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Using Clay in PA-Based Intumescent Formulations. Fire Performance and Kinetic Parameters

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Summary : The improved fire performance of polyamide-6 clay nanocomposite compared with polyamide-6 are correlated with their degradation kinetic parameters. Moreover substituting polyamide-6 by polyamide-6 clay nanocomposite in an intumescent blend enables to improve its fire properties. Once again, the improved fire performance can be correlated with the kinetic degradation parameters. The advantages of using nano-dispersed clay are shown.

Introduction

Polyamide-6 clay nanocomposite (PA-6 nano) was shown to present enhanced fire properties compared with PA-6[1,2 and references therein].

Ethylene-vinyl acetate (EVA) copolymers are used in low-voltage electrical wires. But their major shortcoming remains their flammability. A solution to reduce it consists in using additives which develop an intumescent shield under heat flux[7-8] : intumescent materials form on their surface a foamed cellular charred layer, limiting the heat, mass and oxygen transfers between the gas and the condensed phases. Intumescent formulations generally contain three active ingredients : an acid source (for example, ammonium polyphosphate (APP)) , a carbonization agent (like a charring polymer : PA-6 for instance) and a blowing agent (ammonia evolved during the degradation of APP). The EVA / APP / PA-6 intumescent formulation was shown to present excellent fire properties[9]. The purpose of this part is to improve the fire properties of the blend by substituting PA-6 by PA-6 nano. The fire properties obtained will be compared with those of the equivalent blend using clay as a classical filler. The IKP method[3-5] will be applied to the thermo-oxidative degradations of the blends, to attempt to correlate their kinetic parameters with their fire properties.

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Experimental

Materials : EVA 24 wt.% copolymer (EVA-24, Evatane 24-03) is supplied as pellets by Elf Atochem. PA-6 and PA-6 nano are supplied as pellets by UBE. APP ($(NH_4PO_3)_n$, n=700, Hostaflam, powder as supplied by Clariant) is also used. Potassium montmorillonite K-10 is supplied by Aldrich. Powders (particles size lower than 200.10^{-6} m) for thermogravimetric (TG) analyses are obtained using a Retzsch cryogenic grinder at about –196°C.

Processing : The following materials EVA-24 (100 wt.%), EVA-24 (60 wt.%) / APP (30 wt.%) / PA-6 (10 wt. %), EVA-24 (60 wt.%) / APP (30 wt.%) / PA-6 nano (10 wt. %) are mixed at 230 °C using the Brabender Laboratory Mixer measuring head (type 350/EH, roller blades, Brabender Plasticorder PL2000 system, constant shear rate : 50 r.p.m.). The K-10 containing formulation : EVA-24 (60 wt. %) / APP (30 wt. %) / PA-6 (10 × (98)/100 wt. %) / K-10 (10 × 2/100 wt. %) is processed using a Brabender DSK 42/7 intermeshing conter-rotating twin-screw extruder (50 rpm, between 220 and 235°C along the screws).

Sheets are then obtained using a Darragon press at 190°C with a pressure of 10^6 Pa.

Cone calorimetry : Samples are exposed to a Stanton Redcroft Cone Calorimeter according to ASTM 1356-90 under a heat flux of 50 kW/m^2,. corresponding to the evolved heat during a fire[10-11]. The rate of heat release (RHR), and the residual weight are obtained using a software developed in our laboratory.

TG analyses : they are performed using a Setaram MTB 10-8 thermobalance at four heating rates β_v (5 ; 7.5 ; 10 and 15°C/min) from 20°C to 800°C under air flow (Air Liquide grade, $5\times10^{-7}m^3/s$ measured in standard conditions). Samples (about 10^{-5}kg) are placed in vitreous silica pans. Precision on temperature measurements is ±1,5°C.

The Invariant Kinetic Parameters Method : it is applied to the thermal and thermo-oxidative degradations of PA-6 and PA-6 nano and to the thermo-oxidative degradation of the blends.

