FLAME IGNITION MECHANISMS IN POLYMER NANOCOMPOSITES: EXPERIMENTAL EVIDENCES AND INTERPRETATION

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Abstract

In this work, flaming ignition of montmorillonite clay polymer nanocomposites and microcomposites was addressed, showing variable trends in the time to ignition, as compared with the reference polymers. Temperatures on the surface layer of specimens irradiated in the cone calorimeter were measured during the test, to investigate the surface temperature at ignition. Viscosity measurement and in depth radiative absorption measurements were also carried out and correlated with ignition of polymer. Additionally, physical and chemical characterization of the condensed phase at different time, either before or after ignition, were carried out to investigate the evolution of the material during the combustion process.

1 Introduction

Ignition of polymers has been extensively studied since the '60s [1], but fundamental aspects concerning their chemical and physical evolution, prior and during the combustion process are not yet understood in details. Indeed, especially in the case of complex polymer-based formulations containing fire retardants and/or nanoparticles, the thermophysical evolution of the condensed phase before ignition in a fire test has been rarely studied, also owing to experimental difficulties in such properties measurement. On the other hand, polymers containing additives or nanoparticles often exhibit unpredictable time to ignition if blind reference is made only to the material thermal behaviour such as that shown in thermogravimetry.

As an example, variable trends for time to ignition have been reported for polymer/layered silicate nanocomposites: a reduction of ignition time was often observed [2,3,4], compared to the reference polymers, but the opposite effect is also reported in many other cases [5,6,7,8].

Despite different proposals have been made to interpret modification of ignition time in nanocomposites, including thermal instability of layered clays organic modifiers [9,10,11], polymer degradation triggering by catalytic effects [12,13] and molten polymer viscosity [14,15], little work has been devoted to materials evolution experimental investigation during fire tests. The use of temperature measurements in the condensed phase has been recently shown [16] to help in understanding phenomena controlling ignition in polymer nanocomposites, providing insights in the melting, which controls the time to reach the decomposition temperature in semicrystalline polymers, and decomposition, which controls the production of volatile fuel. Furthermore, the analysis of residues quenched before or soon

after ignition were shown to deliver information on the thickness of material contributing to volatiles production as well as on material chemical evolution.

2 Materials and testing methods

Polyethylene terephtalate and Polypropylene PP (containing 5% of PP grafted with maleic anhydride-PPgMA, used as a compatibiliser for nanoclays) were used to prepare intercalated nanocomposites with organomodified montmorillonite clays (Cloisite 30B and Cloisite 20A by Southern Clays, respectively). Microcomposites were also prepared for comparison in both polymers, using unmodified montmorillonite (Sodium Cloisite by Southern Clays).
All formulations were melt compounded in a Leistritz ZSE 18 HP 40D twin screw extruder
Surface temperature measurements were performed during cone calorimeter tests, using K-type 0.5 mm stainless steel sheathed thermocouples by Tersid (I). Thermocouples were carefully placed and supported to keep contact with the upper surface of the sample throughout the experiment. Heat transmitted through the material was measured by Schmidt-Boelter heat flux meter below specimens with variable thickness (0.5, 1, 1.5 mm), under cone irradiance.
Interrupted combustion tests were performed by quenching the flame just after ignition, directing a stream of nitrogen at room temperature on the material surface. Fragile fracture were obtained after immersion in liquid Nitrogen to oberve the specimen cross-section.. On such residues, visual and optical microscopy observation were carried out, as well as infrared analyses, by Attenuated Total Reflectance (ATR).

