

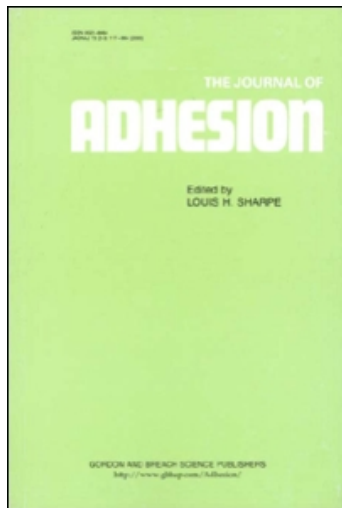
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Magnesium hydroxide filled EVA: The effects of filler surface modification on the strength of filler/matrix adhesion and the consequences for composite structure and properties

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MAGNESIUM HYDROXIDE FILLED EVA: THE EFFECTS OF FILLER SURFACE MODIFICATION ON THE STRENGTH OF FILLER/MATRIX ADHESION AND THE CONSEQUENCES FOR COMPOSITE STRUCTURE AND PROPERTIES

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The interaction of ammonium stearate (AS) and γ -aminopropyltriethoxysilane (APS) treatments with a magnesium hydroxide flame retardant filler and their effects on its use in an ethylene vinyl acetate copolymer compound have been investigated.

The work has shown clear evidence of changes in the structure of the surface layers formed on the filler as the amount of additive is increased and the levels at which these occur can be correlated with theoretical monolayer quantities. Infrared (IR) spectroscopy data suggest that the stearate coating changes from a half salt to a full salt as the coating level is increased and that the APS coating on the filler initially has a significant bicarbonate content, presumably due to reaction with atmospheric carbon dioxide.

The effect of coating level on the melt flow rate, insoluble matrix content, crystallisation behaviour, tensile properties, limiting oxygen index, and ageing of the filled compound has been studied. Distinct trends have been observed, many of which can be correlated with the structure of the filler surface layers. Of particular importance is the observation that, unlike APS, excess stearate appears to promote detrimental ageing effects.

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This is one of a collection of papers honoring Hatsuo (Ken) Ishida, the recipient in February 2001 of *The Adhesion Society Award for Excellence in Adhesion Science*, Sponsored by 3M.

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Keywords: Magnesium hydroxide filler; Ethylene vinyl acetate; Stearate; Gamma-aminopropyltriethoxysilane; Compound properties; Ageing

INTRODUCTION

Over many years Professor Ishida's work has been a constant source of inspiration to all who work in the area of adhesion, and the authors were delighted to be asked to contribute a paper to this special Collection. This paper is very much based on the ideas and techniques pioneered by Professor Ishida and deals with the effect of surface modifiers on a flame retardant filler in an ethylene vinyl acetate (EVA) copolymer.

Due to their benign environmental effects, flame retardant fillers such as aluminium and magnesium hydroxide are becoming widely adopted in many polymer applications [1]. The cable industry is a major user, with EVA being a favoured polymer matrix. High filler loadings are needed to achieve the required flame retardancy, and hence filler surface treatments are widely used to improve both processing and mechanical properties.

The two most commonly used filler treatments for EVA compounds are fatty acids and amino-silanes; the former is assumed to decrease filler/polymer interaction and the latter to increase it. This paper examines the effect of these two types of treatment for a synthetic magnesium hydroxide in a typical cable grade of thermoplastic EVA (containing 18% m/m (mass/mass) vinyl acetate).

There are no studies reported in the academic literature that cover such a comprehensive comparison of the interaction of these two coatings with magnesium hydroxide and their effect on the properties of an EVA compound. Furthermore, no previous work has investigated the aqueous coating procedure for applying the fatty acid, despite frequent use of such coating methods in industry.

Fatty acids (such as stearic acid) and their salts are widely used filler surface treatments, and there have been many studies of their effects with various filler and polymer combinations [2]. Hornsby and Watson [3] have reported on the effect of varying levels of stearic acid and metal stearates, added to magnesium hydroxide by a dry coating method, on some properties of a polypropylene compound. They found good improvements in impact strength at high coating levels, with the metal stearates being more effective than stearic acid. They did not characterise the surface structures or relate the effects observed to filler surface area. Gilbert and Petiraksakul [4] have also reported some studies on the dry blending of magnesium hydroxide with fatty acids and their salts, including stearic acid and magnesium stearate,

and the effect of such coatings in polyolefin compounds. Using the same grade of magnesium hydroxide as in the present work, they found that the best impact properties in polyethylene were obtained at about 1 theoretical monolayer coating level. Harper et al. [5] have studied the coating of a high surface area magnesium hydroxide with decanoic, stearic, and behenic acids and their effect in polyethylene. The coating was carried out in the dry powder state, using a high speed mixer. Using diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), they showed that all of the acids were converted to the salt form under the dry blending conditions used; however, no surface saturation level was found. They did, however, find an optimum level of coating for mechanical properties of the composites at about 1 theoretical monolayer. The acid of longest chain length (behenic) was found to produce the greatest effect on composite properties. Liauw et al. have reported on the coating of magnesium hydroxide with stearic and other fatty acids using an organic solution as the coating medium [6, 7]. This work indicated that, under the conditions used, stearic acid formed a vertically-oriented chemisorbed layer, which was more than 1 molecule in thickness. There was no evidence of free acid in this layer.

APS is widely used as a surface treatment for glass fibres and silane-responsive mineral fillers. Its reaction with such surfaces has received a great deal of study, and the early results in this area were reviewed by Ishida [8]. Most of the scientific work has dealt with deposition from aqueous solution, where the structures can be better controlled and characterised. There has been little scientific study of the surface structures produced by the dry coating method, even though this is widely used in industry. An important finding to emerge has been that, when coated onto a surface, the primary amine group is prone to undergo reaction with atmospheric carbon dioxide. This was first postulated by Boeiro et al. [9], but there has been great controversy about the exact nature of the reaction product. Among the structures suggested are the carbonate, bicarbonate, and carbamate. Ishida et al. [10] carried out a detailed study which showed that, under normal conditions, the bicarbonate was the most likely species to form but that this could be reversed by heating above 95°C.

EXPERIMENTAL

Materials and Reagents

The magnesium hydroxide filler used was DP 393, a development grade product from Premier Periclase (Ireland). The average particle

size given by the manufacturer was 0.7 μm . As the specific surface area was important in interpreting the additive adsorption data, this was measured by the authors, using the BET method, and found to be $10.5 (\pm 0.5) \text{ m}^2 \text{ g}^{-1}$.

The EVA copolymer used was Grade VNS 050 from Ato Fina. It contained 18% m/m of vinyl acetate.

The ammonium stearate used was prepared from 99.9% pure stearic acid obtained from Aldrich Chemicals. The amino-silane used was γ -aminopropyltriethoxysilane (A 1100, APS) from OSI Specialities. It was used as received.

The reference magnesium stearate (technical grade) was obtained from Aldrich Chemicals (catalogue no. 41505/7). It is described as MgSt_2 , where the acid content is 65% m/m stearic acid and 25% m/m palmitic acid. The IR spectrum showed no evidence of a hydroxyl peak, confirming the absence of any significant basic salt content.

