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Thermal Evolution of Nanocomposites. When Nanoparticles are effective in polymer fire retardancy

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It is generally agreed that the combustion behavior of polymer nanocomposites strictly depends on the interface between polymer condensed phase and the gas phase. Since the first studies on the nanocomposites' behavior in fire [1,2], it was pointed out that the behavior under forced combustion for different nanocomposites were quite similar: a reduction of the heat release rate consequent to a lower fuel feed rate often without substantial modifications of the polymer bulk degradation pathway. Such a behavior is related to the formation of a physical shield built up by the inorganic nanoparticles left behind by polymer ablation, which acts as a barrier, slowing down the release of generated gas fuel. However, limited understanding of fundamental of physical and chemical process occurring in the condensed phase is available at present. Indeed, complex phenomena can take place in the surface mesophase during nanocomposite burning, affecting accumulation of inorganic particles and their interaction with the polymer while building of a surface structured ceramic phase takes place. Furthermore, the effectiveness of these phenomena on the fire performance of the nanocomposite strictly depends on the specific features of the considered test, such as geometrical setup, presence or absence of external heating source and the possibility of dripping.

At present, the fire retardance scientific community basically takes advantage of three different fire tests, namely vertical UL94, LOI and Cone Calorimeter. UL94 and LOI are generally referred to as flammability tests, in which the material behaviour exposed to a small flame is addressed, in terms of capability to ignite and to self-sustain a flame, thus representing a scenario in which the material is at the origin of a fire. On the other hand, cone calorimeter test is representative of a forced combustion, in which the material is forced to burn under controlled heat flux. This test addresses the ignition time, the rate of combustion and the total heat released, modelling the contribution of the material to a fire started on other items.

Moreover, these flammability and combustion tests also differ for the specimen positioning, the formers being vertical tests, the latter most often being an horizontal test, despite vertical configuration is even provided for by the standard methods [3,4]. Considered these differences, it is certainly reasonable to expect different performances of a given fire retarded formulation compared with the reference material, when testing in different fire tests, expected to be representative of different fire scenarios. With polymer nanocomposites, the differences in performance obtained in flammability and forced combustion test are usually very significant, this having caused an ongoing discussion on the actual effectiveness of nanoparticles as fire retardants [5,6].

The consequence of these facts is twofold: on the one hand, the relevance of different fire tests to real fire scenarios becomes crucial for the final application of polymer nanocomposites and, on the other hand, the scientific significance of standard tests must be carefully evaluated. In this section, a critical comment of phenomena behind the bare ranking results of some standard fire tests is proposed.

Ignition

Polymer nanocomposites show variable trends for time to ignition have been reported: a reduction of TTI compared to neat polymers is often observed, but the opposite effect is also reported in many cases. A number of proposals have been made to interpret reduction of TTI in nanocomposites when it occurs, such as thermal instability of nanofiller alkylammonium organic modifiers, releasing fuel at relatively low temperature by Hoffman reaction [7], triggering polymer degradation by catalytic effects [8], enhanced radiant heat absorption [9], improved thermal conductivity [10] as well as viscosity increase hindering convective flow in the molten polymer [11, 12]. However, similar changes in thermophysical properties (thermal conductivity, viscosity) have been proposed in cases when time to ignition is observed to be higher than the reference polymer [13,14], leading to a puzzling scenario, in which none of the interpretations supplied so far in the literature result in a general rule and where no solid experimental evidences are reported.

PET- and PA6-based nanocomposites containing layered nanoclays showing anticipated ignition were studied in details by the measurement of ignition temperatures and observation of physical and chemical phenomena occurring prior to ignition for polymer and polymer nanocomposites. Surface temperature profiles suggested that in nanocomposites, ignition may be controlled by nanoparticle-catalyzed oxidation of the gases generated at the surface of the condensed phase by volatilization of the polymer. Conditions for ignition are thus created as soon as the polymer decomposition temperature is reached, in contrast with pristine polymer in which enough volatiles from bulk polymer pyrolysis have to be produced to mix with air above the specimen to reach the lower flammability limit.

Flammability

Flammability tests such as UL94 and LOI on polymer nanocomposites usually evidence significantly lower or no dripping from the ignited specimen, significantly lower rate of combustion and higher residue at the end of test, compared to the reference polymer.

However, the same or worse material ranking for nanocomposites compared to reference polymer are usually obtained in UL94 test. This depends on the fact that UL94 methods are pass/fail tests which aim at ranking the materials in terms of fire risk in selected scenarios but ranking by itself is useless in development of fire retardant materials because of its ambiguity in terms of detailed combustion behaviour. For example the same V-0 ranking is attributed either to a material burning without dripping or to a material that heavily drips but does not ignite underlying cotton. Moreover, such test was originally developed for devices and appliances, and the standards themselves state that the method is not intended to cover plastics when used as materials for building construction or finishing, whereas the test has become of general use in both industrial product specifications and in the scientific literature, because the test is extremely simple and cheap.

