Interphase Structure Development in Impact Modified PP/$Mg(OH)_2$ Composites Reactively Processed with 1, 3-Phenylene Dimaleimide

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Summary: Interphase modification of impact modified isotactic poly(propene) (IMPP)/ magnesium hydroxide ($Mg(OH)_2$) composites, via use of the reactive modifier 1, 3 phenylene dimaleimide (BMI) has led to the formation of compsites that have strength and toughness more than twice that of the unmodified composite. These significant improvements in properties were found (via response surface analysis, DSC and matrix extraction-DRIFTS studies) to be due to encapsulation of the filler particles with the elastomeric poly(ethene-co-propene) impact modifier phase of the IMPP. Acceptable processing characteristics can be realised together with excellent mechanical properties, via judicious addition of a lubricant (a fatty acid amide/ester blend) to the formulation.

Introduction

Halogen free flame retardants such as magnesium hydroxide are becoming commercially more significant as legislation regarding the use of halogenated polymer additives continually tightens. There are many reviews on the mode of action of such halogen free flame retardants and the reader is referred to Roger Rothon's book[1)]. In order to be effective, high loadings (60% w/w) of flame retardant fillers are required this causes a significant reduction in mechanical properties and poor melt rheology. The necessarily high level of filler causes the interfacial properties to be the major determinant of the bulk mechanical properties of the composites. In composites based on unmodified filler, interfacial properties are usually unsuitable for attainment of the required property profile. In many cases the situation is also exacerbated by poor dispersion of filler particles caused by poor wetting of the polar filler surfaces by the non-polar matrix

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melts. Therefore PP/$Mg(OH)_2$ composite properties can be improved and controlled via tailoring of the interphase.

The authors have published work on BMI modification of similar composites based on LLDPE[2)] and PP homopolymer[3)]. These latter studies have highlighted important differences in the mode of action of BMI that is dependent on the response of the given matrix to mechano-oxidative degradation. Therefore investigation of a copolymer of ethylene and propylene, where the polypropylene forms a continuous phase and ethene rich random poly(ethene-co-propene) (E co P) forms a dispersed elastomeric impact modifier phase, was considered worthwhile, and has resulted in composites with outstanding strength and toughness.

The aim of this paper is to gain insight into how the interphase structure develops in these composites and to understand how the excellent strength and toughness, that exceeds levels obtainable with silane based systems, is achieved.

Experimental

A central composite design approach 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. The levels used are presented in Table 1. The composites in this study were formed from ICI GXM216 IMPP (40 - (lubricant + BMI) (% w/w)) and untreated $Mg(OH)_2$ (Duhor N) (60% w/w) from 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 and 3.0 mm thickness (for production of tensile and impact test pieces, respectively).

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 (22°C (±1°C)) 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), in order to isolate the toughening effect of the elastomeric domains.

The level of bound matrix was determined via Soxhlet extraction with n-decane. In order to maintain a high extraction temperature and rapid reflux rate, the apparatus was thoroughly lagged with glass wool and aluminium foil. Extraction with decane continued for three days and was followed by extraction with hexane for 24 hours. The composite residues were then dried to constant mass at 70 °C and the bound matrix content then determined by ignition at 1000 °C, after taking account of the mass loss of on ignition of pure $Mg(OH)_2$, due to dehydration.

The composite residues (powdered by abrasion with silicon carbide paper and diluted to ca. 5 % w/w in KBr) were analysed using DRIFTS (Spectra-Tech DRIFTS cell in Nicolet 510P). Spectra were made up of 150 scans and resolution was set to 4 cm^{-1}. The crystalline content of the bound matrix on the composite residues (10 mg samples of residue in sealed aluminium pans) was assessed by DSC (Perkin-Elmer DSC-7) using a heat-cool-heat cycle under an N_2 atmosphere. Heating/cooling rate was 20 °C min^{-1} and start and end temperatures were 30 °C and 220 °C, respectively. The sample was held for 5 minutes at 220 °C after the first heat.

Results and Discussion

Examination extrapolated data (Fig. 1-3) from the maximum processing temperature (X_1), maximum BMI level (X_2) axis of the contour plots yields very interesting trends that afford considerable insight into how the interphase structure develops. Interestingly, there is a discontinuity in the MFR data (Fig. 1) between 0.2 and 1.4 % w/w lubricant. Within this range (region B), the melt viscosity can be considered zero. In region A the melt viscosity reduces to zero but in region C melt viscosity increases.

