FIRE RETARDANT BEHAVIOUR OF POLYLACTIC ACID NANOCOMPOSITES

S. Bocchini, G. Camino

sergio.bocchini@polito.it Dipartimento Scienze dei Materiali e Ingegneria Chimica Politecnico di Torino sede di Alessandria, Viale Teresa Michel 5, 15121 Alessandria, Italy

In the nex few years biobased polymers are expected to substitute commodity plastics in sectors such as transportation and electrical/electronic applications in which the fire hazard is a relevant issue and flame retardancy is required.

The addition of a small amount of well dispersed clay (exfoliated/intercalated) has been shown to reduce the rate of combustion in forced combustion test in PLA. On the other hand, performance of polymer materials and nanocomposites in a fire test strongly depends on test scenario i.e. on the fire model. At present, the fire retardance scientific community takes advantage of basically three different fire tests, namely Cone Calorimeter, vertical UL94, Limiting Oxygen Index (LOI). The last two are generally referred to as “flammability” tests, in which the behaviour of the material 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. The cone calorimeter test, referred to as a “combustion test” is representative of a forced combustion, in which the material is burned under controlled external heat flux and supplies a full set of the combustion parameters characterising the combustion of the material. Ignition time, rate of combustion and total heat released, are most often those reported for an essential characterisation of the material contribution to a fire started on other items. Moreover, these flammability and combustion tests also differ for the specimen positioning, the formers being vertical tests (bottom ignition,UL94; top ignition, LOI) the latter most often being an horizontal test, despite vertical configuration is even provided for by the standard procedures.

Taking into account the different fire scenario of the three tests, it is expected that they give different results for the comparison of a given fire retarded formulation with the reference material. 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. 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.

Indeed, scientific understanding of polymer combustion will accelerate the highly desirable transition from the present “prescriptive codes” approach to materials application which is based on blind ranking typical of UL94 or LOI, to “performance evaluation” based on parameters characterising the combustion of the material in the fire scenario likely to occur in each specific application.

The oxygen index test (LOI) is widely recognized as a most useful tool for studies of fire retardance mechanism in polymer materials. As compared to the numerous tests proposed for measuring flammability of polymers, LOI has the advantage of ranking of materials by numbers. LOI is the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports candle-like combustion of a specimen, can indeed be measured with a relative standard deviation below 10%. Besides LOI, other measures can be performed on the specimen burning in the LOI apparatus which may be useful in the characterization of flammability and combustion behavior of polymer materials. The time interval between the removal of the ignition flame and the extinction of the burning specimen which is named “Self-Quenching Time”(SQT) is a function of oxygen concentration (OC). Usually the OC vs SQT plots can be separated in two successive regions on showing an approximately linear dependence. In the first region a much larger increase of OC is required to increase SQT than in the second. The transition between the two regions, which has been attributed to transition from unstable to stable burning generally occurs at SQT < 60 s, depending on type of polymer and fire retardant additive. This the reason why LOI is defined as the OC at which combustion is self-sustained for at least 180 seconds. While measuring LOI, it is useful to evaluate OC and the time at which the transition from unstable to stable combustion occurs which is called self quenching time at transition (SQTt). Another parameter which could be calculated from the data collected to measure OI is the OC corresponding to SQT = 0. This parameter would have the physical meaning of the minimum oxygen concentration below which ignition of the material does not occur whatever the flame application time to the specimen. By analogy with OI this parameter was defined as "ignition oxygen index" (IOI) which might give an indication of ease of ignition of a material. IOI is obtained by extrapolation of OC data to SQT to 0 in the first region of OC-SQT linear dependence, before transition to stable burning. In the case of PLA the regions of stable and unstable burning can be recognized. The addition of a flame retardant based on hindered ammines increases the OI of PLA, similarly, the OC of SQTt increases. On the contrary, the IOI is practically the same as that of PLA. Thus it seems that the fire retardant action is due to the destabilization of the flame. Indeed, both samples ignite at the same OC but, the OC should be increased in order to have a stable burning for samples with flame retardant.

PLA-based nanocomposites instead burn without showing an unstable flame depending on OC. Indeed, once the nanocomposites ignite, they burn with a stable flame with a negligible dependence of SQT on OC, so that LOI and IOI are practically coincident. In other words: once nanocomposites ignite, they burn without self-extinguishment. This behavior confirms what already reported on TTI in forced combustion [1] concerning the presence of dispersed nanoclays into other polymers. Conditions for ignition are created in nanocomposites as soon as the polymer decomposition temperature is reached by the specimen surface, 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. The suggested explanation for this behaviour, involves catalysis of the oxidation of the volatiles produced by polymer decomposition, due to the clays present at the surface of the specimen In the case of LOI test, the OC necessary to ignite the sample (IOI) is quite similar for both nanocomposites and PLA, but in the case of PLA and PLA containing flame retardants an increase of OC is necessary to have a stable burning, on the contrary, the nanocomposites combustion is already stable at ignition conditions. The overall effect that is usually recorded in the standard LOI reporting, is the decrease of the LOI for the nanocomposites as compared to the polymer matrix.

With the LOI apparatus it is possible also to evaluate the burning rate of the materials which is easily measured as a function of OC above LOI, when the specimen buns steadily, by measuring the time required by the flame to cross two marks at measured distance on the specimen length. For all the samples the burning rate increases linearly with the OC. PLA is the material which shows the highest increase of the burning rate (BR) with increasing OC that is the incremental ratio: burning rate/oxygen concentration (ΔBR). The addition of the flame retardant decreases ΔBR of PLA, In nanocomposites, accumulation of clay on the surface e.g. by migration in the hot matrix leads to a strong decrease of the BR of PLA. The BR of nanocomposites at the same OC could be from 10 to 20 times lower that of pure PLA. Moreover the effect of clay on the BR is directly related to the quantity of clay present in the nanocomposite. Thus the presence of clay in the PLA matrix anticipates ignition both under forced combustion (Cone calorimeter) or self-sustained conditions (LOI). This effect is attributed to nanoparticles-catalyzed oxidation of the gases generated at the surface of the condensed phase by thermal volatilization of the PLA matrix. The same catalytic effect also promotes stable combustion in LOI test at lower oxygen concentration than in pure PLA. On the other hand, the presence of clay decreases combustion rate. This effect seems strictly linked to the ability of clay to form a stable char on the surface of the burning nanocomposite which insulates the underlying polymer from the heat transfer from the flame, reducing its rate of volatilization.

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[1] Fina A, Camino G. Ignition mechanisms in polymers and polymer nanocomposites (2011) Polym. Adv. Technol. 22(7): 1147-1155.