Filler Surface Treatment

Ammonium Stearate (AS)

Ammonium Stearate was added from aqueous solution. The filler (150 g) was first deagglomerated by use of a Phillips domestic blender and then made into a 10% m/m slurry in hot deionised water. The slurry was kept agitated and maintained at 80°C. The ammonium stearate was prepared by adding stearic acid and then a slight excess of ammonium hydroxide to hot water with stirring. The resulting solution of ammonium stearate was added over a 60-min period to the hot filler slurry. The treated filler was separated by filtration, washed with deionised water, and dried in an oven at 110°C for 24 h. The oven-dried filter cake was finally deagglomerated in the Phillips blender. Filler coating levels were based on the amount of stearic acid used, not on ammonium stearate.

γ -Aminopropyltriethoxysilane (APS)

APS was added by a dry blending method. The DP 393 filler (150 g) was agitated in the Phillips blender for 5 min. The required amount of APS was then added dropwise, followed by a further 5 min of agitation.

Determination of Amount of Additive Bound to the Filler

Determining the amount of additive bound to the filler was carried out by a combination of gravimetric and extraction methods. For both the ammonium stearate and APS, the total amount of additive present after treatment was confirmed by an ashing procedure identical to that described in the section "Determination of Insoluble Matrix

Content" below. The amount of extractable material was then determined by stirring the treated filler in ethanol for 5 min and then leaving to stand for 24 h. The filler was then removed by centrifugation. The amount of extractable additive from the ammonium stearate coating was determined by IR analysis of the extract. The amount of bound coating was then determined by subtracting the extracted amount from the initial amount. For the APS, the amount of coating remaining after extraction was directly determined by the ashing method.

DRIFTS Analysis

The filler samples were prepared as 10% m/m mixtures with finely ground spectroscopic grade KBr. A Nicolet 510 P FTIR spectrophotometer bench-fitted with a Spectra-Tech DRIFTS cell and deuterated glycine sulphate (DTGS) detector was used to carry out the analysis. The spectra were obtained from 150 scans with a resolution of 4 cm^{-1} .

Dye Adsorption

The dye Ponceau 3R was used to assess the degree of surface coverage achieved by the additives. This dye adsorbs strongly onto the surface of magnesium hydroxide at a level of 1.27 mg m^{-2} [11].

The degree of coverage of the filler by the surface modifiers was determined by adding 13.5 cm^3 of a 100 mg dm^{-3} aqueous solution of Ponceau 3R to 1.000 g of filler. The resulting slurry was agitated for 48 h to ensure equilibration of the adsorption process. The supernatant liquor was then removed and added, along with filler washings, to a 100 cm^3 volumetric flask and made up to 100 cm^3 with deionised water. The solution was then added to a 1 cm path length glass cell, and the absorbance of visible light at the absorbance maximum of 508 nm was measured using a Perkin-Elmer Lambda 7 UV-VIS spectrophotometer. The amount of dye adsorbed was determined via a calibration curve constructed using absorbance data from standard solutions in the range 0 to 14 mg dm^{-3} Ponceau 3R. This technique had a detection level of 0.5 mg m^{-3} of the dye, and the untreated filler was found to adsorb 11.3 mg m^{-3} of the dye.

Composite Preparation

A 2-roll mill was used to incorporate the filler. The front roll was maintained at 140°C and the back one at 120°C . The friction ratio was 1:1. Blending time was 20 min with cross blending being used. Sample specimens were prepared by compression moulding of flat sheets using a temperature of 160°C and with 10 min pressing time. The pressed

sheets were cooled in a water-cooled press. The samples were allowed to stand in sealed bags for 24 h before testing.

The filler loading used was 60% m/m (excluding coating). The twin roll compounding procedure is generally very efficient in achieving the desired filler level, but it was checked by ashing and all the compounds were found to contain between 59 and 61% m/m of filler.

Differential Scanning Calorimetry (DSC)

DSC was carried out using a Perkin Elmer DSC-7 energy balance instrument, controlled by a TAC-7 linked to a PC running Perkin Elmer PC-TA software. A nonisothermal method was employed. Sealed aluminium pans were used and the DSC head was purged with oxygen-free nitrogen at a flow rate of 30 cm³ min⁻¹. The composite samples were cut transversely from the centre of the tensile test pieces. The program sequence was as follows: Hold at 5°C for 5 min, heat from 5°C to 200°C at 20°C min⁻¹, hold at 200°C for 5 min, cool from 200°C to 20°C at 20°C min⁻¹, hold at 20°C for 2 min, heat again from 20°C to 200°C at 20°C min⁻¹. The various crystallisation parameters (i.e., temperature at the melting endotherm peak [during the first heating segment] (T_m), the corresponding crystalline content (X_c), and the temperature at the crystallisation endotherm peak (T_c)), were determined using the analysis menu of the Perkin Elmer PC-TA software.

Determination of Insoluble Matrix Content

The insoluble matrix content was determined by 48 h Soxhlet extraction with toluene. The residue in the thimble was dried to constant mass at 70°C and the mass loss on ignition at 1100°C (maintained for 4 h) was then determined. By taking account of the mass loss on dehydration of pure magnesium hydroxide (under the latter conditions), it was possible to calculate the amount of polymer in the composite residue. The accuracy of this method is typically $\pm 5\%$.

Melt Flow Rate (MFR)

MFR was determined according to ASTM (American Society for Testing and Materials) D-1238-90b, using a temperature of 190°C and a load of 2.16 kg.

Tensile Testing

Tensile testing was carried out at 20°C ($\pm 1^\circ\text{C}$) after a post-moulding conditioning period of 24 h. A Hounsfield M-Series tensometer fitted with a laser extensometer was used to measure all samples according to British Standard (BS) 2782 Part 3, Method 320 A (1986). The cross-head speed was 500 mm/min. The specimens were BS 903 Part A2,

Type 2 dumbbells die cut from 2 mm thick compression-moulded sheets. The gauge length of the test pieces ran parallel to the mill direction. The results reported are based on the average of a minimum of 10 specimens, and the error margins are based on 95% for confidence limits.

Limiting Oxygen Index (LOI) Determination

The LOI was determined according to BS 2782 Method 141. Test pieces were prepared by cutting a 3 mm-thick compression-moulded sheet into strips 6.5 mm wide and 150 mm long.

Heat Ageing

Precut test pieces were suspended in a circulating air oven at 70°C for 168 h.

RESULTS

Terminology Notes

As will be discussed later, the apparent monolayer coverage for the stearate and amino-silane on the DP 393 filler are 30 mg/g⁻¹ and 15 mg/g⁻¹, respectively. Where it makes interpretation of the results clearer, surface modifier levels are expressed as fractions of these values rather than as weight percentages. They are then referred to as equivalent monolayers.

Interaction of Surface Treatments With the Filler Surface

Adsorption Isotherms

The isotherms for AS and APS adsorption onto the filler are presented in Figure 1. They are based on the amounts remaining after solvent extraction.

