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Reactive processing of particulate filled polymers: *m*-phenylene bismaleimide modified polyethylene/magnesium hydroxide composites

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Summary

The influence of processing temperature and the presence of the reactive modifier, m-phenylene bismaleimide (BMI), on the formation of highly filled polyethylene/$Mg(OH)_2$ composites has been investigated using central composite design methods. Infrared spectroscopic and differential scanning calorimetric evidence produced suggests that maleimide C=C bonds are involved in a free radically induced process which leads to extended and crosslinked polyethylene chains being produced, some of which encapsulate the filler particles, resulting in formation of a crosslinked interphase. This effect resulted in increased tensile strength and reduced composite melt flow rate (MFR).

Introduction

Presently, considerable interest is being shown in the use of magnesium hydroxide based polyolefin composites for the production of flame retardant mouldings which not only meet the UL94 VO (vertical burn) rating, but also meet the various political and environmental demands for artefacts which display low smoke and toxic gas emissions when in a fire (1). However, the large amount (at least 60% by weight) of the flame retardant magnesium hydroxide required in the composite, to achieve these desirable features, creates major difficulties in relation to filler-matrix mixing and melt processing, as well as potentially severely compromising final composite mechanical properties, particularly tensile and impact strengths (2). To a some extent these difficulties can be overcome by treatment of the filler particles with special coatings that modify the filler's surface characteristics such that its dispersibility in the matrix and/or filler-matrix adhesion are significantly improved (3-9).

In our laboratories, a variety of filler coating/coupling agents are currently being investigated, as it is now widely recognised that the filler-polymer matrix interphase is a critical region in relation to optimisation of composite mechanical properties. Certain vinyl silanes, maleanised polybutadiene and m-phenylene bismaleimide (BMI) (10-12) are proving to be particularly interesting agents, as they appear to facilitate the chemical or

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physical bonding of filler particles to the polymer matrix and offer scope for the production of composites with acceptable mechanical properties. Indeed, our studies of vinyl silane or maleanised polybutadiene treated $Mg(OH)_2$/rubber modified polypropylene (PP) composites indicate that when the materials are blended in the presence of a peroxide initiator, the individual filler particles are encapsulated by the dispersed rubber phase which is also chemically bonded to the polyolefin matrix (13,14). We believe that this rubbery interphase between the filler particle surface and the thermoplastic matrix is an important pre-requisite in achieving a good balance between composite strength and toughness. Currently, we are investigating the use of BMI as an alternative to a vinyl silane or maleanised polybutadiene in the $Mg(OH)_2$/PP system.

The purpose of this paper, which is one of a number of closely related papers we are publishing in this topic area, is to report on studies that we have been undertaking on the incorporation of BMI in a $Mg(OH)_2$/polyethylene (PE) composite at the blending stage, and the impact that this can have on composite processing and product mechanical properties. During the blending of the materials, we believed that thermo-mechanically generated PE free radicals react with the BMI C=C groups to produce extended or crosslinked PE structures. Of particular interest in our studies has been the nature of the interphase between the filler particle and the PE matrix, the type and level of bonding between filler surface and the matrix, and the amount of polymer physically or chemically bound to filler particles.

Experimental

Materials Linear low density polyethylene (LLDPE) - Escorene LL 1004 YB was supplied by Exxon Chemicals, US; its Melt Flow Rate was 2.8 dg min^{-1} (190 °C, 2.16 kg). Magnesium hydroxide was supplied by Duslo Sala, Slovakia. m-Phenylene bismaleimide was a commercial product supplied by VUAS, Pardubice, Czech Republic.

Experiment design Factorial experimental design was used to assess the influence of BMI concentration and blending temperature on composite Melt Flow Rate (MFR) and tensile strength. Relevant data for the two-factorial rotatable central composite design with its five levels for both BMI concentration and blending temperature are given in Table 1. Thirteen trial formulations were investigated and the general form of the associated second order polynomial was as follows:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2 + b_{22}X_2^2 + b_{11}X_1^2$$

Composite formation $Mg(OH)_2$ (60% w/w), LLDPE and BMI were melt blended with using a two roll mill the temperature region of 160-189°C (10 minutes mixing time) and 0.8 mm thick test plaques were formed by compression moulding. A composite containing the filler but no BMI, and an unfilled matrix control was also prepared.

