Surface Analysis of Zinc Hydroxystannate-Coated Hydrated Fillers

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Introduction

Zinc hydroxystannate ($Zn[Sn(OH)_6]$, ZHS)-coated fillers are novel flame retardant and smoke suppressant additives for polymeric materials. The application of ZHS coating to various hydrated inorganic fillers, in particular magnesium hydroxide or aluminium hydroxide, allows significant reduction to be made in the overall filler loading, with no loss in their flame retardant properties.[1-3] In order to help to rationalise this effect, in this work a surface characterisation of zinc hydroxystannate-coated magnesium hydroxide and aluminium hydroxide fillers was performed by XPS, including the determination of the surface coverage and the average layer thickness values of the ZHS coating.

Sample preparation

ZHS-coated fillers were prepared according to the 'standard' route as follows. In a typical example, 1000 g of alumina trihydroxide (ATH, Alcan SF4, produced by Alcan Chemicals, UK) filler were slurried in 8 litres of an aqueous solution containing 103 g sodium hydroxystannate. One litre of an aqueous solution, containing 53 g zinc chloride, was added dropwise into the slurry, and the resulting mixture was stirred for 2 hours. The resulting solid product was separated from the solution by centrifugation, washed three times with distilled water and dried in air at 110 °C. The dried cake was crushed in a mortar with pestle to give 1110 g of a fine white powder (ZHS-coated ATH). ZHS-coated magnesium hydroxide (MH, Magnifin H5, produced by Martinswerke AG, Germany) powders were prepared using a similar method.

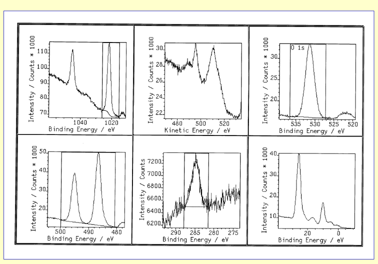
Surface analysis

X-ray Phototoelectron Spectroscopy

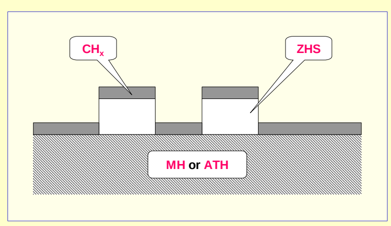
Kratos XSAM 800 spectrometer
Mg K$\alpha_{1,2}$ excitation
Fixed Analyser Transmission, 80 and 40 eV pass energy
Referencing: CH_x type C1s (BE = 285 eV)
C1s, O1s, Zn2p, Mg2p or Al2p

Data processing: Kratos Vision2000 data system
Model calculation: XPS MultiQuant, version 2.0 [4]
Cross sections: Evans et al. [5]
IMFP calculation: Seah and Dench [6]
Morphology: SEM [1,2]

Characteristic spectra of zinc hydroxystannate



The scheme of the *Islands-on-Plane model applied for the quantification of the ZHS-coated MH and ATH samples**



* Lamelliform particles

Calculation of concentration of ZHS

The theoretical ratio of the mass of the coating, m_c to the mass of the substrate, m_s is:

$$m_c / m_s = ahAr \quad (1)$$

where
a - calculated coverage
h - calculated layer thickness
A - surface area of the substrate (6.2 m^2/g by BET)
r - mass density of the coating (3.3 g/cm^3 by product specification)

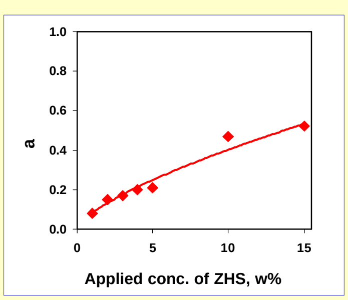
The bulk weight concentration (*c*) of the coating is:

$$c = 100\, m_c / (m_c + m_s) \quad (2)$$

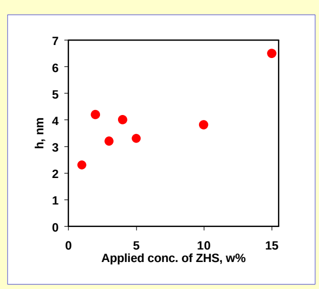
$$100 / c = (m_c + m_s) / m_c = 1 + m_s / m_c = 1 + 1 / Aahr \quad (3)$$

$$c = 100 / (1 + 1 / Aahr) \quad (4)$$

Surface coverage (a) of ATH by ZHS versus applied bulk concentration of ZHS



Thickness (*h*) of ZHS islands as a function of its applied bulk concentration

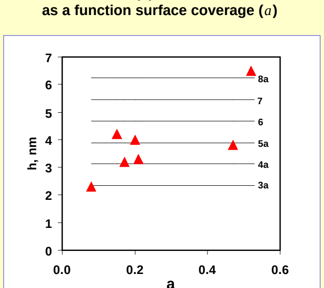


Summary

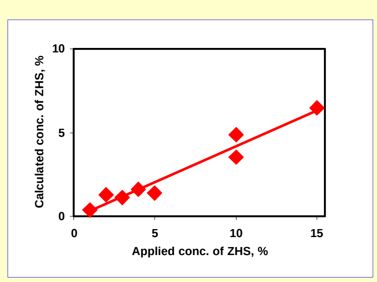
Magnesium hydroxide and aluminium hydroxide powder samples coated by zinc hydroxystannate (ZHS) to various extents have been studied by X-ray photoelectron spectroscopy. For quantification of the XPS results a model was applied, in which the substrate was covered by islands of ZHS, and this system was considered to be covered by a uniformly thin carbonaceous contamination overlayer. The surface coverage by ZHS and the thickness values of the carbonaceous and ZHS layers were determined for each sample by the recently developed XPS MultiQuant program. Relationships were established between surface coverage, layer thickness and applied bulk concentration of ZHS.

Low coating thickness values in the range of several nanometres have been obtained, which may account for the previously observed high flame retardant and smoke suppressant efficacy of zinc hydroxystannate-coated fillers when applied in various polymeric formulations.

Thickness (*h*) of ZHS islands as a function surface coverage (a)



Calculated versus applied concentrations of ZHS



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