Plastics Research Online
10.2417/spepro.006916

Improving flame retardancy of epoxy resins

Loris Giorgini, Tiziana Benelli, Mauro Comes Franchini, and Laura Mazzocchetti

New nitrogen-rich bentonite organoclays are used to improve the behavior of traditionally flammable materials, such as epoxy resins in carbon fiber-reinforced polymers.

Carbon fiber composite polymers (CFRPs) are increasingly replacing steel and aluminum alloys in a wide range of applications (e.g., in construction, transportation, aerospace, and electronics). This is because they can be used to produce high-quality and durable products that have good physical, thermal, chemical, and mechanical properties.[1] Nonetheless, both the polymer matrix and the reinforcing fibers in CFRPs have poor fire resistance characteristics when they are exposed to moderately high temperatures (i.e., 300–400°C).[2] In these circumstances, CFRPs tend to ignite and thus produce heat, smoke, soot, and toxic volatiles. It is estimated that fires account for about 1% of global annual gross domestic product, and that thousands of fire-related deaths occur in Europe every year. There are thus strong economic, sociological, and legislative demands for the production of materials (including CFRPs) that have greatly reduced fire risks.

Rather than obtaining completely non-flammable products, the major emphasis in the production of materials with reduced fire risks is making them less likely to ignite (or to delay the ignition point). Fire retardancy is therefore one of the key challenges in the fabrication of safe materials. Indeed, flame retardants (FRs) are intended to inhibit the polymeric thermal decomposition and combustion process. Although the development of inherently flame-resistant polymers appears to be the most efficient way to overcome flammability problems, this approach is not always feasible, and FRs are often required for commercial polymer formulations. The precise chemical nature of the FR is important because it can strongly influence the toxicity of fumes released during combustion (e.g., recently there has been concern over halogen-based FRs).[3] There is thus an increasing interest in the development of alternative FRs to meet new health and environmental regulations. For instance, there have been efforts to prepare and characterize polymeric nanocomposites in which the dispersion of nanofillers can be used to improve mechanical performance.[4]

Figure 1. *Left: Several examples of samples used in the study. The pure epoxy resin samples are shown on the far left (labeled A–E). The nanocomposite samples containing 3wt% bentonite-6-(4-butylphenyl)-1,3,5-triazine-2,4-diamine (R-BeBFTDA) and bentonite-11-amino-N-(pyridine-2yl)undecanamide (R-BeAPUA) are shown in the center (A–G) and on the right (A–D), respectively. Right: Photograph illustrating the transparency of the 3wt% R-BeAPUA panel used in the fire behavior tests.*

In our work, we built upon earlier studies to synthesize new flame-retardant organomodified bentonites.[5] Previous results showed that exfoliated clays (in which the hydrated cations are ion-exchanged with lipophilic organic cations) can be used to promote the infiltration of polymer chains between clay lamellae at the nanometric scale.[6,7] In this way, the nanoscale interactions between organoclay and a polymer matrix can be increased. Moreover, if the organic cation used in the exchange has flame-retardant properties, the functionality can be imparted to the final composite. We thus chose nitrogen-rich molecules—because they are known to be inherently fire retardant—to produce two new FR nanoadditives. In particular, these nano-FRs are based on organically modified clays and can be dispersed within a final polymer to impart fire retardancy.

To synthesize our nano-FRs, we used an ion exchange process (starting from pristine bentonite, Be) with either 6-(4-butylphenyl)-1,3,5-triazine-2,4-diamine (BFTDA) or 11-amino-*N*-(pyridine-2yl) undecanamide (APUA). We then added the BeBFTDA and BeAPUA in different amounts (3 and 5wt%) to an epoxy resin (see Figure 1) and characterized the mechanical properties and fire behavior of the

Continued on next page

samples. To analyze the effect of the additives and to better understand the contribution of each component to the overall performance, we compared the results to the behavior of both the neat resin (R) and the resin that contained pristine clay, i.e., with no organic modification.

To assess the efficacy of the curing process for our nanocomposites, we subjected each of the samples to differential scanning calorimetry analyses. We found that there is an absence of any exotherm transition across the whole range of investigated temperatures. Our results thus confirm that there is no detrimental effect on the curing process of our thermosets or on the thermal properties of our samples. Furthermore, at the lower concentrations (3wt%), the nanoadditives seem to improve the thermomechanical properties of the polymer matrix.

In our study we also used an oxygen consumption calorimeter to perform flame behavior measurements. We conducted these tests under conditions that are comparable to a small-scale fire (i.e., with a heat flux of 25kW/m^2). Specifically, we measured the peak of heat release rate (pHRR) of the samples. This is a good indicator of the ability of an ignited material to spread fire to a neighboring material. Our results (see Figure 2), for example, indicate that the R-BeAPUA sample has a pHRR that is 17% less than than of the R sample. Together with encouraging results for other parameters (not shown), we found that the R-BeAPUA composite is less prone to the propagation of fire than the neat resin. In addition, we noted that the nanofiller content necessary to improve the thermomechanical properties of the resin is the same as for achieving the best fire-resistant behavior.