Table 1 Coded and real values for experimental design

	factor	-1.414	-1	0	1	1.414	Li
X_1	temperature (°C)	160.86	165	175	185	189.14	10
X_2	BMI (wt. %)	0.286	0.7	1.7	2.7	3.114	1

Mechanical testing ASTM D 638M Type M-III tensile dumbbell test pieces were cut from the compression moulded sheets and tensile strength was measured using a crosshead speed of 50 mm min^{-1}.

Physico-chemical Analyses Filler-bound polymer level was deduced by extracting a sample of composite with xylene in a well lagged Soxhlet apparatus for 72 hours, with the thimble carrying the composite sample kept at 130°C. After this period, traces of xylene were removed from the composite residue by subjecting it to Soxhlet extraction with hexane for 24 hours. Finally, the composite residue was dried overnight in an oven at 70°C. Diffuse reflectance Fourier transform infrared spectra (DRIFTS) of the residues were obtained using a Nicolet 510P FTIR bench fitted with a Spectra-Tech DRIFTS cell. Spectra were made up of 150 scans with a resolution of 4 cm^{-1}. Specimens were diluted with finely ground KBr. The bound matrix content was determined by mass loss on ignition of the composite residues at 1100°C.

Composite MFRs were measured at 190°C using a 17.0 kg load, with a 5 minute equilibration period prior to measurement. All other parameters were to ASTM D 1238.

Differential scanning calorimetry (DSC) studies were carried out using a Perkin-Elmer DSC-7. Samples were heated from 20°C to 150°C at 20°C min^{-1}, held at 150°C for 5 minutes, cooled from 150°C to 20°C at 20°C min^{-1} and reheated from 20°C to 150°C at 20°C min^{-1}. Crystalline content was determined from first heat melting endotherms, taking the heat of fusion of perfectly crystalline PE as 277 J g^{-1}.

Results and discussion

Figure 1 displays contour plots yielded by the factorial experiment design analysis of the blending of the $Mg(OH)_2$ and PE in the presence of BMI. The influence of processing temperature and BMI concentration on composite MFR and tensile strength are quite clear. Composite tensile strength increases significantly with BMI concentration and blending temperature. The data indicate that with the maximum BMI concentration of 3% w/w and a maximum blending temperature of 189°C, a composite tensile strength 50% higher than the unmodified composite can be obtained. The unfilled matrix and unmodified composite achieved tensile strengths of 24.4 and 19.4 MPa, respectively.