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

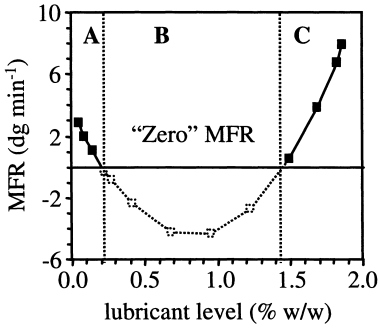

Fig. 1: Effect of lubricant level on extrapolated values of MFR (at max. X_1, max. X_2 line)

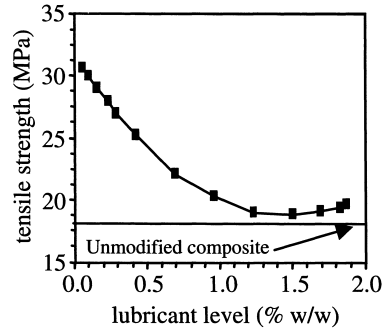

Fig. 2: Effect of lubricant level on extrapolated values of tensile strength (at max. X_1, max. X_2 line)

Within Region A composite strength and toughness are at least double that of the unmodified composite (Fig. 2+3). Once into region C, impact strength had fallen below that of the unmodified composite and tensile strength reaches the level of the latter composite. The reduction in MFR within region A is thought to be due hindrance of interphase formation caused by preferential adsorption of the lubricant on to the filler. In the absence of lubricant, the BMI is able to adsorb on to the $Mg(OH)_2$ via an amide carboxylate[3)], and the interphase structure then develops via addition of PP and preferentially, random (E co P) macro-radicals to the maleimide alkene[2,3)]. Blockage of adsorption of BMI will therefore cause these addition reactions to occur within the bulk matrix; with both maleimide alkene groups readily accessible to macro-radicals, chain extension and branching proceeds more rapidly than chain scission, with the result that melt viscosity sharply increases. This effect was confirmed by TGA studies (Fig. 4) on composites containing 1.05 % BMI with no lubricant and with 0.96 % lubricant, a level right in the middle of region B. It is readily evident that the composite containing no lubricant degrades far more rapidly, indicating the bulk matrix consists of low molar mass chains, possibly resulting from a predominance of chain scission during processing. The composite containing lubricant is far more stable due to the presence of chain extended and crosslinked structures arising from addition reactions with free BMI in the matrix. Within Region C, the melt viscosity is reduced to such an extent, via plasticisation by the lubricant, that insufficient shear forces for chain scission, and hence

macro-radical production are developed. Therefore the rate of BMI addition reactions reduces and matrix plasticisation becomes the dominant effect.

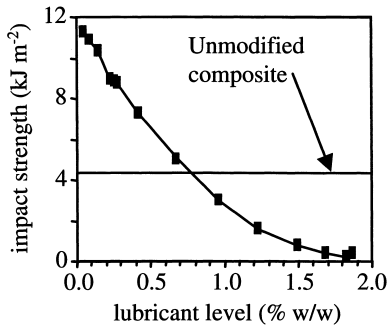

Fig. 3: Effect of lubricant level on extrapolated values of impact strength (at max. X_1, max. X_2 line)