The stearate isotherm is initially linear, with virtually all the added acid being adsorbed. Small amounts of extractable material start to appear at about 20 mg/g⁻¹, and above a limiting value of about 30 mg/g⁻¹ of filler all of the additional coating can be extracted. IR examination showed that the extracted material was almost exclusively in the salt form.

The APS isotherm is only linear to about 15 mg/g⁻¹, but up to this level there is again virtually no removable additive. Above this level the amount of extractable material increases faster than with the AS, tending towards a similar plateau adsorption level of about 30 mg/g⁻¹.

Completeness of Surface Coverage

The isotherm data referred to above shows distinct adsorption plateaus, but they cannot provide information on the way the coating

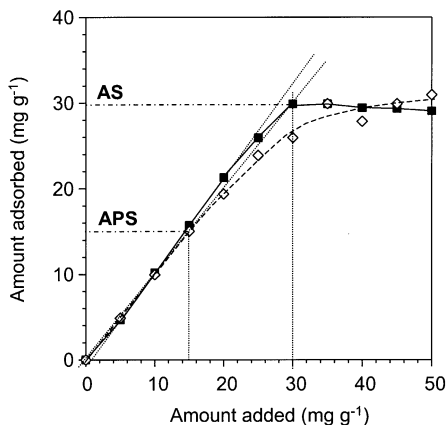


FIGURE 1 Adsorption isotherms for ammonium stearate [AS] (■) and APS (◇) onto the DP 393 filler.

is distributed on the filler surface. In particular, the coating could be patchy rather than uniform. Useful additional information is provided by the dye adsorption results presented in Figure 2. The results for stearate treatment are in good agreement with the adsorption data presented above, with a steady decrease in dye absorption reaching a zero level at 30 mg/g^{-1} . This strongly indicates that there is a true, uniform monolayer at this coating level, although the dye molecule is quite large and it is somewhat surprising that complete surface blockage is not observed at levels lower than an equivalent monolayer.

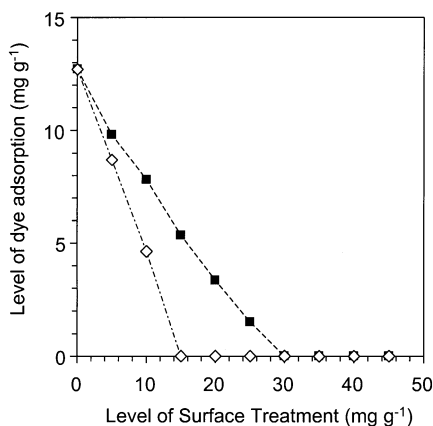


FIGURE 2 The effect of additive coating level on the dye adsorption of the DP 393 filler. (■) ammonium stearate coating, (◇) APS coating.

The results for APS indicate that complete blocking of the surface is reached at only 15 mg/g^{-1} . Again, this indicates that there is a uniform monolayer at this coating level. At first sight it is somewhat surprising that the dye is not adsorbed onto the amine groups of the coating. As shown later, this may be due to neutralisation of the amine groups with atmospheric carbon dioxide during the coating process.

Infrared Spectroscopy Studies

The relatively clean spectrum of magnesium hydroxide makes infrared spectroscopic techniques especially useful for characterising surface treatments. The DRIFTS technique is also especially useful for detecting surface layers on powdered materials, with the spectral subtraction facility allowing the contribution of the surface treatment to be isolated.

The hydroxyl peak of magnesium hydroxide in the unsubtracted spectra can be used as a convenient internal standard, and the ratio of the peak area for the C-H stretch to the area of this peak for AS-treated filler is presented in Figure 3. This ratio is seen to increase linearly up to about 30 mg/g^{-1} of added coating but tails off rapidly afterwards. This indicates that, while the first 30 mg/g^{-1} largely goes to coating the filler surface, any further additive is mainly forming a separate phase rather than being retained on the filler surface.

Substrate-subtracted DRIFTS spectra for the carbonyl region of the magnesium hydroxide treated with increasing amounts of added AS

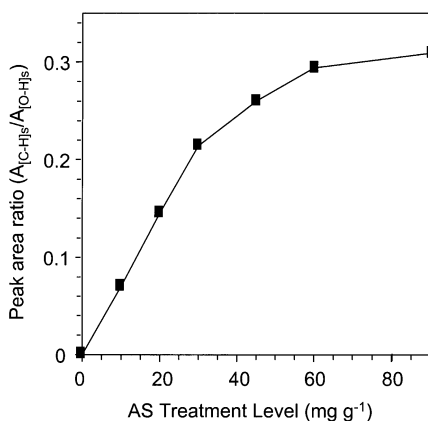


FIGURE 3 Infrared absorption peak area ratio (C-H stretch [from AS] ($A_{\text{C-H}(s)}$)/O-H stretch [from $\text{Mg}(\text{OH})_2$] ($A_{\text{O-H}(s)}$), obtained from DRIFTS spectra of ammonium stearate-treated magnesium hydroxide.

are presented in Figure 4, together with spectra of stearic acid (h) and magnesium stearate (MgSt_2) (g) for comparison. It is immediately evident that the vast majority of the AS is present as a carboxylate salt, as the carbonyl asymmetric stretching frequency was reduced from ca. 1715 cm^{-1} (of the hydrogen bonded dimer form of stearic acid) to $1540\text{--}1575\text{ cm}^{-1}$. As the ammonia initially present would have been driven off in the coating and drying procedure, it can be assumed that we now have a magnesium salt. However, at stearic acid levels greater than 20 mg/g^{-1} some free acid may also be present as the undissociated dimer (1644 cm^{-1} , asymmetric carbonyl stretch and $1408\text{--}1414\text{ cm}^{-1}$ symmetric carbonyl stretch). This is entirely consistent with Thistlethwaite's study [12] of sodium oleate-modified titanium dioxide.

Together with the increase in the overall intensity of the asymmetric and symmetric carboxylate carbonyl stretching vibrations, observed with increasing AS level, there are also small but important shifts in these frequencies. In some cases, these shifts result in partial

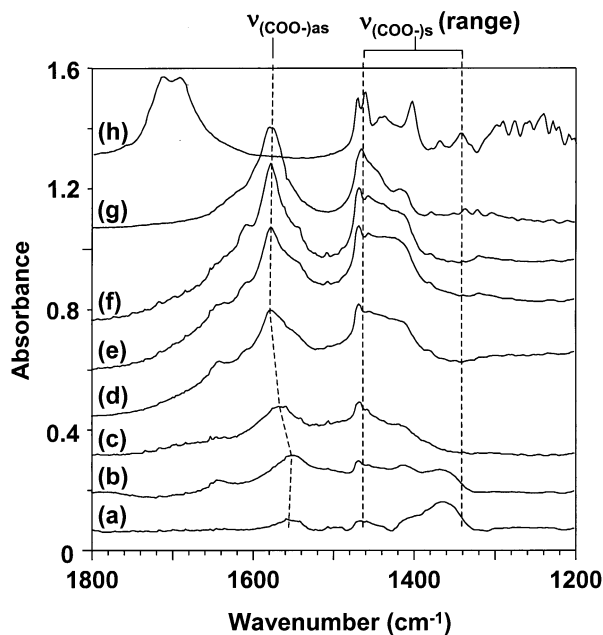


FIGURE 4 Substrate-subtracted DRIFTS spectra for the carbonyl region of magnesium hydroxide treated with increasing amounts of ammonium stearate: (a) 10 mg/g^{-1} , (b) 20 mg/g^{-1} , (c) 30 mg/g^{-1} , (d) 45 mg/g^{-1} , (e) 60 mg/g^{-1} , (f) 90 mg/g^{-1} , (g) magnesium stearate, and (h) stearic acid.

splitting of the symmetric carbonyl stretch. Such effects afford insight into the type of salt formed and are discussed in more detail below.