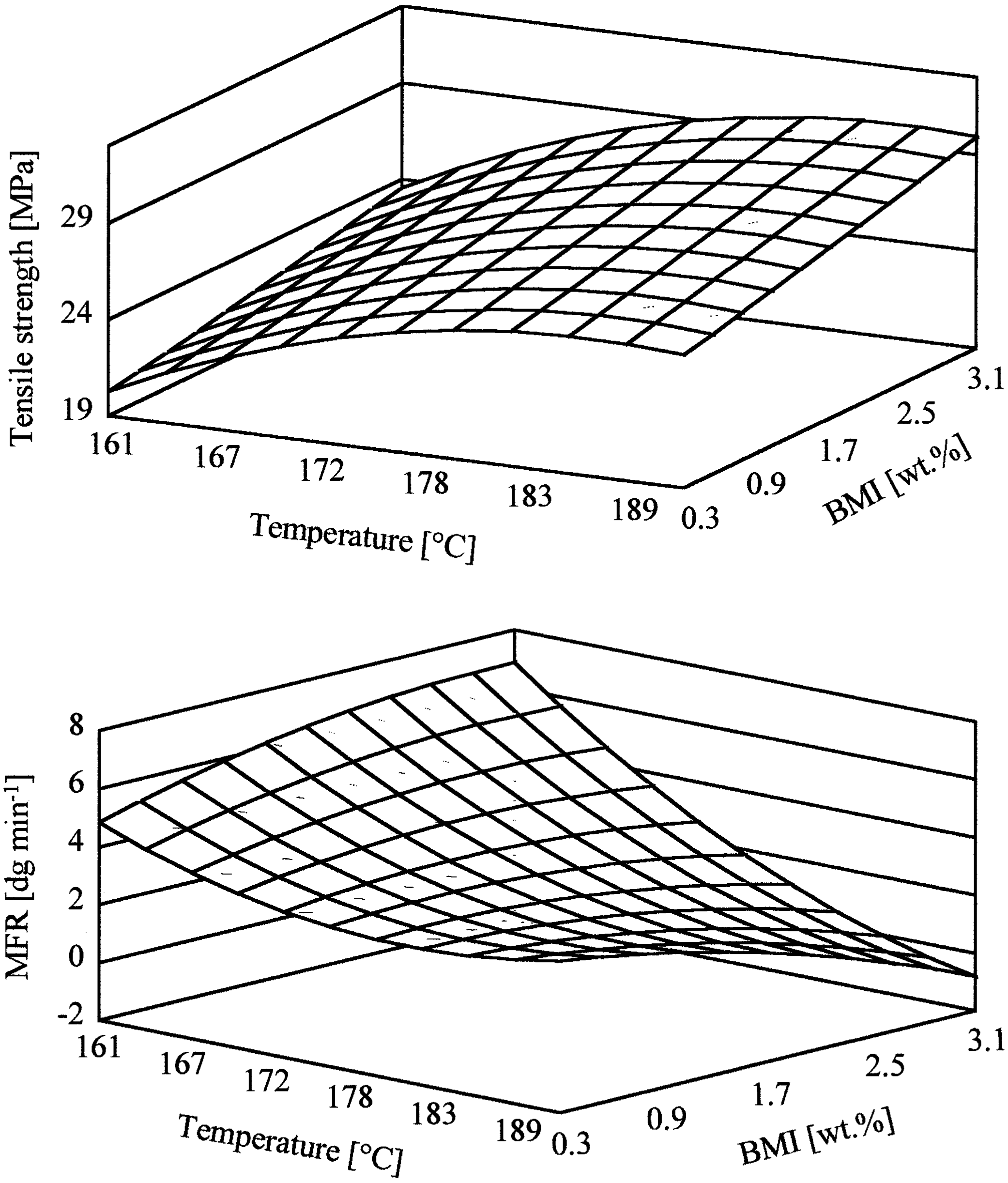

Figure 1 Contour plots showing the influence of BMI concentration and processing temperature on the tensile strengths and MFR of $Mg(OH)_2$/LLDPE composites.

At high BMI levels and low blending temperatures the composite MFR is greater than that of the unmodified composite (4.6 dg min^{-1}) and reflects a lubrication effect afforded by the BMI in the melt. However, as the BMI concentration and blending temperature increase composite MFR falls significantly, as the likelihood of the development of extended or crosslinked PE chains increases to a point where the composite MFR falls to such a low level that the composite would be very difficult to process.

The following studies focus on two composites, denoted A and B, which contain the lowest (0.3% w/w) and highest levels (3.1% w/w) of BMI, respectively. Blending temperature for both was 175°C.