In summary, we produced two new organoclays in which we included bentonite that was modified with nitrogen-based organic compounds (BFTDA and APUA) within an epoxy resin matrix. Our resultant nanocomposites do not exhibit any detrimental effects on the curing process or the thermal properties of the resin. Indeed, the samples containing 3wt% of the nano-FRs have improved thermomechanical properties. In addition, we found that the nanocomposites containing Be-APUA, in particular, are substantially less prone to the propagation of fire than the neat and pristine samples. These preliminary results are very encouraging and suggest that APUA-modified organoclays have the potential to be used as flame retardants. In our future work we plan to optimize the dispersion of the nanofillers with the matrix of the samples and to thus realize even better mechanical properties and improved flame-retardant behavior.

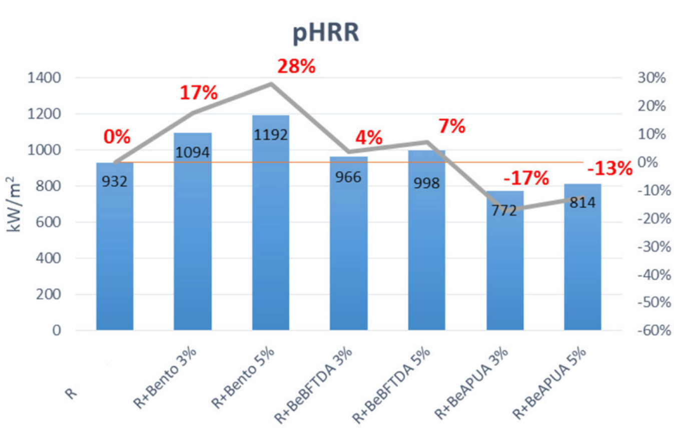

Figure 2. *Measured peak of heat release rate (pHRR) for the pure epoxy resin (R) and nanocomposite samples containing 3 and 5wt% of the pristine clay (Bento) and modified clay (BeBFTDA) and (BeAPUA) additives. Values in red represent the variation with respect to the R sample.*

Author Information

Loris Giorgini, Tiziana Benelli, Mauro Comes Franchini, and Laura Mazzocchetti
Department of Industrial Chemistry
University of Bologna
Bologna, Italy

Loris Giorgini has been an associate professor in the Department of Industrial Chemistry since 2014. He is the leader of the department's Polymer Group, which includes researchers, postdoctoral researchers, and PhD students who have interests encompassing different fields, e.g., polymer synthesis and characterization, materials science, (nano)composite materials, and industrial chemistry.

Tiziana Benelli obtained her PhD in industrial chemistry in 2002 and is now an assistant professor in the department. Her research activity is focused on the application of living polymerization techniques, and materials for advanced technological applications (including nonlinear optics, optical storage, and optoelectronics).

Mauro Comes Franchini has been an associate professor in the Department of Industrial Chemistry since 2014. He coordinates a group with interests in synthetic organic chemistry and in nanotechnological applications for advanced materials and medicine.

Laura Mazzocchetti is an assistant professor. Her interests are centered on the structure/properties relationship in polymers. In particular, she deals with biodegradable polymers from renewable resources. Recently she has focused her attention on composite materials for advanced applications and on their end-of-life recycling processes.

Continued on next page

References

1. L. Mazzocchetti, T. Benelli, E. D'Angelo, S. Ligi, G. Minak, E. Poodts, F. Tarterini, V. Palermo, and L. Giorgini, *Managing heat phenomena in epoxy composites production via graphenic derivatives: synthesis, properties, and industrial production simulation of graphene and graphene oxide containing composites*, **2D Materials 4**, p. 015020, 2017.
2. A. P. Mouritz and A. G. Gibson, **Fire Properties of Polymer Composite Materials**, Springer, 2006.
3. B. Biswas, B. K. Kandola, A. R. Horrocks, and D. Price, *A quantitative study of carbon monoxide and carbon dioxide evolution during thermal degradation of flame retarded epoxy resins*, **Polym. Degrad. Stability 92**, pp. 765–776, 2007.
4. L. Sisti, J. Belcari, L. Mazzocchetti, G. Totaro, M. Vannini, L. Giorgini, A. Zucchelli, and A. Celli, *Multicomponent reinforcing system for poly(butylene succinate): composites containing poly(L-lactide) electrospun mats loaded with graphene*, **Polym. Test. 50**, pp. 283–291, 2016.
5. T. Benelli, L. Mazzocchetti, E. D'Angelo, M. Lanzi, F. Saraga, L. Sambri, M. Comes Franchini, and L. Giorgini, *New nitrogen-rich heterocycles for organo-modified bentonites as flame retardant fillers in epoxy resin nanocomposites*, **Polym. Eng. Sci.**, 2017. doi:10.1002/pen.24565
6. G. Beyer, *Nanocomposites: a new class of flame retardants for polymers*, **Plast. Addit. Compound. 4**, pp. 22–28, 2002.
7. P. Kiliaris and C. D. Papaspyrides, *Polymer/layered silicate (clay) nanocomposites: an overview of flame retardancy*, **Prog. Polym. Sci. 35**, pp. 902–958, 2010.