At the submonolayer level of 10 mg/g^{-1} (Figure 4a) the carboxylate carbonyl asymmetric stretching absorption ($\nu_{(\text{CO}_2\text{-})_{\text{as}}}$) appears at 1550 cm^{-1} . The symmetric stretch ($\nu_{(\text{CO}_2\text{-})_{\text{s}}}$) is difficult to determine accurately, but appears to peak at ca. 1360 cm^{-1} . Increasing the AS level to 20 mg/g^{-1} (0.67 monolayers, Figure 4b) has minimal effect on $\nu_{(\text{CO}_2\text{-})_{\text{as}}}$. However, the corresponding symmetric stretching band appears to be split into two components; one of these is at ca. 1360 cm^{-1} and the other is at ca. 1415 cm^{-1} . This splitting implies that there may be two forms of salt present. Thistlethwaite [12] used the difference between the asymmetric and symmetric carboxylate carbonyl stretching frequencies ($\Delta\nu = \nu_{(\text{CO}_2\text{-})_{\text{as}}} - \nu_{(\text{CO}_2\text{-})_{\text{s}}}$) of the adsorbed carboxylate, relative to that in pure unbound stearate, to assess the coordination of the metal ion. At an AS level of 10 mg/g^{-1} , the predominant $\nu_{(\text{CO}_2\text{-})_{\text{s}}}$ component at 1360 cm^{-1} gives a $\Delta\nu$ value of 190 cm^{-1} ; as this value is greater than that for pure MgSt_2 (165 cm^{-1}), it can be implied that the stearate interacts as a single salt. Doubling the amount of AS to 20 mg/g^{-1} gives rise to two $\Delta\nu$ values; 190 cm^{-1} and 135 cm^{-1} (corresponding to the $\nu_{(\text{CO}_2\text{-})_{\text{s}}}$ component at 1415 cm^{-1}). The latter component may be due to formation of some double salt. These findings are consistent with earlier work [6, 7].

Increasing the added ammonium stearate level to the monolayer level (30 mg/g^{-1}) (Figure 4c) causes an increase in $\nu_{(\text{CO}_2\text{-})_{\text{as}}}$ to 1560 cm^{-1} . This may reflect an increase in the proportion of vertically-adsorbed molecules and/or a change in the mode of adsorption that modifies the interaction of the carboxylate carbonyl group with the substrate. A definite value for $\nu_{(\text{CO}_2\text{-})_{\text{s}}}$ is difficult to resolve, but the noticeable peak at ca. 1360 cm^{-1} , seen at submonolayer levels, has turned into a broad shoulder that shows two knees before rising up to meet the C-H deformation vibration at 1468 cm^{-1} . The smallest of these knees is at 1380 cm^{-1} , and the largest, perhaps incorporating a contribution from $\nu_{(\text{CO}_2\text{-})_{\text{s}}}$ of the free acid monomer, is at 1415 cm^{-1} . The corresponding $\Delta\nu$ values (in the range 180 to 145 cm^{-1} but skewed heavily towards 145 cm^{-1}), together with the value of $\nu_{(\text{CO}_2\text{-})_{\text{as}}}$ observed, are likely to be consistent with vertical adsorption, mainly via the double salt.

Increasing the level of AS addition beyond the monolayer level (Figures 4d to 4f) results in an increase in $\nu_{(\text{CO}_2\text{-})_{\text{as}}}$ to the limiting value of 1575 cm^{-1} (the same value as for pure magnesium stearate [Figure 4g]), whilst $\nu_{(\text{CO}_2\text{-})_{\text{s}}}$ is in the range 1441 – 1414 cm^{-1} , with a small shoulder still present at ca. 1380 cm^{-1} . The increase in $\nu_{(\text{CO}_2\text{-})_{\text{as}}}$ may reflect a change in environment from magnesium stearate

associated with the filler surface to the layer of magnesium stearate where the magnesium ion is not associated with any hydroxyl ions, i.e., the formation of $\text{Mg}(\text{st})_2$. The latter condition is likely to be satisfied at addition levels greater than the monolayer level. The increasing sharpness of the asymmetric carboxylate carbonyl stretching absorption, as the AS addition levels rise above monolayer, may be explained by a predominance of the nonhydroxyl-associated magnesium ion, i.e., formation of a magnesium stearate layer on top of the layer of stearyl groups adsorbed via the single salt. The values of $\Delta\nu$ for the carboxylate carbonyl absorptions for addition levels $\geq 45 \text{ mg/g}^{-1}$ are predominantly in the range 159 to 134 cm^{-1} , thus suggesting that the double salt (with similar structure to pure magnesium stearate) is the major product. This is consistent with earlier data [7] generated from adsorption isotherm studies (from heptane) and flow-microcalorimetry studies.

The C-H stretching region of the above substrate-subtracted spectra is shown in Figure 5. Only at the submonolayer level of 10 mg/g^{-1} is the asymmetric C-H stretch absorption ($\nu_{(\text{C-H})\text{as}}$) shifted to slightly higher energy, relative to the unbound stearic acid and magnesium stearate, suggesting a disordered arrangement of adsorbate molecules; the latter is also implied by the carboxylate carbonyl shift. Similar shifts in $\nu_{(\text{C-H})\text{as}}$ have also been observed in our previous work [6, 7].

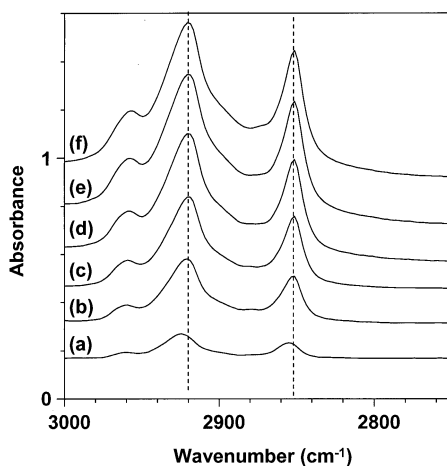


FIGURE 5 Substrate-subtracted DRIFTS spectra showing the C-H stretching region of magnesium hydroxide treated with increasing amounts of ammonium stearate: (a) 10 mg/g^{-1} , (b) 20 mg/g^{-1} , (c) 30 mg/g^{-1} , (d) 45 mg/g^{-1} , (e) 60 mg/g^{-1} , and (f) 90 mg/g^{-1} .

The increase in intensity of the C-H stretching bands as the AS level increases is in agreement with the increasing thickness of the magnesium stearate layer.