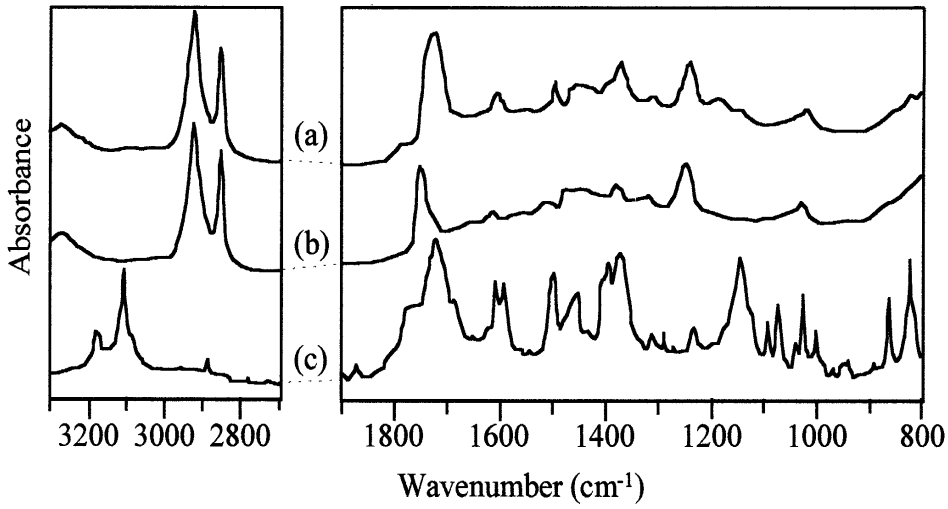

Figure 2 DRIFTS spectra of dried composite residues; (a) composite B, (b) composite A, and (c) BMI alone in KBr for comparison. (a) and (b) are normalised to the OH stretch of $Mg(OH)_2$ at 3697 cm^{-1}.

Following the removal of soluble materials from Composites A and B, via hot xylene Soxhlet extractions, bound polymer levels for these composites were determined to be 6.1% and 9.8%, respectively. These values are in line with bound polymer levels that we have found with other systems we have investigated (5).

FTIR analyses of each of the dried composite residues left after hot xylene extraction of Composites A and B (Figure 2 (a) and (b)), indicate the presence of an imide carbonyl stretching absorption centred at 1725 cm-1, with the absorption being strongest for the residue from Composite B, the composite containing the highest level of BMI. In both these spectra, there is little evidence for the presence of the maleimide alkene C-H stretching bands at 3110 cm^{-1}. In addition, the C=C stretch at 1600 cm^{-1} and C-H bending at 1397 cm^{-1} are also reduced in intensity relative to pure BMI (Figure 2(c)). These changes indicate that the maleimide alkene has reacted, presumably in the radical based mechanism discussed below. Other changes associated with the BMI in the extracted composites are also apparent and are further evidence for the formation of new bonds, these are as follows: The imide carbonyl band shape in the extracted composites is different to that of pure BMI and the band centred at 1240 cm^{-1} appears to grow in intensity at the expense of the pure BMI band at 1146 cm^{-1}. Chemical interaction between the $Mg(OH)_2$ surface and the BMI could potentially occur via a carboxylate salt that forms from base ($Mg(OH)_2$) catalysed fission of the C(O)-N bond (15). However, infrared evidence for formation of a carboxylate salt is weak, though a carboxylate salt carbonyl may form a component of the reduced C=C stretching absorption at ca. 1600 cm^{-1}. Further studies on these reactions are ongoing and will be reported soon.

The crystallinity in the unfilled matrix and the composite based on untreated filler was found to be 33% and 28%, respectively (Figure 3(a) and (b)). However, following blending of the polymer and filler in the presence of BMI, the crystalline content and maximum melting peak temperature had reduced to 12-15% and ca. 75°C, respectively. Figure 3(c) shows fusion behaviour typical of all BMI based composites within the range investigated.