Results and discussion

PA-6 and PA-6 nano : PA-6 nano presents enhanced fire properties compared with virgin PA-6[11]. The IKP method is used to compute the kinetic parameters of their thermal and thermo-oxidative degradations. *Under nitrogen flow*, PA-6 and PA-6 nano roughly have the same activation energy (respectively 180+/-10 and 200+/-10 kJ/mol), and they both degrade according to phase boundary reactions. Moreover, whatever the temperature and conversion degree the degradation rate is higher for PA-6 than for PA-6 nano. Oxygen plays a major role in the stabilisation process of PA-6 nano. Indeed *under air flow* the activation energy of PA-6 nano is higher than that of PA-6 (300 +/- 20 against 250 +/- 20 kJ/mol). Moreover the thermo-oxidative degradation of PA-6 can be represented by a potential law model (classical degradation mode of a polymer), whereas it can mainly be represented by a diffusion model with a plane symmetry for PA-6 nano. This would be in accordance with the formation of a physical barrier. In addition PA-6 nano degrades more rapidly than PA-6 at high temperatures and then at lower temperatures and at high conversion degree PA-6 degrades more rapidly than PA-6 nano (Fig. 1). A protective barrier is thus formed during the thermal degradations of PA-6 nano which decreases its rate of degradation via a diffusion process (lowers the escape of fuels). According to the shapes of the degradation rates and of the kinetic laws the coating formed by PA-6 nano may be more efficient than that formed by PA-6, what could explain its better fire properties. The formation of a barrier for PA-6 nano may correspond to a change phase of the clay, from a delaminated to an intercalated structure[12].

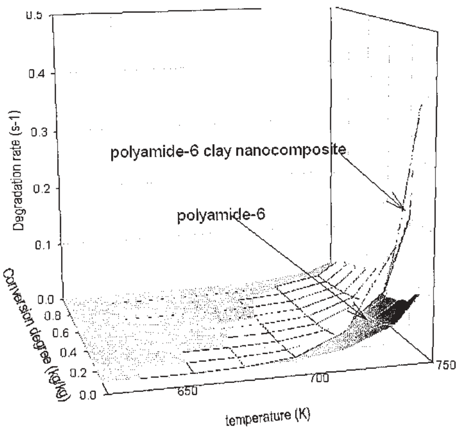

Fig. 1. Degradation rate of PA-6 and PA-6 nano under oxygen.

The intumescent blends

Fire Properties : as shown by Fig. 2, the RHR values of the intumescent EVA-based materials are reduced by about 80% compared with virgin EVA. Using PA-6 nano instead of PA-6 in the blend improves the fire properties with a decrease in the RHR peak from 320 to 240 kW/m^2. Adding K-10 to the blend enables a decrease in the RHR peak in the first step of the combustion similar to that obtained using PA-6 nano. However, around 300s, K-10 is causing increased degradation (increase in the RHR peak from 200 to 400 kW/m^2).

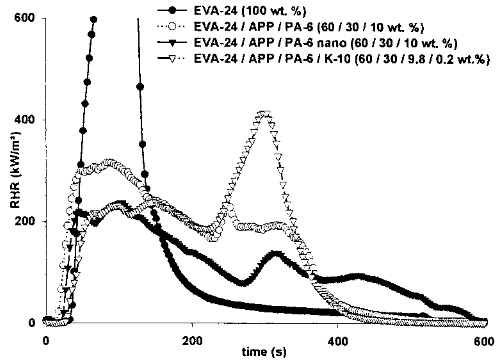

Fig. 2. RHR values versus time of the formulations EVA-24 / APP / PA-6, EVA-24 / APP / PA-6 nano and EVA-24 / APP / PA-6 / K-10 in comparison with virgin EVA-24 (heat flux = 50 kW/m²).

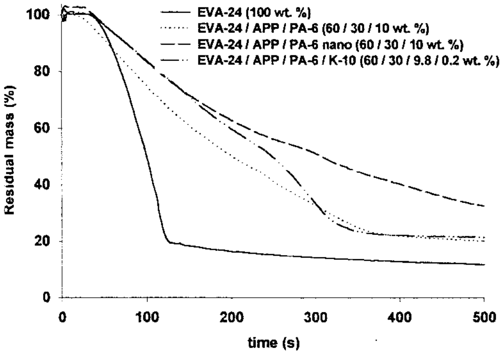

Fig. 3. Residual mass versus time of the formulations EVA-24 / APP / PA-6, EVA-24 / APP / PA-6 nano and EVA-24 / APP / PA-6 / K-10 in comparison with virgin EVA-24 (heat flux = 50 kW/m²).

