Interphase Control in Poly(styrene-*block*-butadiene-*block*-styrene) Copolymer/Magnesium Hydroxide Composites

Paul Dumitru, Graham C. Lees, Christopher M. Liauw, Roger N. Rothon*

Department of Chemistry and Materials, Faculty of Science and Engineering,
The Manchester Metropolitan University, Manchester M1 5GD, UK

Summary: The role of isostearic acid (ISA) and maleinised polybutadiene (MPBD) in the interphase control of SBS/magnesium hydroxide composites was investigated. Infrared studies showed that both ISA and MPBD interact chemically with the magnesium hydroxide. Flow microcalorimetry studies showed that model polymers that resemble the two phases of SBS (polybutadiene and polystyrene), were absorbed irreversibly on the surface of magnesium hydroxide. Differences in mechanical responses showed that filler surface modification with MPBD led to increased filler-matrix adhesion compared to the composite based on untreated. ISA treatment of the filler led to reduced melt viscosities and filler-matrix interaction, but resulted in higher levels of strain induced crystallization, relative to the composites based on untreated and MPBD treated magnesium hydroxide.

Introduction

Magnesium hydroxide is now recognized as one of the major inorganic flame retardant and smoke suppressant fillers. In order to achieve flame retardancy, at least 60% w/w must be incorporated into the polymer matrix[1-3)]. These systems have two principal disadvantages: difficulties in melt processing, due to high melt viscosity, and a significant reduction in the mechanical properties. In order to surmount these problems the interphase region between the filler and the polymer matrix must be modified and the dispersion quality of the filler must be maximized. These objectives can be achieved via surface modification of the filler[4)]. Poly(styrene-b-butadiene-b-styrene), SBS, is a tri-block polymer consisting of a two phase morphology which is responsible for its mechanical and rheological properties[5-7)]. It is used in a wide range of applications, from adhesives, sealants and coatings, to medical and automotive applications and for wire and cable coatings. The latter three applications require flame retardancy that can be afforded by incorporation of flame retardant fillers (e.g., magnesium hydroxide). Highly filled SBS has received very little attention in the literature with respect to the effects of filler surface modification[8-9)]. Therefore the purpose of this

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paper is to investigate effect of filler surface modification on the interfacial properties of highly filled (60% w/w) SBS/magnesium hydroxide composites.

Experimental

Materials. Poly(styrene-b-butadiene-butadiene) (SBS) – Kraton D1102 CU was supplied by Shell Chemicals UK Ltd. Its styrene content was 27.5% (w/w) and its melt flow rate was 6 g min^{-1} (200°C, 5 kg). Magnesium hydroxide ($Mg(OH)_2$) – Magnifin H10 was supplied by Martinswerk Gmbh, Austria. The surface modifiers used were: isostearic acid (ISA) – Prisorine 3505, provided by Unichema Chemie, the Netherlands, and maleinised polybutadiene (MPBD) – Lithene N4-9000 (LX-16) - 10MA supplied by Revertex Ltd, UK.

Filler studies. For characterisation of layer structure magnesium hydroxide was coated with different levels of ISA and MPBD by deposition from toluene. The monolayer levels of the two surface modifiers were determined using a sedimentation volume approach developed by Liauw10). Diffuse reflectance Fourier transformed infrared spectroscopy (DRIFTS) of the coated filler were obtained using a Nicolet 510P FTIR filled with a Spectra-Tech DRIFTS cell. The samples used for DRIFTS were diluted to 5% treated filler in KBr and the spectra were recorded using 150 scans with a resolution of 4 cm^{-1}. Flow microcalorimetry (FMC) studies were conducted using a Microsal 3V (PTFE fluid path). FMC experiments were carried out at 30 ± 1°C. The carrier fluid was heptane, stored over freshly activated 4A molecular sieves. The absorbents used were low molar mass polybutadiene ($\overline{M}_n = 3680$) and polystyrene ($\overline{M}_n = 1800$) from Aldrich.

