Measurement of kinetics and thermodynamics of the thermal degradation for flame retarded materials: Application to EVA/ATH/NC

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ABSTRACT

The modelling of the behavior of a material exposed to fire is very complex and needs the coupling of fluid dynamics, combustion, heat and mass transfer, kinetics and so forth. A growing amount of studies and numerical models are reported in this field since the last decade. The aim of these models is to predict the fire behavior of wood, charring or non-charring polymers and even intumescent materials. However, these studies are seldom applied to formulated materials and especially flame retarded materials. In this study, an ethylene-vinyl acetate copolymer was formulated with a flame retardant (aluminum tri-hydroxide) and a synergist (nanoclays). A systematic approach for the characterization of the thermo-physical properties of the material as well as of its optical properties and the heat capacity of the decomposition gases is proposed and applied in this study. It is shown that it is possible to evaluate the input data required for pyrolysis modelling, even for multi decomposition steps materials. It is also shown that the diffusion of the gases inside the material had to be considered on the opposite of the classical assumption found in other studies. Indeed, using low mass diffusivity was the sole way to predict in the same time the temperature distribution and the mass loss rate of the material in a gasification experiments.

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1. Introduction

Fire is an important hazard in the industry, public transport and building facilities because it can lead to loss of lives and goods. Given the number and extent potentially flammable materials encountered in everyday life, fire safety is of main concern in terms of both human deaths and also economical loss [1]. In that frame, the use of numerical models in fire protection engineering appears has an important topic that is more and more considered. Partially because of the increase of computer power, fire modelling has reached the point that fire development can be predicted. These models associate a gas-phase model that include heat transfer, fluid dynamics and combustion with a condensed phase model that simulate the heating and pyrolysis of the condensed phase. Nowadays even if numerical models of the development of fires are more often reported in the literature, the predictive capabilities for condensed phase phenomena are more limited compared to

these of gas phase phenomena. Indeed, the Navier-Stokes equation governs fire induced gas fluid flow and huge progresses were made in turbulence modelling and numerical methods. Non-premixed combustion models were also developed, and combustion is now understood in terms of elementary reactions for simple fuels such as methane or hydrogen [2,3].

A large variety of models for the condensed phase action, including mass and heat transport, have been developed during the last decade (Fire Dynamics Simulator pyrolysis sub-model [4], Gpyro [5], ThermaKin [6], or Pyropolis [7], for example). Despite those developments, pyrolysis models are seldom applied to complex objects or formulated materials. Indeed, to represent how a material behaves under a thermal constraint, several phenomena should be taken into account which are not necessarily applicable from one type of material to another. As an example, delamination can occur for composites or fiber-reinforced materials, but is uncommon for pristine or filled polymers which involve dripping and/or charring [8]. For input data, these models require values that describe the chemical and physical phenomena occurring when a material burns. While some progress has been made in the development of experimental procedures for the measurement of these prop-

Nomenclature

General parameters/variables

t	Time
T	Temperature
N_r	Number of decomposition reactions of the material
x	Depth
m	Mass
N_g	Number of gaseous component released by the material

Optical properties

M	Black body exitance
α	Reflectivity
ε	Emissivity
λ	Wavelength
d	Thickness
I	Irradiance
A	Absorption coefficient
T	Transmittance
R	Reflectance

Kinetic parameters

$\dot{r}_r$	Reaction rate for reaction r
A_r	Pre-exponential factor for reaction *r*
E_r	Activation energy for reaction r
R	ideal gas constant
n	Order of reaction
ν_r^i	Stoichiometric coefficient of component i in reaction r

Thermo-physical properties

Cp	Heat capacity
k	Thermal conductivity
D_{gasi}	Mass transfer coefficient of component *i*
ρ	Density
H_r	Enthalpy of reaction r

erties [9–16], accuracy, comprehensiveness or robustness of these procedures clearly require further refinement.

