Abstract PhD

“The role of intumescent flame retardants on the fire behavior of poly(vinyl acetate) and poly(ethylene-co-vinyl acetate): a mechanistic and kinetic study.”

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The fire behavior of polymer model systems poly(vinyl acetate) and poly(ethylene-co-vinyl acetate) with 73 and 60 weight% vinyl acetate, PVAc and EVA 73 and EVA 60 respectively, are studied in combination with three different solid-state flame retardants: ammonium polyphosphate (APP), melamine isocyanurate (MIC) and silicate nanocomposites. The fire performance of these flame retardants (FRs) is tested with cone calorimetry. The relationship with lab-scale thermal analysis is made by means of difference thermograms calculated out of the oxidative degradation as measured with thermogravimetric analysis (TGA). Thermogravimetry combined with Differential Thermal Analysis (TGA-DTA) is used to measure the production or absorption of heat during the degradation of the composites.

A simplified mechanistic degradation model of both the inert and oxidative degradation of the pure polymer and flame retardant composites is developed using the combination of thermogravimetric analysis coupled with mass spectrometry (TGA-MS) and solid-state NMR measurements performed on partially degraded samples. This degradation mechanism is used for modeled kinetic analysis. The model is built-up in such a way that addition of other materials like flame retardants can be incorporated by means of parallel or combined degradation reactions. Thermogravimetric data originating from isothermal, constant heating rate and Hi-Res™ measurements were used for this purpose. An optimization routine is used to obtain a best fit between calculated and measured weight profiles by the software program FITME. The resulting findings are then compared with the fire behavior of the composites.

In an inert environment PVAc and EVA copolymers first undergo a deacetylation reaction between 300 and 400 °C: acetic acid is eliminated from the polymer backbone, leaving a double bond. For PVAc, EVA 73 and EVA 60 this process is autocatalytic. In the mechanistic model, this is described by three different reactions: a non-catalytic deacetylation, a catalytic deacetylation reaction and a deactivation step for the catalytic sites. For EVA with a weight% vinyl acetate (VAc) of 9, 19 and 33, only the non-catalytic deacetylation reaction is observed. Rate parameters of this reaction are therefore studied with these copolymers. By the study of the kinetics of the catalytic deacetylation and deactivation of PVAc, EVA 73 and EVA 60, it is observed that the importance of this last step depends on the (co)polymer composition: the more ethylene entities incorporated into the EVA copolymer, the higher the rate of the deactivation step.
After deacetylation, the formed polyene-like structure degrades upon further heating with chain scission reactions producing both aliphatic and aromatic volatiles (between 400 and 500 °C). Ethylene entities degrade into aliphatic volatiles, unsaturated entities into aromatics. The rate parameters of the chain scission reactions were optimized simultaneously for a range of copolymer compositions between 9 and 100 % VAc. In an oxidative environment, the rate of the catalytic deacetylation increases, influenced by the presence of oxygen. After deacetylation, the polyene is reformed into a fully aromatic structure or char between 400 and 500 °C. Ethylene entities are not incorporated into this charred structure and degrade similar to inert conditions. The formed char is degraded into CO₂ upon further heating (between 500 and 600 °C). The rate parameters of the charring step and oxidation into CO₂ are optimized simultaneously for EVA 73 and PVAc. Both have a similar thermostability.

PVAc, EVA 73 and EVA 60 / APP composites posses excellent fire behavior. The earlier ignition of the plates is explained by an acceleration of the deacetylation process of PVAc and EVA 73; the combination with EVA 60 leads to a further destabilization of the ethylene entities. The lowered burning intensity is linked to an improved thermostability of the polymer matrix when combined with APP. During deacetylation of these copolymers, APP is activated and cross-links with the polymer. In the model this deacetylation and cross-linking process is described by five parallel reactions: the three reactions of the deacetylation process, the activation of APP and the crosslinking reaction of APP with the polymer. The kinetic evaluations reveal an acceleration of the non-catalytic reaction. After deacetylation the PVAc and EVA 73 / APP composites undergo charring in oxidative conditions, followed by the breaking of the phosphate cross-linked structure and oxidation of the remaining organic char. The kinetic evaluation learns that the thermostability of the cross-linked material is independent of the mixing ratio. Furthermore, the thermostability of both PVAc and EVA 73 / APP composites is equal. Only if the amount APP added to PVAc is lowered to 5 phm, the char looses its stability.

If MIC is added to PVAc as a flame retardant, good FR activity is obtained with the addition of at least 40 phm MIC. Similar to the APP composites, for EVA 73 and EVA 60 this effect is already observed with lower mixing ratios. TGA-DTA analysis reveals the absorption by MIC of the produced heat originating from degrading polymer during deacetylation and charring. A large part of MIC evaporates during these steps; MIC acts as a heat-sink and crosslinking FR. All mixing ratios of the PVAc and EVA 73 / MIC composites have identical degradation rates, indicating that small amounts of MIC acting as crosslinking agent are sufficient to stabilize the polymer matrix. The part of MIC not incorporated into charring acts as heat-sink flame retardant. The more MIC acts as heat-sink FR, the more the influence on the fire behavior of the composite.