Substrate-subtracted DRIFTS spectra of the Si-O-X stretching region ($1300\text{--}800\text{ cm}^{-1}$) of magnesium hydroxide treated with increasing levels of APS are shown in Figure 6, together with a spectrum of unbound APS for comparison. In the unbound silane the Si-O-C asymmetric stretching bands are apparent at 1102 and 1080 cm^{-1} . These absorptions are sharp and well defined. The other bands at 1168 and 958 cm^{-1} are also characteristic of an alkoxy silane.

The spectra for the coated filler have two broad absorptions, with peaks at 1024 and 1121 cm^{-1} ; these are labelled I and II in Figure 6. Reaction of APS with magnesium hydroxide would be expected to result initially in hydrolysis followed by formation of Si-O-Mg and Si-O-Si bonds, in the course of chemisorption and self-condensation reactions, respectively. In earlier work conducted by Ishida [13], Si-O-Pb bonds absorbed at 960 cm^{-1} , and Anderson [14] gives a range of 900 to 1000 cm^{-1} for Si-O metal with metals in the range Na to Pb. It is envisaged that Si-O-Mg will absorb closer to 1000 cm^{-1} and is therefore likely to be superimposed on the residual silanol (1035 cm^{-1}) and Si-O-Si absorptions.

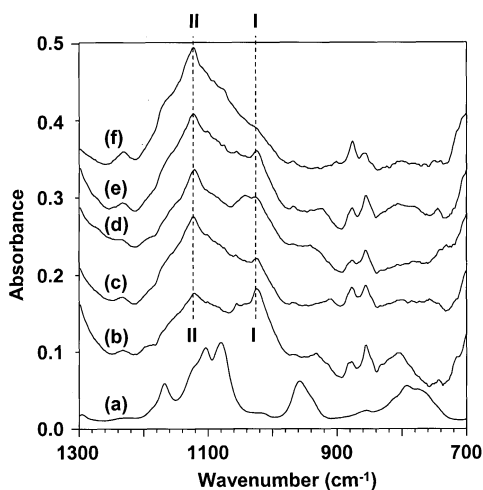


FIGURE 6 Substrate-subtracted DRIFTS spectra showing the Si-O-X stretching region for magnesium hydroxide treated with increasing amounts of APS: (a) unbound APS (transmission, liquid film), (b) 10 mg/g^{-1} , (c) 20 mg/g^{-1} , (d) 30 mg/g^{-1} , (e) 40 mg/g^{-1} , and (f) 50 mg/g^{-1} .

At the lowest added APS level (10 mg/g^{-1}), the absorption at 1024 cm^{-1} is slightly greater in intensity than the Si-O-Si absorption at 1121 cm^{-1} ; there is also a shoulder at 1059 cm^{-1} . The two lower energy absorptions are tentatively assigned to Si-O-Mg, residual silanol, and Si-O-Si. The absorptions at 1168 and 958 cm^{-1} , characteristic of an alkoxy silane, are absent, indicating hydrolysis and evolution of ethanol. The position of the siloxane absorption, centred at 1100 cm^{-1} , can provide insight into the degree of structural ordering of the polymer, and values in the range 1115 to 1130 cm^{-1} have been quoted [15], representing random and ordered ladder polymer structures, respectively. In this study, the position of the siloxane absorption remains constant (1121 cm^{-1}) at all added APS levels and reflects a degree of structural ordering. As the added level of APS increases beyond the monolayer level (ca. 15 mg/g^{-1}), the siloxane absorption at 1122 cm^{-1} grows in intensity whilst the intensity of the absorption at 1024 cm^{-1} stays sensibly constant. This is consistent with formation of a polysilsesquioxane network of increasing thickness.

As mentioned in the introduction of this article, reactions of the amine functionality of APS have been the subject of much controversy in the literature concerning the formation of carbonate and bicarbonate species that result from reaction of the amine with atmospheric carbon dioxide and moisture. The 2300 to 1300 cm^{-1} region of the above spectra, which covers absorption bands associated with such species, is shown in Figure 7. At all added APS levels a complex collection of bands between 1770 and 1200 cm^{-1} is apparent. The bulk of these bands are indeed associated with reaction products of the primary amine with atmospheric carbon dioxide and moisture, forming principally the amine bicarbonate. The major absorptions associated with the latter species are as follows: 1642 cm^{-1} and 1356 cm^{-1} , OCO_2 asymmetric and symmetric stretching, respectively, of the bicarbonate carbonyl; 1585 cm^{-1} (weak shoulder) and 1488 cm^{-1} , asymmetric and symmetric N-H stretching respectively, of $-\text{NH}_3^+$. The weak broad absorptions centred at 2100 cm^{-1} and 2900 cm^{-1} (with C-H stretching absorptions superimposed), can be assigned to combination vibrations of NH_3^+ and hydrogen bonding interactions of the amine bicarbonate salt with residual silanol and possibly the magnesium hydroxide substrate itself. This result is consistent with that reported by Ishida et al. [10]. The presence of some amine carbonate $[(\text{RNH}_3^+)_2\text{CO}_3^{2-}]$ cannot be ruled out, as in the majority of the spectra there is an absorption at 1432 cm^{-1} that is likely to be too strong to be solely assignable to CH_2 scissoring vibrations.

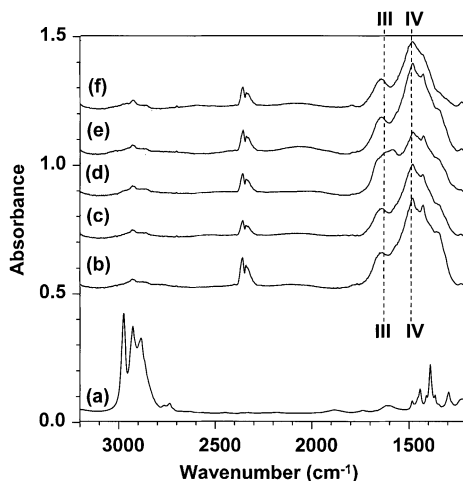


FIGURE 7 Substrate-subtracted DRIFTS spectra of magnesium hydroxide treated with increasing amounts of APS showing the region where amine/carbon dioxide reaction product absorptions are found: (a) unbound APS (transmission, liquid film), (b) 10 mg/g^{-1} , (c) 20 mg/g^{-1} , (d) 30 mg/g^{-1} , (e) 40 mg/g^{-1} , and (f) 50 mg/g^{-1} .

Effect of the Filler Treatments on Composite Properties

Processing as Indicated by the MFR

The effect of treatment level on the MFR of the compound is presented in Figure 8. Although not shown, the uncoated filler, as expected, produced a large decrease in MFR. Unexpectedly, while the stearate coating did produce an increase, this was much smaller than would normally be expected, with no apparent step change at any coating level. The APS treatment, on the other hand, led to a steady drop in MFR, again with no apparent step change. The absence of any step changes indicates that the surface structure of the coating does not play a significant role in determining the MFR of the compounds.