However, in a recent paper [17] we have developed methods for the measurement of the inputs data including kinetics of decomposition, thermo-physical properties of the condensed phase as a function of the temperature and decomposition state but also other parameters such as optical properties or heat capacity of the decomposition gases. Those methods for instance include thermogravimetric analysis (TGA), simultaneous thermal analysis (STA), modulated (mDSC) or non-modulated differential scanning calorimetry (DSC) and transient plane source methods (TPS). On the opposite of other studies, these methods were applied to flame retarded material. An ethylene vinyl acetate copolymer (EVA) flame retarded with 65 wt% of aluminum tri-hydroxide (ATH). Even if it was possible to simulate the gasification of a flame retarded material, industrial materials are even more complex and their modelling is more challenging. Indeed, they are also formulated with other additives such as plasticizers, pigments, antioxidants or synergists for the fire performances and/or mechanical properties. As an example, it was shown that nanoclays, such as montmorillonite, exhibit synergistic effects with mineral fillers [18–27], especially for cable applications [25,26]. The use of such type of synergist may modify the decomposition pathway of materials and/or add additional decomposition state that would then have to be considered in the numerical models.

The aim of this study is thus to model of the fire behavior of a complex flame retarded material. Thus, an EVA flame retarded with 60 wt% of ATH and 5 wt% of nanoclays (NC) was chosen. The decomposition of this material was first investigated with an emphasis on its decomposition pathway but also kinetics and enthalpies of decomposition. Then, the thermo-physical and optical properties of the material as well as the heat capacity of its decomposition gases were characterized as a function of temperature. Afterward, the thermal decomposition of EVA/ATH/NC was investigated in a controlled-atmosphere mass loss cone in anaerobic atmosphere e. Finally, the simulation of the gasification experiments allowed us to validate our experimental approach and the values obtained for EVA/ATH/NC.

2. Experimental section

2.1. Materials and sample preparation

The polymer used in this study is an EVATANE® 28-05 (hereafter called EVA), corresponding to an ethylene-vinyl acetate copolymer containing 28 wt% of vinyl acetate (MFI = 5–8 g/10 min). Aluminum trihydroxide (hereafter called ATH) was supplied in powder form from Nabaltec AG as Apyral® 40CD (BET = 3.5 m²/g, D_{50} = 1.3 μm). The nanoclay (NC) used in this study is an organo-modified montmorillonite (Cloisite 30BTM) supplied by Southern Clay Product. The loadings of ATH and NC were fixed at 60 and 5 wt% respectively. More information about the processing method can be found elsewhere [17].

In order to characterize the dispersion of the additives (ATH and NC) in the EVA matrix, Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) experiments were performed. The samples were first ultra microtomed with a diamond knife on a Leica ultracut UCT microtome, at cryo temperature (−120 °C) to obtain smooth surfaces. For TEM experiments, films with a nominal thickness of 70 nm were then transferred to Cu grids of 400 meshes. Bright-field TEM images of composites were obtained at 200 kV under low dose conditions with a FEI TECNAI 62 20 microscope, using a Gatan CCD camera. TEM pictures were taken at 88 000x. SEM images were taken at 2 200x using a Hitachi S4700 SEM at 6 kV. It can be seen in the SEM presented in Fig. 1 that the dispersion of ATH is evenly dispersed in the EVA matrix. The dispersion of NC was determined with TEM pictures. It can be seen that the NC platelets are mainly exfoliated with few tactoids of 3–5 platelets in size.

A high-speed rotor mill (Retsch – Ultra Centrifugal Mill ZM200) was used to obtain fine powder from the formulations pellets. This powdered material will be used for further analyses including TGA, py-GC/MS or STA experiments. Before grinding, the materials were dipped in liquid nitrogen. The fed materials only remain in the grinding chamber for a very short time and so, the features of the samples were not modified.

Specimens for the fire testing were obtained by pressing the appropriate mass of material, previously extruded and pelletized, with a hydraulic hot press using specific molds at 170 °C and under 20 kN for 2 min and 40 kN for 8 min.

2.2. Thermo-gravimetric analysis and kinetic analysis

Thermo-gravimetric analysis (TGA) were performed on a TA Instruments Discovery TGA, using 250 μL open alumina pans. Experiments were carried out under nitrogen to mimic pyrolytic decomposition. The balance purge flow was set to 15 mL/min nitrogen to avoid the oxidation of the balance. The balance temperature was set at 40 °C to have controlled conditions and optimum sensitivity. All samples of 5.0 ± 0.5 mg underwent an isotherm at 50 °C