Fig. 3 shows that the residual mass of EVA-24 / APP / PA-6 nano is strongly increased compared with EVA-24 / APP / PA-6. The same stabilization is observed in the 200 first seconds of the combustion when using K-10 but after 300 s, no stabilization is observed anymore. Thus a tougher intumescent char is formed in the first step of the combustion when using PA-6 nano or K-10. However when using K-10 it may be assumed that the intumescent barrier is not as strong or less thermally stable as when using PA-6 nano. Thus some cracks may be formed leading the char to collapse around 300 s.

The stabilization under air when using PA-6 nano was not observed under nitrogen[13]. This could be correlated with the effect of oxygen on PA-6 nano degradation. Thus the modeling will be performed upon the thermo-oxidative degradations of the blends.

Under air, the degradation of the materials is a three-step process. The second step is assumed to govern the fire properties and thus will be studied.

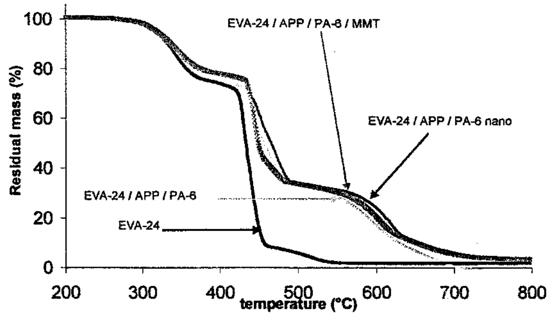

Fig. 4. TG curves of the intumescent blends compared with virgin EVA. Under air ; 10°C/min.

The degradation rates are plotted from the IKP method results against conversion degree and temperature on Fig. 5. On the whole temperature range, whatever the conversion degree the degradation rates of the formulations containing clay (PA-6 nano, or K-10) are quite identical. They degrade more rapidly than EVA / APP / PA-6 at high temperature and then at lower temperature, whatever the conversion degree, EVA / APP / PA-6 degrades slightly more rapidly. The protective behavior of the EVA-based formulations is observed at low conversion degree values when the temperature increases. It is stronger for the clay-containing formulations. The blend degrades rapidly to form the material presenting barrier properties.

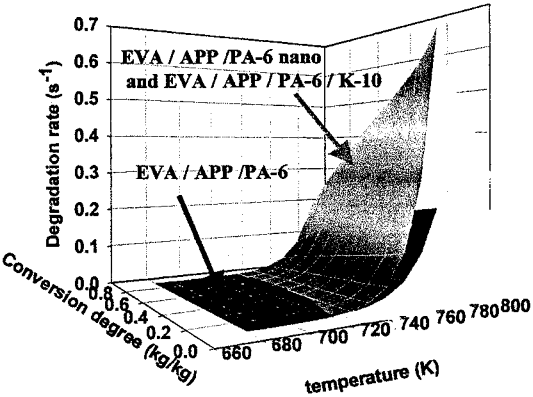

Fig. 5. Degradation rate of the EVA-based formulations under air in the 660-800K temperature range.

Discussion

EVA / APP / PA-6 / K-10 and EVA / APP / PA-6 nano present the same degradation mode and rate. They both display a protective behavior stronger than EVA / APP / PA-6. Even though the thermogravimetric analyses conditions are different from the conditions of a fire it is assumed that the kinetic considerations are responsible for the improvement of the fire behavior in the first step of the combustion : adding K-10 to the intumescent blend enables to obtain the same fire properties as when using PA-6 nano. APP reacts[13] with the clay to form an alumino-phosphate structure and a ceramic-like structure in a higher temperature range. We may assume that using PA-6 nano enables to obtain a better dispersion of these species in the char than when using K-10 dispersed in the blend. Thus using PA-6 nano leads to the formation of a homogeneous surface ceramic-like material nanocomposite providing a nanoscale reinforcement which enables the protection of the material all along the combustion. On the contrary, using K-10, the clay is in µm size and even if it is achieved good dispersion of K-10 micronclay, it fails to provide the nanoscaled flame retardant reinforcement needed.

Conclusion

This study shows the role played by oxygen in the stabilisation role played by nanoclay. Moreover the advantages of using nanoclay rather than micron-sized clay in an intumescent system are shown. Correlations are shown between the fire performance and the kinetic data.

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