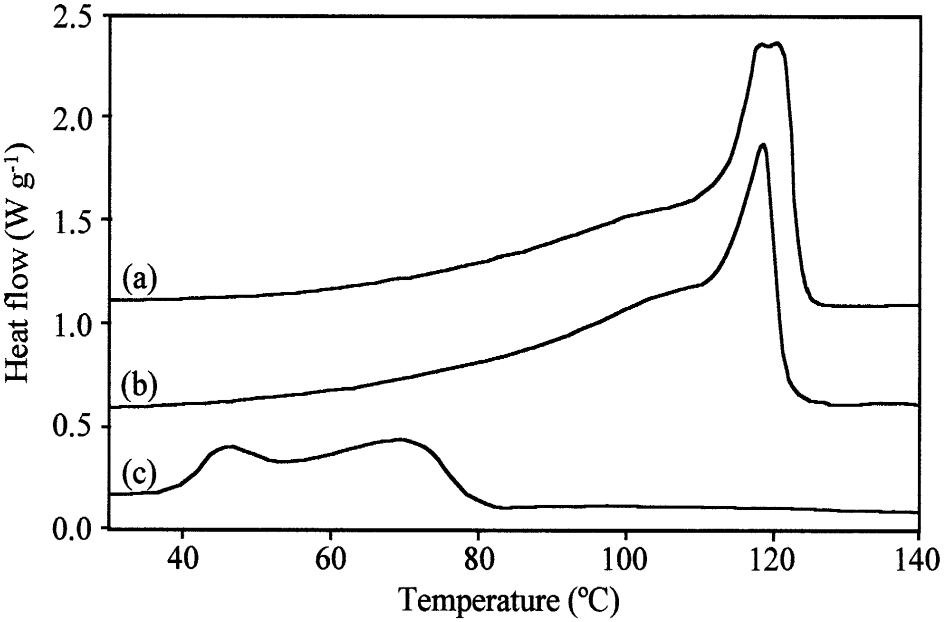

Figure 3 Matrix mass normalised DSC data (first heat) for; (a) unfilled matrix, (b) composite based on untreated $Mg(OH)_2$, (c) composite containing BMI and $Mg(OH)_2$.

The polymer found bound to the $Mg(OH)_2$ filler particles, however, was, as might be expected, substantially lower in crystallinity; the two samples analysed (Composites A and B) showed crystallinity values of 3.7% and 5.5%, respectively.

We are interpreting the above evidence to suggest that free radicals, generated by the thermo-mechanical degradation of the PE, consume the vast majority of maleimide alkene groups in the formation of branched/extended or crosslinked PE structures, some of which become bound to the filler particles. The significant reduction in melting point and crystalline content arising from BMI addition shows that the chain branching/extension and crosslinking effects are likely to pervade throughout the matrix. If the crosslinking were confined to the interphase region only, the effect on matrix crystallisability would not be so profound. This could be verified by melt blending of BMI and PE, followed by DSC and xylene extraction of the blend, however, our studies with other polyolefins (to be published soon) have indicated that reaction will not occur if $Mg(OH)_2$ is absent. The latter statement reflects an enhanced rate of thermo-mechanical degradation caused by the high viscosity of the composite melt, relative to an unfilled matrix/BMI blend. Given the apparently high level of BMI associated PE crosslinking, the bound matrix contents obtained for the composites are unexpectedly low and may be an artefact associated with crosslink degradation during the high temperature xylene extraction. The nature of the bonding of this polymer to the filler particles is far from clear. Ongoing work, which will be reported in the near future, has indicated the existence of some form of interaction. However, our data also suggests that the filler-matrix interaction within these composites may not be entirely associated with chemical interactions; a physical/entrapment process may also be involved. A similar mechanism has been postulated by Demjén and co-workers (16,17) for the silane coated calcium carbonate/PP composites they have investigated, where they considered the filler particles to be physically linked to the polypropylene matrix through an interphase of crosslinked polymer.

Conclusions

Reactive melt processing of magnesium hydroxide and low density polyethylene with m-phenylene bis-maleimide, particularly where the filler is the dominant phase, can afford acceptable and useful composites, with higher tensile strengths than the unfilled polymer. These results are in line with those achieved by us with similar based polypropylene systems, and once again reflect the effectiveness of the maleimide in promoting encapsulation of filler particles with an extended or crosslinked polyethylene interphase which, in the system being reported, is responsible for physically binding the polyethylene matrix to the filler particles and enhancing tensile properties.

Obituary During the course of writing this paper Dr Joe Hurst sadly died whilst on University business in the Slovak Republic. This paper is dedicated to his memory.

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