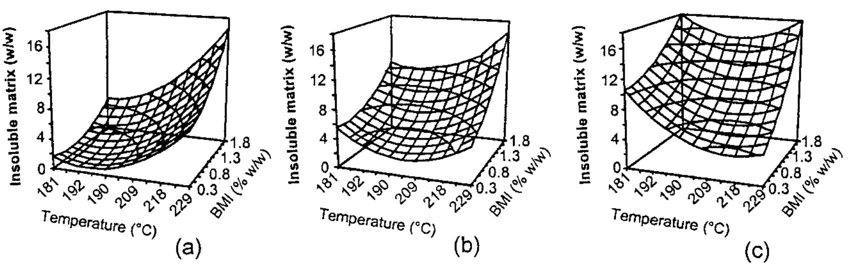

Fig. 1: Response surfaces showing the effect of processing temperature and BMI level on the insoluble matrix content at lubricant levels of; (a), 0.05%; (b), 0.96% and (c), 1.87%.

somewhat less detrimental effect. Therefore the fatty acid amide/ester based lubricant used in this study may be involved in reactions associated with degradation, particularly if it is hydrolysed back to the fatty acid. It may therefore be envisaged that chain scission of the PP phase particularly, will occur more rapidly than addition reactions to BMI, resulting in an overall decrease in the molar mass and a possible increase in the level of chain branching. Such an effect may explain the observed decrease in insoluble matrix content arising from increasing processing temperature at low BMI levels. At higher BMI levels the lubricant associated effects are balanced by addition reactions to BMI.

These data generally confirm the MFR (at max. temp and Max. BMI) versus lubricant level) data given in the previous paper[3], here the MFR decreased to zero then increased again at higher lubricant levels. These observations were explained by a change in the locus of BMI addition reactions from the filler surface, i.e., interphase structure development with minimal crosslinking of the bulk matrix, (at the lowest lubricant levels), to the bulk matrix itself (at intermediate to moderately high lubricant levels). At the highest lubricant levels the MFR increased due to an increase in the level of degradation and the conventional effect of a lubricant.

The crystalline content of the insoluble matrix in the composite residues was determined from the heats of fusion of PP determined by DSC and the insoluble matrix content determined from TGA. The insoluble matrix residue of the unmodified composite was 6% crystalline and the unfilled matrix was 35% crystalline. Response surfaces for the crystalline content as a function of processing temperature and BMI level at the three lubricant levels are given in Figure 2. The overall shape of the response surfaces was not significantly affected by the level of lubricant, though the position on the y-axis, i.e., overall crystalline content, was significantly affected by this parameter. Increasing lubricant level from the minimum to the middle level causes almost a step reduction in the crystalline content, whereas a further increase to the maximum lubricant level causes a rather more progressive decrease. On first examination these observations may seem a little unexpected, especially compared with the data obtained from samples that were solvent extracted under harsher conditions using decane[3]. Decane extraction is likely to result in more thorough extraction of the PP component, partly due to the higher temperature (175°C) and due to more rapid degradation of the PP during extraction. Extraction with xylene is likely to leave behind more PP and possibly preserve a greater proportion of linkages between PP blocks and EP blocks. Therefore the increased crystalline content observed at the lower lubricant level may be explained by preferential BMI and degradation induced crosslinking of the EP phase at the filler surface and the attachment of this phase to the filler surface (via the adsorbed BMI), thus forming the elastomeric interphase. These effects are likely to further increase the degree of phase separation and leave the PP layer surrounding the EP covering of the filler more depleted in ethylene than at an equivalent distance from an EP domain in the unfilled matrix; therefore resulting in a higher crystalline content in the surrounding PP layer. Increasing the level of lubricant such that the BMI adsorption sites on the filler are blocked causes a greater proportion of addition reactions to BMI in the bulk matrix, the EP phase cannot encapsulate the filler so readily and the driving force for enhanced phase separation is lost. Additionally reaction of PP macroradicals with BMI will increase the level of branching which together with the increased rate of degradation associated with the fatty acid derived component of the lubricant, will ultimately result in mixed structures of limited structural regularity being formed. These factors explain the observed reduction in crystalline content.