Insoluble Matrix Content

Quite high levels (about 10% m/m) of insoluble EVA matrix arise from melt processing operations. The results obtained for increasing amounts of the 2 surface treatments are presented in Figure 9. Untreated filler is seen to lead to a small increase in the level of insoluble polymer. The stearate treatment is seen to lead to a steady decrease up to a level of about 0.8 of a monolayer (25 mg/g^{-1}). Immediately above this there is a sharp increase, followed by a plateau. The APS treatment,

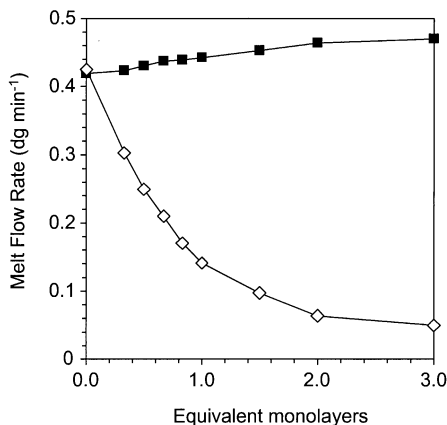


FIGURE 8 The effect of ammonium stearate (■) and APS (◇) filler treatments on the melt flow rate of EVA/DP393 (60% m/m) composites.

however, only leads to a steady increase in the amount of insoluble polymer.

Polymer Crystallinity

This was determined by DSC methods. The first heat segment of the cycle with samples cut from moulded specimens gives the most relevant information regarding the structure of the composite as used for mechanical property tests. The crystalline content of the EVA matrix (X_c) and the position of the melting endotherm peak (T_m), as determined in this way, are presented in Figure 10. X_c is seen to initially decrease slightly with stearate coating level and to stabilise at about a monolayer of additive (Figure 10a). Interestingly, T_m drops to a limiting value at the lowest coating level, but at the monolayer level a step increase to a sensibly limiting value (similar to that observed with untreated filler) is observed. The APS treatment (Figure 10b) appears to lead to a small increase in X_c at high treatment levels, but shows similar variation in T_m to that observed with the stearate treatment, with the step change occurring at about an equivalent monolayer (15 mg/g^{-1}).

The data obtained on the recoiling of a melted specimen gives some more information about the interaction of the filler surface treatment and the coatings with the polymer matrix. The main interest is in the temperature of crystallisation as indicated by the peak value (T_c), and this is also presented in Figure 10. The first level of ammonium stearate and APS treatment are seen to inhibit nucleation. No further

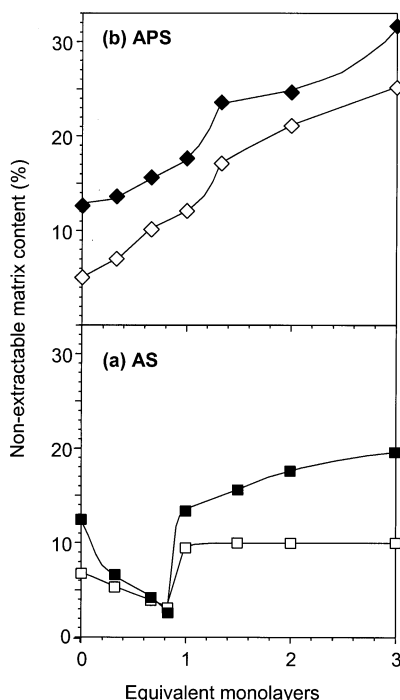


FIGURE 9 The effect of ammonium stearate and APS filler treatments on the bound polymer content of EVA/DP393 (60% m/m) composites: (\diamond) APS before ageing, (\blacklozenge) APS after ageing, (\square) ammonium stearate before ageing, and (\blacksquare) ammonium stearate after ageing.

change is then observed until about the monolayer level of AS (30 mg g^{-1}) and about 1.5 monolayers of the APS, when there is a significant step increase in the onset of crystallisation with both coatings. Again, there is no further effect arising from increasing coating levels above the monolayer level.

Mechanical Properties

Illustrative stress-strain curves are presented in Figure 11. In this figure, error bars for the last data point only are shown so as to show the spread of ultimate property data. These show that the uncoated filler significantly increases the stiffness and reduces elongation at the break of the composite, indicating quite strong filler/polymer interaction. The stearate treatment is seen to cause an apparent reduction in this interaction, while the APS appears to increase it.

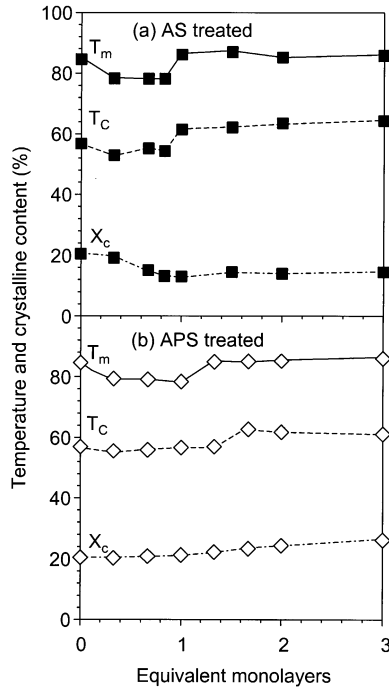


FIGURE 10 The effects of ammonium stearate and APS filler treatments on the crystallisation of EVA/DP393 (60% m/m) composites. T_m = peak melting temperature, T_c = peak cooling temperature, and X_c = total crystallinity determined from the heating curve.

Detailed results are presented in Table 1 and Figures 12 and 13. The lowest stearate coating level is seen to reduce tensile strength and elongation without any appearance of yielding. Yielding starts to appear at about 15 mg/g^{-1} treatment, and the yield strength progressively decreases, accompanied by increased elongation, until about the 30 mg/g^{-1} monolayer level, after which there is little further change. The secant modulus is progressively decreased with coating level up to about 30 mg/g^{-1} , after which there is no further change.

With APS the trends are different. The secant modulus increases with additive level, up to the highest values studied, with some evidence for step changes at about 15 and 30 mg/g^{-1} levels. The composite based on untreated filler shows no yielding, but yielding occurs with even the lowest amount of additive used. The yield strength then increases with additive level, with some indication of a step at the

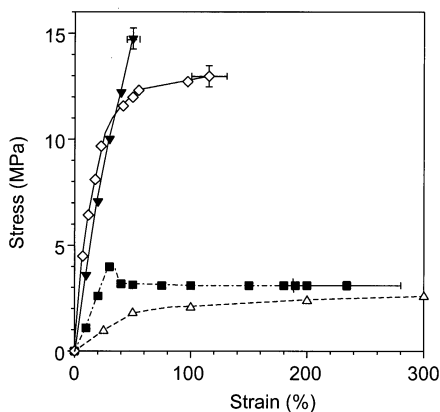


FIGURE 11 Illustrative stress strain curves: (\triangle) Unfilled EVA, (\blacktriangledown) EVA filled with 60% m/m uncoated DP393, (\blacksquare) EVA filled with 60% m/m DP 393 treated with 1 equivalent monolayer of ammonium stearate (30 mg/g^{-1}), (\diamond) EVA filled with 60% m/m DP 393 treated with 1 equivalent monolayer of APS (15 mg/g^{-1}).

monolayer level. The tensile strength decreases with the first addition of APS, then increases steadily until about the 1.5 monolayer level. The elongation to break is little changed by the first amount of additive, but improves sharply in the region from 0.5 to about 1 monolayer and shows a further gradual improvement as the amount of additive is further increased.