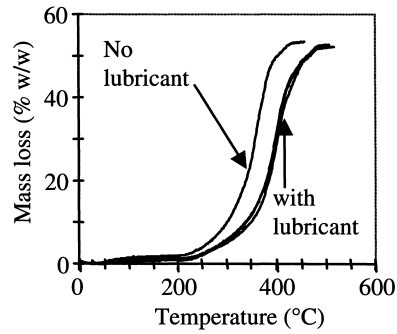

Fig. 4: Effect of lubricant on thermal stability of composites

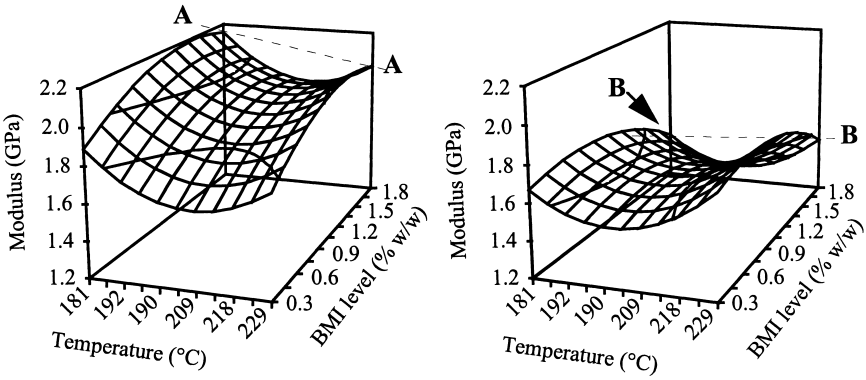

Fig. 5: Contour plots showing effect of lubricant on modulus versus processing temperature behaviour; left, lubricant level is 0.05 % w/w (minimum level); right, lubricant level is 1.87 % w/w (maximum level).

Together with the simultaneous attainment of high strength and toughness, the effect of processing temperature on the tensile modulus at the maximum BMI level provides clear evidence of filler encapsulation by the IMPP elastomeric phase. As the lubricant level

range is traversed (Fig. 5), the change in modulus, from lowest to highest processing temperature, ranges from strongly negative to slightly positive (compare slopes of secants A-A and B-B on Fig. 5). The negative difference at low lubricant levels is due to elastomeric encapsulation, which is confirmed by DRIFTS studies on residues from matrix extracted composites (Fig. 6c), where the methylene C-H stretch (2920 cm^{-1} and 2850 cm^{-1}) is stronger. Similar spectral data has been obtained for vinyl silane modified composites[4]. DSC analysis (Table 2) confirms this assignment as the crystalline content of the residue from the BMI modified IMPP based composite is much lower than that of an equivalent composite based on PP homopolymer. The carbonyl absorption present in the DRIFTS spectrum for the unmodified composite residue (Fig. 6a) may be due to degradation during processing and during extraction. At higher lubricant levels, the modulus difference becomes positive (secant B-B on Fig. 5) because chain extension within the bulk matrix becomes more significant, but not to the extent that the melt plasticisation effect of the lubricant is overshadowed.

Conclusions

The excellent mechanical properties achievable with the IMPP/$Mg(OH)_2$/BMI system can be attributed to elastomeric encapsulation of the filler by the impact modifier phase of the IMPP. For this encapsulation to occur, lubricant levels need to be kept low so that sufficient filler surface is available for BMI adsorption. BMI has significant potential as an interphase modifier for IMPP/$Mg(OH)_2$ composites; the mechanical properties achievable are above those attained with more expensive silane based systems that often require an additional (and hence expensive) filler pre-treatment step. Even greater improvements can be realized by the industrially utilized twin screw extrusion compounding - injection moulding composite formation route. Details of these studies will be published separately.

Table 2. Analysis of composites after Soxhlet extraction with decane and hexane.

Composite	Bound matrix content (% w/w on filler)	crystalline content of bound matrix (%)	$A_{(C\text{-}H)s}/A_{(O\text{-}H)s}$
Unmodified	6.1	no peaks	0.42
3% BMI, 60% $Mg(OH)_2$, 37% IMPP	19.5	3.4	1.73
as above but with PP homopolymer	8.9	14.4	0.81

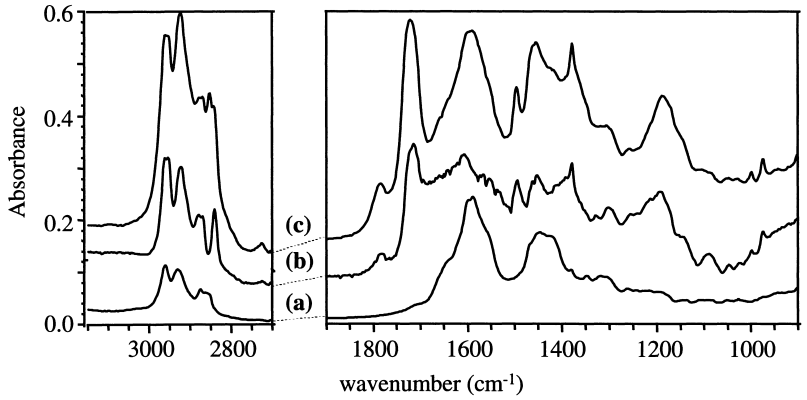

Fig. 6: DRIFTS spectra of filler residues after decane extraction, (a) unmodified composite, (b) BMI modified composite based on PP homopolymer, (c) BMI modified composite based on PP block copolymer.

References

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