A typical DRIFTS spectrum of a boiling xylene insoluble composite fraction displaying the quantified peaks and baselines is shown in Figure 3. The response surface shape for the relative level of BMI ($Abs_{(BMI)}/Abs_{(OH)}$) in the composite residues as a function of processing temperature and BMI level is largely unaffected by lubricant level (Figure 4). However, a step increase in the data is evident as a result of increasing lubricant level from the minimum to the middle level.

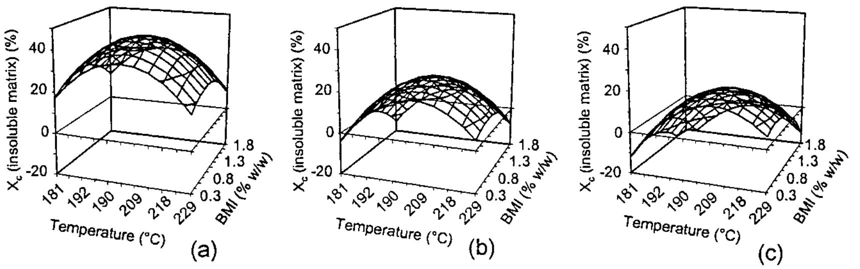

Fig. 2: Response surfaces showing crystalline content of insoluble matrix fraction as a function of processing temperature and BMI level at lubricant levels of (a), 0.05%; (b), 0.96% and (c) 1.87%.

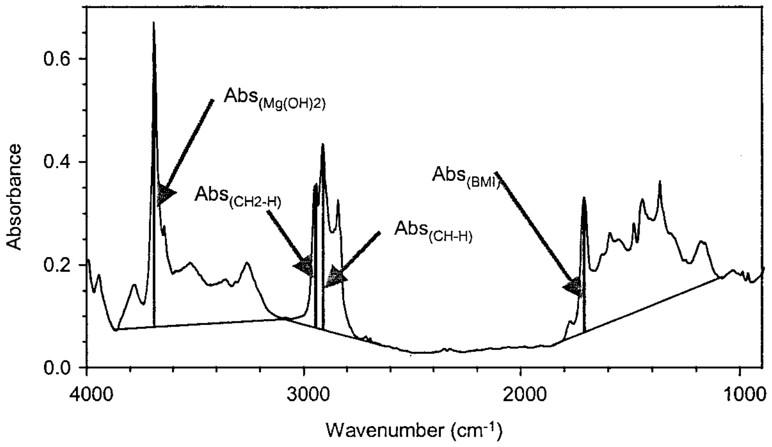

Fig. 3: Example DRIFTS spectrum of composite residue showing measured absorptions.

Whereas, increasing the lubricant level to maximum results in only a minimal change. The reduced level of BMI observed at the lowest lubricant level may be explained by its reaction with the filler surface; ring opening of the imide, to form the amide carboxylate, will result in a decrease in the carbonyl vibration frequency and intensity[4]. Close proximity to the filler surface may also result in the BMI being less resolvable through the relatively thick covering layer of polyolefin; most of the IR radiation will be absorbed in this layer particularly if the angle of incidence is low. Increasing the lubricant level to the extent that there is sufficient available to completely cover the filler surfaces results in an increase in the observed level of BMI in the composite residue, evidence that further verifies a shift in the locus of addition reactions to BMI. A sensible estimate of the level of added lubricant required to cover the filler is almost impossible to make because the structures (and relative proportions) of the fatty acids on which the amide/ester blend is based, are unknown, as is the proportion of lubricant able to reach the filler surface. However, the data given in the previous paper[3] suggest lubricant levels in the range 0.6-0.8% w/w are required to render the filler surface inactive to BMI, at least as far as the impact strength response is concerned.