TABLE 1 The Effect of Additive Level on the Tensile Properties of Magnesium Hydroxide-Filled EVA Composites

Additive level (mg/g^{-1})	AS			APS		
	Tensile (MPa)	Yield (MPa)	Elongation (%)	Tensile (MPa)	Yield (MPa)	Elongation (%)
0	14.7 (0.5)	none	48 (5)	14.7 (0.5)	none	48 (5)
5	—	—	—	11.3 (0.5)	7.9 (0.5)	55 (5)
10	10.5 (0.5)	none	37 (5)	11.8 (0.5)	9.1 (0.5)	97 (15)
15	8.3 (0.5)	trace	51 (5)	13.0 (0.5)	9.6 (0.5)	115 (15)
20	6.9 (0.5)	6.5 (0.5)	121 (15)	14.8 (0.5)	11.6 (0.5)	120 (15)
25	4.9 (0.2)	5.5 (0.3)	187 (20)	15.3 (0.5)	12.1 (0.5)	123 (15)
30	4.0 (0.2)	3.9 (0.2)	234 (46)	15.5 (0.5)	12.7 (0.5)	135 (15)
45	3.9 (0.2)	3.9 (0.2)	210 (38)	15.7 (0.5)	14.8 (0.5)	156 (15)
60	3.8 (0.2)	3.8 (0.2)	200 (41)	—	—	—
90	3.8 (0.2)	3.8 (0.2)	190 (43)	—	—	—

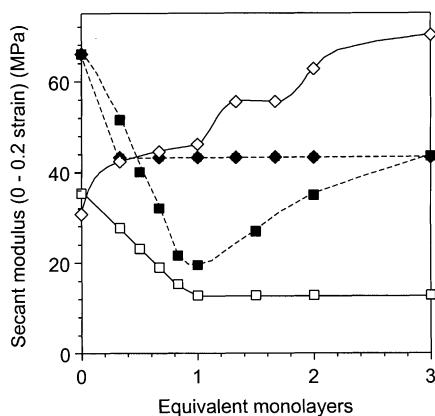


FIGURE 12 The effect of increasing levels of ammonium stearate and APS filler treatments and effect of heat ageing on the secant modulus (0–0.2 strain limits) of composites based on EVA and 60% m/m DP393: (◇) APS before ageing, (◆) APS after ageing, (□) ammonium stearate before ageing, and (■) ammonium stearate after ageing.

Limiting Oxygen Index (LOI)

Magnesium hydroxide is principally used as a fire retardant additive. Filler surface treatment has been reported as influencing fire retardant properties, and hence a brief study was made in this work using the simple LOI test. The results are presented in Figure 14. These show that both types of modifier have a small but detectable effect on this measure of flame retardancy. Thus, the stearate treatment leads to a steady increase in oxygen index, while the APS leads to a steady decrease. There is no evidence here of any step changes.

Many factors contribute to the LOI performance, including filler dispersion, melt viscosity, modulus, and ash structure. These can all be affected by filler treatment. Increased filler/polymer interaction has been reported as reducing oxygen index through the increase in modulus-causing spalling effects [15], and this may be the reason for the decrease in oxygen index seen with APS.

Heat Ageing Performance

Ageing is a very important feature of polymer-based products, but is not often studied in works on filler surface modification. A brief study was made in the present work, using oven heat ageing.

The effect of heat ageing on bound polymer is presented in Figure 9. This shows the same pattern as observed with the unaged composites,

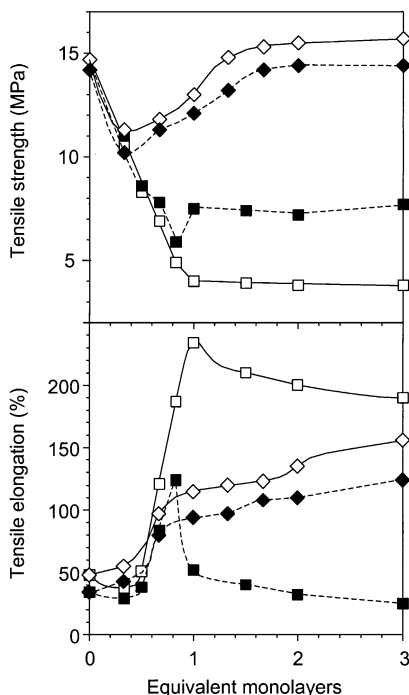


FIGURE 13 The effect of increasing levels of ammonium stearate and APS filler treatments and heat ageing on the tensile strength and elongation of composites based on EVA and 60% m/m DP393: (◇) APS before ageing, (◆) APS after ageing, (□) ammonium stearate before ageing, and (■) ammonium stearate after ageing.

but with significant increases in the absolute values. It is worth noting that, unlike the preaged situation, the amount of bound polymer from the stearate treatment continues to increase after the step change at 30 mg/g^{-1} . The effects of heat ageing on tensile properties are summarised in Figures 12 and 13. With the ammonium stearate treatment, heat ageing led to an increase in tensile strength and a reduction in elongation, indicating increased filler/polymer interaction. The ageing became most marked at levels above the 30 mg/g^{-1} monolayer, and again there was a stepwise change at this level. The aged samples showed a clear optimum performance, with coating levels close to the monolayer.

The APS-treated samples showed much greater stability, with small decreases in tensile strength and elongation and no real effect of coating level.

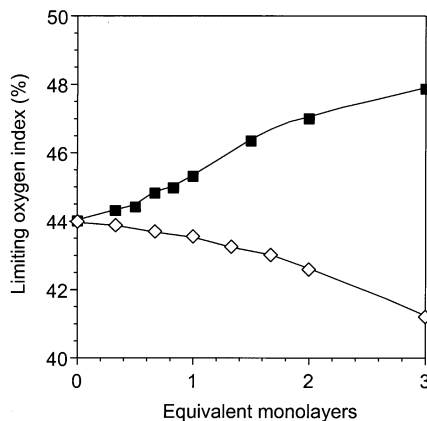


FIGURE 14 The effect of ammonium stearate and APS filler treatments on the oxygen index of composites based on EVA and 60% m/m DP393: (■) ammonium stearate treatment and (◇) APS treatment.

DISCUSSION

The results provide a good insight into the adsorption of the two surface modifiers onto the filler surface and some of the consequences of this for polymer composite properties.

In both cases there is clear evidence of changes in additive structure and performance at certain coating levels, which can be related to the formation of surface layers.

Looking first at the ammonium stearate treatment, the results show strong evidence for surface-bound magnesium stearate, probably largely in the half salt form, up to a coating level of 30 mg/g^{-1} . Above this level there appears to be free magnesium stearate present. This level is consistent with the footprint area of 0.205 nm^2 for the stearate anion in a close-packed, vertically-adsorbed monolayer [16].