Composite preparation. Magnesium hydroxide was coated with ISA by dry blending in a TK Fielder mixer whereas MPBD coating was conducted in-situ during compounding, ensuring one monolayer of coverage for both modifiers. Composites containing untreated and surface modified filler (ISA and MPBD) were formed using a Betol BTS 30 twin-screw extruder. A fractional experimental design (central composite two-factorial rotatable design) was run in order to find the simultaneous effect of the two surface modifiers on the mechanical and rheological properties of the composites. The levels of surface modifiers used in the experimental design are presented in Table 1. For the experimental design the filler was first pre-coated with ISA and then MPBD was added in-situ during compounding. The filler level in all the composites was 60% w/w. The composites were injection moulded using a Negri-Bossi NB 60 injection moulding machine fitted with a gated, 8 mm x 8 mm x 2.5 mm plaque mould.

Table 1. Coded and real values for experimental design

	Factor	-1.414	-1	0	1	1.414
X_1	Number of ISA monolayers	0.50	0.71	1.25	1.79	2.00
X_2	Number of MPBD monolayers	0.20	0.46	1.10	1.74	2.00

Mechanical testing. Tests were carried out according to BS 903 Part A2 (equivalent to ISO 37) using type 2 dumb-bell test. Test pieces were produced by die punching from the moulded plaques and the tensile properties were determined using a Hounsfield M-series (HTE 10) tensometer fitted with a laser extensometer and a 1000 N load cell.

Rheological testing. Rheological studies were carried out using a Rosand RH7-7 capillary rheometer attached to a computer running V6.01 software. The type of test used was a two-barrel test using a 16 mm die with a diameter of 1 mm. The shear rate range was 100 s^{-1} to 5000 s^{-1}.

Results and discussion

Sedimentation volumes of magnesium hydroxide treated with ISA and MPBD versus the level of treatment are presented in Figure 1. It is believed that the surface treatment reduced the agglomerate size thus increasing the packing density of the filler, which resulted in a lower sedimentation volume. When complete coverage was attained (i.e., one monolayer), the excess modifier had negligible effect on the packing density of the magnesium hydroxide, and consequently the sedimentation volume reached a limiting value. Therefore sedimentation volume measurements yielded monolayer levels of 10 mg g^{-1} and 20 mg g^{-1} for ISA and MPBD of respectively. The infrared spectra of ISA treated magnesium hydroxide samples used in sedimentation volume studies are presented in Figure 2. The spectra show the magnesium isostearate carboxylate carbonyl vibration at 1580 cm^{-1}. This peak continued to grow in intensity even though the monolayer level had been exceeded. No free acid carbonyl (1715 cm^{-1}) could be detected, even at the highest treatment level. It is known11) that the excess acid reacted with the magnesium hydroxide forming a salt, which was soluble in toluene. After evaporation of the toluene, the soluble salt was deposited on the filler surface thereby giving rise to the increasing in carboxylate carbonyl absorption, even at coverages beyond monolayer. The infrared spectra of MPBD treated magnesium hydroxide, shown in Figure 3 showed an absorption at 1620 cm^{-1} which was associated with the reaction between the filler and the surface modifier. Compared to ISA, MPBD showed a specific peak for the unreacted acid (found by hydrolysis of the anhydride) (1720 cm^{-1}) beyond the monolayer coverage.

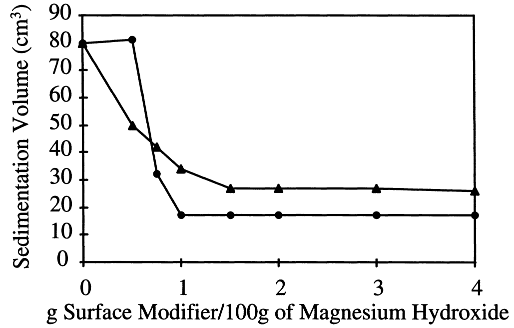

Fig. 1: Sedimentation volume data; (●) ISA treated $Mg(OH)_2$; (▲) MPBD $Mg(OH)_2$ treated.