3 Results and Discussion

3.1 Ignition of pristine polymers

Ignition, i.e. the reaching of the critical fuel production to overcome the lower flammability limit once mixed with air, depends on the rate of volatilization and the amount of material which temperature is sufficient for decomposition. Therefore, ignition is obtained as a consequence of decomposition of a layer with a certain thickness, below the thermally irradiated surface. However, the thickness of the decomposing layer before ignition depends on both the polymer type and the experimental conditions. As an example, very different behaviours were observed for PP and PET. In the case of PET, the presence of bubbles across the whole thickness suggests that the whole specimen contributes to fuel production before ignition. On the other hand, PP shows no bubbles across in the cross-section, suggesting only a thin surface layer is responsible for production of volatiles sufficient for ignition. Further support comes from the observation of deformation observed in cross-section and the texture of the bottom part of the PP specimen, showing the lower part of the specimen is not molten prior to ignition.
These facts evidence for significant differences in terms of in-depth heat transfer. In particular, heat transfer by convection has an important role in the overall thermal transport. By the observation of cross-sections, significant convective flows are found in PET, whereas no evidences of convective flow are shown for PP.
An explanation for these differences can be provided by the large difference in viscosity for the two polymers above melting. Indeed, while PET exhibits a netwonian viscosity plateau at low frequency about 40 Pa·s (at 260°C), compared with the value of about 1300 Pa·s (at 190°C) for PP, thus evidencing a completely different flow behavior. A higher viscosity clearly results in a reduction of convective flows, i.e. a reduction of thermal transfer by convection. Therefore, a slower heat transfer is indeed expected for PP, compared to PET, leading to a limited thickness of the decomposing material before ignition.
The surface temperature plots for PET show a first fast heating to the melting temperature (255 °C), followed by a very well defined temperature plateau of about 250 s is observed,

corresponding to complete melting of the sample. After melting is completed, a very sharp increase in temperature to a new plateau at about 400 °C is observed, corresponding to decomposition of PET. This temperature is kept constant, within the error of experimental measurement, until ignition, i.e. until the thickness of the decomposing layer is high enough to produce the critical flux for ignition.

For PP, a smoother curve with less defined melting and decomposition plateaus is observed. This explained by its higher melt viscosity, which does not allow to keep thermal equilibrium during melting and decomposition of the polymer.

3.2 Ignition of polymer nanocomposites

Intercalated PET/5wt.% organomodified montmorillonite (Cloisite 30B) nanocomposites was compared with correspondent microcomposite prepared with unmodified sodium montmorillonite (Cloisite Na$^+$) and pristine PET [16]. Polyethylene terephthalate shows an average TTI at 730 s and a very sharp increase in the HRR after ignition, with a maximum combustion rate of about 1100 kW/m^2. On the other hand, both composites exhibit lower ignition time and lower peak of HRR. The reduction in both TTI and peak HRR is particularly significant in the intercalated nanocomposite, with TTI at 380 s and peak HRR at about 450 kW/m^2. Surface temperature measurements shows no significant differences in terms of ignition temperature, which remains controlled by the decomposition of PET.

Similarly, intercalated PP/5wt.% organomodified montmorillonite (Cloisite 20A) nanocomposites was compared with correspondent microcomposite prepared with unmodified sodium montmorillonite (Cloisite Na$^+$) and pristine PP [17]. While the nanodispersed clay reduces significantly the heat release rate compared to PP, limited differences in time to ignition were observed, being namely 117 s for PP, 116 s for PP/CNa$^+$ and 125 s for PP/C20A. Surface temperatures at ignition remains constant (322 and 315°C for PP/CNa$^+$ and PP/C20A, respectively), within the experimental errors. With increasing the imposed heat flux, a general reduction of ignition times is generally observed: however, while PP and PP/C20A exhibit almost identical TTI, PP/CNa+ shows lower TTI values, both at 35 and 50 kW/m^2.

Different trends in ignition temperature were also observed for the different materials when increasing the imposed heat flux. The ignition temperature measured for PP at 35 and 50 kW/m^2 is about 387°C, which is significantly higher than the 316°C measured at 25kW/m^2.

The nanocomposite shows a trend similar to that of PP, with increase of ignition temperature towards pyrolysis-controlled PP volatilisation as heat flux increases to 50 kW/m^2. On the other hand, the microcomposite ignites at the same temperature (316-7°C) independently of the irradiation flux, which is close to the temperature (322°C) at which PP ignites at the lowest irradiation (25 kW/m^2).

This complex behavior is the result of the interplay of several physical and chemical processes such as: polymer viscosity control of heat transfer by convection, filler effect on heat absorption, oxygen diffusion, polymer thermal oxidation, polymer pyrolysis and chain fragments volatilization.

Based on these experimental results, the effect of both microdispersed or intercalated nanoclay on ignition time and ignition temperature will addressed and discussed in details in the presentation.

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