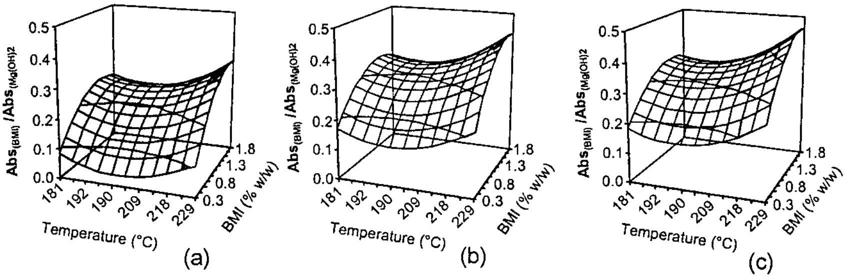

Fig. 4: Response surfaces for relative BMI level as a function of processing temperature and BMI level at lubricant levels of (a), 0.05%; (b), 0.96% and (c) 1.87%.

The relative ethylene content response ($Abs_{(CH-H)}/Abs_{(CH2-H)}$) provides further evidence that confirming elastomeric encapsulation of the filler. This can be seen in the temperature = 220°C plane of Figures 5(a) and (b), where at the lowest lubricant level the ethylene content is higher than at the middle level, this is particularly true at the lower BMI level. Furthermore, the ethylene content actually increases slightly with temperature at the lowest BMI and lubricant level. Under the latter conditions the layer of chain extended/crosslinked PP on top of EP layer is thin because there is just sufficient BMI available to interact with the filler and EP phase. Greater improvement in strength and toughness, however, are observed at higher BMI levels and processing temperatures. In this region the ethylene content decreases as a result of the increased thickness of the covering layer of chain extended/crosslinked PP. At the processing temperature = 181°C plane, however, the ethylene content is seen to increase progressively with increasing lubricant level. This may indicate that the EP phase (and BMI (figure 4)) is displaced from the filler surface and therefore reacts in the bulk matrix. Increases in processing temperature (when lubricant level > 0.05% w/w) may enable the BMI to react more readily with the filler and thus displace the lubricant, this may restore the ability for the filler to undergo encapsulation with the EP phase. However, the level of degradation (associated with the lubricant) and re-arrangement caused by addition reactions of PP and EP macro-radicals to BMI has caused severe damage to the properties of the matrix in this area that is reflected in the increased soluble matrix content and the reduced crystalline content. Previous work[3] has also shown that the composite mechanical properties are also relatively poor as a result of this change in structure.

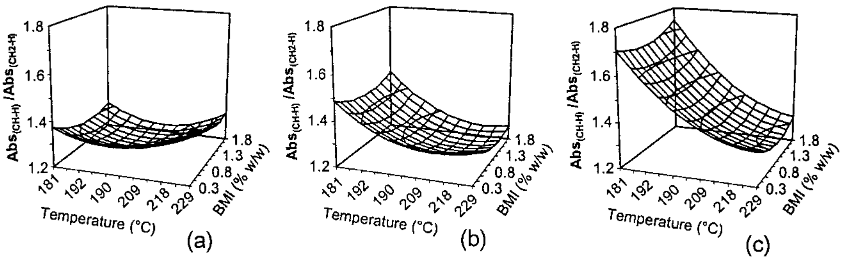

Fig. 5: Contour plots showing the effect of processing temperature and BMI level on the relative ethylene content in the insoluble matrix at lubricant levels of (a), 0.05%; (b), 0.96% and (c) 1.87%.

Conclusion

This study has successfully unravelled the interplay between BMI and lubricant adsorption on the filler and the resultant effect on the locus of addition reactions to BMI. Effective simultaneous improvement of tensile strength and toughness related properties requires a degree of chain extension/branching, and perhaps crosslinking, of the PP phase around the EP phase that encapsulates the filler. Such a condition cannot be met when the lubricant covers a significant proportion of the filler surface area. Under these conditions, adsorption of BMI and the EP phase is inhibited, resulting in a shift in the locus of BMI reactions from the interfacial region to the bulk matrix and thus preventing formation of the latterly described interphase structure.

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