The effects of the filler treatment on composite properties are consistent with reduced filler/polymer interaction and also show trends related to the 30 mg/g^{-1} coating level. Thus, below this monolayer level the coating reduces the amount of bound polymer, modulus, yield, and tensile strengths and increases elongation. Excess coating above this level is seen to lead to an increase in bound polymer and a small reduction in elongation, but it has little effect on modulus, yield, and tensile strength. There are also changes in polymer crystallinity that seem to be related to coating level. As described by Darlington, changes in polymer crystallinity ought to have some correlation with compound properties [17], and it is interesting that changes in crystallinity occur

at about the same point as for some of these properties. More work is required to establish the link and how it might occur.

Surprisingly, the stearate treatment gave only very modest improvement in polymer melt viscosity as determined by the MFR method. The reasons for this are not clear, as one of the main benefits of the stearate treatment is usually improved melt flow [2]. The LOI showed a small, progressive increase with coating level. The factors influencing the oxygen index of filled compounds are not well understood, and hence the reason for this cannot be unequivocally determined; it may be due to improved dispersion.

Heat ageing accentuated the coating level effect, with loss in elongation being more marked above the 30 mg/g^{-1} level. This may be due to the presence of free MgSt_2 in the polymer matrix. Parallel studies reported elsewhere [20] indicate that the purity of the stearic acid has a significant influence on the heat ageing behaviour, with commercial "stearine blends" promoting accelerated ageing relative to the "analytical grade" stearic acid used in this study. Additionally, ongoing studies conducted in our laboratories that focus on the effect of metal stearate processing aids/antacid agents on the thermal and UV stabilisation performance of stabiliser blends in polyethylene, have highlighted some strongly antagonistic behaviour [21, 22]. It is therefore clear that the free MgSt_2 in the studied composites may reduce composite stability via several different routes and that further investigation is required before clear conclusions can be drawn from these observations.

Due to their ability to undergo self-condensation, the monolayer concept is less precise for reactive silanes. Nevertheless, the results here do point to strong surface layer effects. Thus, all the added silane appears to become insolubilised up to a level of about 15 mg/g^{-1} , and Ponceau 3R dye adsorption shows that the filler surface is effectively blocked at this treatment level. After this, progressive amounts remain extractable until about 30 mg/g^{-1} have been deposited. These results, and the DRIFT data discussed in the results section, are consistent with the formation of a chemically-adsorbed monolayer up to treatment levels of 15 mg/g^{-1} . At addition levels between 15 and 30 mg/g^{-1} it appears that, with the dry blending process used, some self-condensation can occur, leading to the chemisorption of oligomers together with the presence of increasing amounts of extractable monomer and unbound oligomers. At still higher levels, all of the extra APS appears to remain extractable, although it may have undergone some self-condensation. This type of effect has been reported previously for dry coating of organo-silanes onto mineral surfaces [8, 19].

The commercial literature indicates that about 30 mg/g^{-1} of the APS would be needed to form a monolayer on the present filler [18], and this is indeed consistent with the limiting value obtained by the extraction isotherm method. On the other hand, the value given by Miller and Ishida in the literature for the area occupied by a silane triol head group from close-packed, vertically-adsorbed, γ -methacryloxypropyltriethoxysilane, a similar molecule to APS, is 0.240 nm^2 per molecule (13) and our own calculations agree closely with this figure. The IR results clearly illustrate that hydrolysis of the alkoxy-silane groups has occurred on the filler surface and, using this value, we arrive at a monolayer level of only about 15 mg/g^{-1} . It is interesting that this is the value at which we start to see some unbound material being formed. The DRIFTS data for the filler show that, under the coating conditions used, the amine group of the APS has reacted with carbon dioxide to form a bicarbonate species. This reaction is now widely recognised [8]. Unfortunately, we were unable to establish the fate of the APS in the final compound, but Ishida [10] has reported that the bicarbonate can be decomposed at 95°C , and thus it might be expected that it would break down under the processing conditions used.

As with the ammonium stearate, it is possible to see a correlation between some composite properties and coating level. Thus, there is a general increase in secant modulus with additive level, with some evidence of step changes at about one and two monolayers. Further work would be needed to confirm this. Up to about half a monolayer of additive there is a reduction in tensile strength and no significant improvement in elongation. Both of these properties then improve significantly with further amounts of additive, with the tensile strength seeming to plateau at about two monolayers (30 mg/g^{-1}). The major improvement in elongation occurs between one-half and one monolayer, with a further progressive small increase beyond this level.

Unlike the fatty acid, the APS treatment appears to increase the amount of bound polymer, which would be consistent with increased filler/polymer interaction. The increase in bound polymer is progressive, with coating level over the range studied. The progressive decrease in MFR observed with APS addition is also consistent with increased filler/polymer interaction and with the increase in bound polymer reported above.

The limiting oxygen index also shows a progressive decrease with additive level. This effect has been noted before for additives that increase the composite modulus [15].

Polymer crystalline structure, as indicated by DSC, also seems to show stepwise changes at about 15 mg/g^{-1} . As with the stearate

coating, more work is needed to establish if there is a link between this and the composite properties.

Interestingly, while heat ageing significantly increases the amount of bound polymer formed in the presence of APS, this does not appear to have any marked effect on mechanical properties.

CONCLUSIONS

There is clear evidence that, with the coating methods employed, the structure of coatings deposited on the filler surface from both ammonium stearate and APS vary in structure with the level of additive used. The dependence on addition level is consistent with the filler surface area and the size of the adsorbing molecules.

Chemisorption of stearate occurs up to a limiting value of about 30 mg/g^{-1} of filler, a level which is consistent with the formation of a close-packed, vertically-adsorbed monolayer. At addition levels above this, free magnesium stearate and possibly some stearic acid are present. There is good evidence that the half salt is the main species below the monolayer level, with the full salt becoming predominant above this level.

Chemisorption of APS also occurs up to a limiting level of about 30 mg/g^{-1} , which is consistent with the surface coverage level given in the commercial literature. There is also strong evidence for a change in structure of the chemisorbed layer at about 15 mg/g^{-1} coverage. This level is that predicted for a vertically adsorbed, fully hydrolysed silane monomer. It is thus postulated that this strongly adsorbed layer is formed at low additive levels, while higher ones lead to the chemisorption of increasing amounts of condensed species and also of increasing amounts of physisorbed monomers and oligomers.

With the coating conditions used, APS appears to hydrolyse fully and also to react with atmospheric carbon dioxide to form a bicarbonate salt. The fate of the bicarbonate during further processing was not studied in this work.

Several composite properties, such as bound polymer, tensile strength, elongation, and crystallisation behaviour, show distinct correlation with the 30 mg/g^{-1} stearate level. Excess stearate above this level also seems to promote deleterious ageing effects. Careful control of coating level is thus necessary if optimum results are to be obtained.

Bound polymer, yield and tensile strength, elongation, and crystallisation behaviour show a distinct step change at about the 15 mg/g^{-1} addition level of APS, with a level of about 30 mg/g^{-1} being needed for optimum performance. This indicates that the presence of some condensed silane species may be beneficial. Unlike stearate, excess

amounts of the silane do not seem to lead to detrimental ageing effects, and thus control of coating level appears to be less critical.

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