



Test method

SEM/EDX: Advanced investigation of structured fire residues and residue formation

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ABSTRACT

Heterogeneous, gradual or structured morphology of fire residues plays an important role in fire retardancy of polymers. A scanning electron microscope with an attached energy dispersive X-ray spectrometer (SEM/EDX) is highlighted as a powerful tool for the advanced characterization of such complex fire residues, since it offers high resolution in combination with both good depth of field and analysis of chemical composition. Two examples are presented: First, comprehensive SEM/EDX investigation on a complex structured fire residue of glass fibre reinforced polyamide 6,6 (PA 66-GF) flame retarded by diethylaluminium phosphinate, melamine polyphosphate and some zinc borate. A multilayered surface crust (thickness $\sim 24 \mu\text{m}$) covers a rather hollow area stabilized by GF glued together. The resulting efficient thermal insulation results in self-extinguishing before pyrolysis is completed, even under forced-flaming combustion. Second, sophisticated, quasi online SEM/EDX imaging of the formation of residual protection layer in layered silicate epoxy resin nanocomposites (LSEC). Burning specimens were quenched in liquid nitrogen for subsequent analyses. Different zones were distinguished in the condensed phase characterized by distinct processes such as melting and ablation of organic material, as well as agglomeration, depletion, exfoliation and reorientation of the LS.

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1. Introduction

Pyrolysis in the condensed phase plays a major role in fire behaviour of polymeric materials. The mass loss rate and the effective heat of combustion of the volatiles determine the heat release rate, and thus fire risks such as flammability, flame spread and heat release. Increasing char yield is equivalent to decreasing fuel production; back in the 70s van Krevelen reported the correlation between the char yield of pure halogen-free polymers and their fire properties such as LOI [1]. This approach has been refined since by considering additionally the effective heat of combustion of the fuel [2,3]. However, when the fire behaviour is considered, especially of polymers containing

fillers and flame retardants, this is not the whole story. Physical mechanisms such as re-radiation, thermal insulation, mechanical stability of the char, transport of volatile products, melt flow, dripping and wicking are additional significant factors. Indeed, in some systems they even become the controlling mechanisms [4–7].

All residue formed during a fire also acts as barrier against heat and mass transport. The effectiveness of such a residual protection layer depends not only on the amount of char, but also on its properties, such as morphology, which determines gas permeability and thermal conductivity. Indeed, such protection properties were observed quite independently of the amount of thermally stable char [8]. Further, the properties of residue may be tailored by adding inorganic adjuvants and synergists [9–12]. Hence, the complex, heterogeneous or gradual morphology of the fire residue plays a key role. The design of a fire residue consisting of multicellular structures or closed glassy

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surface layers is a promising approach for flame retardancy. Further, such physical mechanisms influence different fire properties quite differently and are of different utility in different fire tests [13,14]. Residual protection layers strongly influence properties such as heat release rate, whereas other fire risks such as total heat evolved remain largely unchanged [15]. To improve the understanding and directed development of flame retarded materials, the accurate investigation of complex fire residues with respect to their chemical composition and morphology is crucial, as is the investigation of their formation during fire.

Scanning Electron Microscopy (SEM) provides high resolution in combination with good depth of field, and with an energy dispersive X-ray spectrometer (EDX) attached it identifies chemical composition within the microstructure at one location simultaneously. Thus, SEM/EDX has become widely used in material science and engineering. Because viscous smut, char or slug are not the preferred samples for investigation in a SEM apparatus, investigating fire residues was rather rare in past, but probably gained momentum more recently. SEM investigations focus mainly on special surface layers [16–21]. It is the aim of this paper to highlight SEM/EDX as an advanced powerful tool for the investigation of complex fire residues and their formation by presenting two extraordinary examples.