Flow microcalorimetry was used in order to characterize the adsorption/desorption chemistry of the SBS polymer chains on the filler. As SBS consists of two phases, there is a possibility of preferential absorption by either the polybutadiene or polystyrene phase. In order to afford some insight into which component will preferentially absorb, FMC studies were carried out using low molar mass polybutadiene and polystyrene as model systems. The FMC results are presented in Table 2. Comparison of the heats of adsorption and heats of desorption and levels of adsorption and desorption shows that significant amounts of these model polymers are retained on the filler surface. The heat of adsorption for the polybutadiene was higher than polystyrene and it may therefore be argued that polybutadiene (from SBS) may preferentially adsorb onto the magnesium hydroxide and thus encapsulate the filler. Adsorption of the model polymers onto magnesium hydroxide having a FMC deposited layer of ISA results in a five-fold return in heat of adsorption (Table 3). This data confirmed that the strength of the interaction with either of the phases of SBS is likely to be significantly reduced if a fatty acid pre-coating is present. This observation confirms the work of Pukánszky(12). In such cases preferential encapsulation may not take place. Filler surface modification with MPBD led to an increase in tensile yield stress of the SBS/magnesium hydroxide composite suggesting enhanced filler-matrix adhesion, whilst ISA modification resulted in a decrease of this parameter relative to the control composite based on untreated filler (Figure 4). Stress-strain curves showed that the fatty acid treatment promoted strain induced crystallisation of the composite matrix, a phenomenon that led to the increased ultimate tensile properties relative to the unmodified composite and composites modified with MPBD. Melt rheological characterization (Figure 5) of the composites showed that filler surface modification led to a decrease in the shear viscosity, relative to when untreated filler is used.

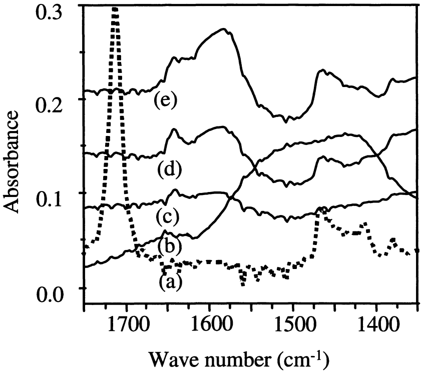

Fig. 2: Family of substrate subtracted DRIFTS spectra for ISA treated $Mg(OH)_2$; (a) pure ISA (shrunk to fit), (b) untreated $Mg(OH)_2$, (c) 5.0 mg g^{-1}, (d) 10.0 mg g^{-1}, (e) 20 mg g^{-1}.

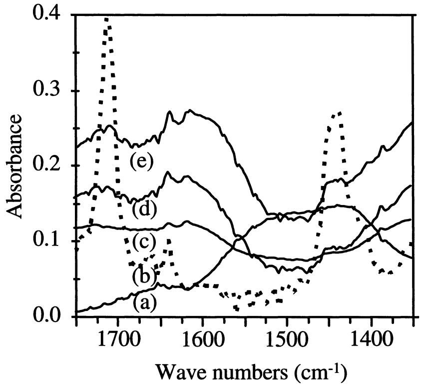

Fig. 3: Family of substrate subtracted DRIFTS spectra for MPBD treated $Mg(OH)_2$; (a) pure MPBD (shrunk to fit), (b) untreated $Mg(OH)_2$, (c) 5.0 mg g^{-1}, (d) 20.0 mg g^{-1}, (e) 30 mg g^{-1}.

Table 2. FMC data for adsorption and desorption of low molar mass polystyrene and polybutadiene onto magnesium hydroxide from n-heptane

	Adsorption		Desorption	
	Heat of adsorption (mJ m^{-2})	Amount adsorbed % (w/w)	Heat of Desorption (mJ m^{-2})	Amount desorbed % (w/w)
Polybutadiene	-75.5	0.23	19.9	0.02
Polystyrene	-59.7	0.56	15.5	0.19

Table 3. FMC data for adsorption and desorption of low molar mass polystyrene and polybutadiene onto ISA precoated magnesium hydroxide from n-heptane

Adsorption of polystyrene		Adsorption of polybutadiene	
Heat of Adsorption (mj m^{-2})	Amount Adsorbed % (w/w)	Heat of Adsorption (mj m^{-2})	Amount Adsorbed % (w/w)
-13.7	0.013	-8.4	0.023

A response surface study was conducted in order to determine whether there is any synergism between the ISA and MPBD treatments (Figures 6-7). From these response surfaces it is evident high strength together with good flow properties can be obtained using middle to high levels of ISA and lower levels of MPBD. The ultimate tensile properties are dominated by strain induced crystallization arising from poor filler-matrix adhesion resulting from ISA treatment. It is also interesting to note that use of high levels of ISA affects the increase in melt viscosities observed when MPBD levels are high and ISA levels are low. This trend may be explained via the interplay that must exit between the following factors; formation of macro-radicals in the melt (caused by mechanical shear); lubrication of the melt, (caused by excess ISA); and coupling of filler and matrix (via entrapment of SBS chains in the web of absorbed MPBD and/or addition of SBS macroradicals to the absorbed MPBD).