In order to properly take into account the material performance behind the specific scenario for which the UL94 was designed for, complementary description of polymer materials burning process should be considered, such as times of combustion, amount of material burned and rate of combustion.

Forced combustion

Cone calorimetry has been by far the most used test for the study of nanocomposite's fire behaviour, allowing quantitative testing of materials in controlled and repeatable conditions.

Among the many parameters supplied by cone calorimetry, attention has been focused primarily on Peak of Heat Release Rate (pkHRR) during combustion because of its relevance to fire risk related to time to flashover. Typical nanocomposite's results reported in literature show a decrease in the pkHRR of about 50 to 70% compared to reference unfilled polymer, with either nanoclays [1,5,15,16], carbon nanotubes [17,18,19,20,21] or other inorganic nanoparticles [22, 23, 24, 25]. The general experimental observation is that the presence of dispersed nanoparticles switches the typical non-charring behavior of most thermoplastic polymers to that of charring materials, intended as materials which develop a surface protective layer when exposed to heat. Such surface layer generally grows in thickness thanks to progressive accumulation of nanoparticles upon polymer volatilization, often leading to the formation of a solid residue at the end of the test, with variable degree of compactness, ranging from isolated floccules to fully solid char with shape and size similar to the unburned specimen. The compactness of the residue during burning is generally related to the efficiency in HRR reduction, the higher the compactness, the lower HRR.

In most of the cases, the reduction of combustion rate of polymer matrix in nanocomposites is explained with the barrier effect obtained upon nanoparticle and polymer char accumulation on the surface of the burning sample by the mechanisms described in the previous section of this chapter. The ceramic-char barrier reduces the rate of fuel feed to the flame, either by the reduction of the effective incident heat flux onto the polymer, owing either to reradiation by the ceramic-char surface layer or by the slow diffusion of volatiles through the surface layer, by labyrinth effect, entrapment into porosity or adsorption. These phenomena are very effective in the horizontal confined sample configuration of the cone calorimeter test, because no material macroscopic flow occurs since the specimen is confined in the sample holder. Morover, the in-depth advancing of flame front allows the ceramic-charred residue to be effective in protecting the underlying polymer, but this is a very specific conditions which does not relate, as an example, with lateral flame spread.

The use of other combustion tests, such as the cone calorimeter performed with vertical specimen setup and the radiant panel tests [26, 27], will certainly help in completing the assessment of nanocomposite behaviour under forced combustion.

Smoke and Evolved Gases

The inclusion of nanoparticles in polymers is often reported to deliver minor effects on the smoke production and toxic gases evolution compared to the unfilled polymers.

Relatively little understanding is available on the effect of these additives on toxic product developed during burning. A few detailed studies are focused on the smoke and gases evolution in different fire scenarios, i.e. in different temperature and ventilation conditions [28,29,30]. On the basis of these reports, nanoclays does not show adverse effect on the toxicity of the material studied in term of development of carbon monoxide and HCN, but the presence of clay increased the concentration of uncombusted hydrocarbons developed. Moreover while the total amount of smoke is not significantly affected the presence of clay seems to promote production of finer soot particles, mainly within 0.5-1.0 μm range, which however show a high tendency to aggregate in larger particles.

Conclusions

The combustion behaviour of nanocomposites is one of their most attractive characteristics. Indeed, nanocomposites containing a few percent of well dispersed nanofiller burn at a much lower rate than the corresponding polymer without dripping of flaming particles, thus reducing the contribution of polymer materials to fire propagation. Nanocomposites are therefore effective fire retardant materials, which are defined as those materials which extend the time to flashover in fires.

The comprehensive assessment of fire retardant behaviour of nanocomposites cannot be evaluated by a single test but should include different tests representing different fire scenarios, ranging from ignition to well developed fires. Each testing setup may show a different behaviour of nanocomposites: as an example, flammability tests such as UL94 and LOI typically evidence for lower dripping, whereas cone calorimeter shows the reduction of burning rate during forced combustion. Moreover, from a material research perspective, test providing quantitative data on ignition and combustion behaviour, such as the cone calorimeter, are essential for development of fire retardant materials, with progressive replacement of prescriptive codes with performance evaluation in materials selection for specific fire retardant applications.

Nanocomposites, make thus a step forward towards reduction of fire risk and hazard for polymers because they avoid flame spreading by flaming dripping and reduce the rate of combustion.

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