A glass fibre reinforced polyamide 6,6 (PA 66-GF) was investigated, flame retarded using a mixture consisting of metal phosphinate/melamine polyphosphate/zinc borate. Such mixtures have become increasingly typical for modern materials, raising particular questions of fire residue's chemical composition and heterogeneity. A structured residue is formed with very effective heat insulation so that the specimen extinguished before the polymer was consumed completely [22]. In the SEM/EDX examinations presented, the morphology and microstructure and the associated distribution of elements in different parts of the residue were investigated. The second material investigated is a layered silicate epoxy resin composite (LSEC). For such nanocomposites, different mechanisms for protection layer formation have been proposed, including polymer ablation, transport mechanisms of silicate directed to the surface, and reassembly of the particles into a surface layer [23–27]. Through interrupting the burning by quenching the specimen in liquid nitrogen the different stages in the condensed phase are conserved, including intact pure material, decomposing material, and residue. Cross sections were investigated by means of SEM/EDX characterizing structure and concentration profiles at the same time to get information on directed transport, reassembly, polymer ablation, etc. The approach aspires to a quasi online characterisation of residual protection layer formation.

2. Experimental

The fire residue of a PA 66/30 wt.-% GF was investigated, with a total flame retardant loading of 18 wt.-% consisting of diethylaluminium phosphinate, melamine polyphosphate, and some zinc borate (PA 66-GF/FR). The polymeric samples (plates; $100 \times 100 \times 5 \text{ mm}^3$) were

provided by Clariant GmbH and were burnt under forced flaming conditions, using an irradiation of 35 kW m^{-2} in a cone calorimeter (Fire Testing Technology, East Grinstead, UK). A significant increase in thickness occurred during burning and extinguishing before the polymer was consumed completely. The fire residue was taken for the SEM/EDX investigations as received from the combustion.

Samples displaying the condensed phase during the burning of a LSEC were obtained by interrupting the burning process. The material consisted of an aromatic epoxy-resin/5 wt.-% organically modified LS (sodium ions of Nanofil 757 (Süd-Chemie) were exchanged with equimolar amounts of tetraphenylphosphonium). 4,4'-dihydroxy-2,2-diphenylpropane "Bisphenole A" diglycidylether (Araldite GY 250 from Huntsman) was used as epoxy and 4-methyl hexahydrophthalic anhydride (MHHPA, Aldrich) as curing agent. The composite was cured at $90 \text{ }^\circ\text{C}$ for 2 to 3 h. The composites were prepared and provided by IFAM in Bremen. A detailed description of the preparation and characterisation has been published previously [28]. The materials were reported to be somewhere between microcomposites and nanocomposites. Specimens with dimensions of $45 \times 45 \times 5 \text{ mm}^3$ were ignited in a cone calorimeter set-up (irradiation = 50 kW m^{-2}), and burnt for a while under forced flaming conditions. After about 50 wt.-% mass loss, the burning specimens were quenched in liquid nitrogen. The samples obtained were prepared to investigate cross sections by embedding them in a bromine-rich epoxy resin (solid epoxy resin of the tetrabromobisphenol-A epichlorohydrin type, D.E.R. 542, Dow Chemical Company). The resin provided low viscosity while embedding and good contrast for SEM/EDX investigations. Further, the mechanical properties of the resins were similar, which facilitates the subsequent polishing with various emerald abrasive papers (increasing the fineness up to a value of 1600).

An Environmental SEM (FEI XL30 ESEM, Eindhoven, The Netherlands) was used, equipped with an energy dispersive X-ray spectrometer (EDAX sapphire detecting unit with Super UTW window and Genesis 4.61, Tilburg, The Netherlands). In case the ESEM mode (up to 3 mbar partial water vapour pressure) did not produce satisfactory results with respect to resolution or intensity, an evaporation chamber (BOC-EDWARDS, Crawley, U.K.) with electron beam evaporator was used to metallize the samples. For metallized samples, secondary electron contrast mode (SE) or the "backscattered secondary electron detector" (BSE) are used; in the case of ESEM mode the so-called "gas secondary electron detector" is applied (GSE). To minimize degradation and drift due to thermal expansion, fast mapping with dwell times (i.e. the time for electron exposure at one certain position) of $200 \mu\text{s}$ per pixel were used whenever possible.

A special two-step analysis procedure was necessary to obtain quantitatively reliable results for the element profiles over the entire cross sections consisting of 8–11 square images: First, the raw intensities of each square image were recalculated to a scale enabling a comparison between them and, second, the intensity drift of the illumination, i.e., the stability of the cathode, had to be considered as well as the efficiency of the excitation and

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