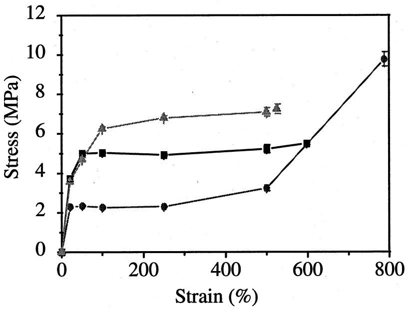

Fig. 4: The effect of surface modification on the tensile properties of SBS/$Mg(OH)_2$ composites; (■) untreated $Mg(OH)_2$, (▲) MPBD treated $Mg(OH)_2$, (●) ISA treated $Mg(OH)_2$.

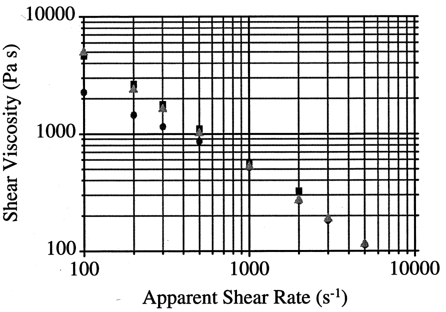

Fig. 5: The effect of surface modification on the flow behavior of SBS/$Mg(OH)_2$ composites; (■) untreated $Mg(OH)_2$, (▲) MPBD treated $Mg(OH)_2$, (●) ISA treated $Mg(OH)_2$.

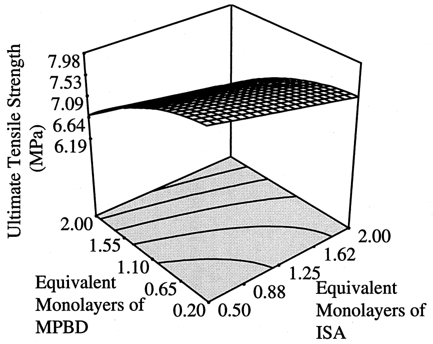

Fig. 6: The effect of ISA and MPBD on the ultimate tensile strength of $SBS/Mg(OH)_2$ composites.

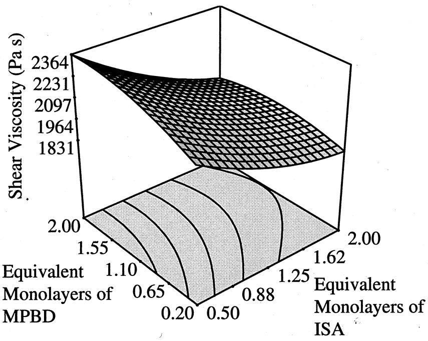

Fig. 7: The effect of ISA and MPBD on the shear viscosity (apparent shear rate = 100 s^{-1}) of $SBS/Mg(OH)_2$ composite.

Conclusions

Isostearic acid and maleinised polybutadiene interact via chemical bonding with the magnesium hydroxide surface. The FMC studies showed that the interaction of the filler surface with the two phases of the polymer matrix can be controlled by filler surface modification. Maleinised polybutadiene surface modification increases the filler-matrix adhesion relative to that afforded by untreated filler and leads to decreased strain induced crystallization and hence to reduced ultimate tensile properties. Isostearic acid surface modification of the filler leads to reduced filler-matrix interaction and melt viscosities, and also enhanced strain induced crystallisation, relative to the composites based on untreated and maleinised polybutadiene treated filler. The simultaneous use of maleinized polybutadiene and isostearic acid suggests that medium to high levels of isostearic acid and low levels of maleinized polybutadiene should be used in order to obtain reduced melt viscosities together with high ultimate tensile strength to render in the SBS/magnesium hydroxide composites investigated.

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