

Improving the flame retardance of microcellular nanocomposites by employing layered nanoclays

Xin-Chao Wang, Tie Geng, Hai-Hong Wu, and Lih-Sheng Turng

Incorporating fully oriented layered nanoclay within microcellular thermoplastic polyurethane foam achieves an excellent thermal-shielding performance that significantly enhances its flame retardance.

Microcellular thermoplastic polyurethane (TPU) foams have been widely used in the construction, sporting goods, and automotive industries because they are very lightweight and have great heat insulation, energy absorption, and resiliency characteristics.^{1,2} With the wider use of TPU flexible foams, however, a number of fields (e.g., aerospace) have higher requirements on their flame-retardant properties. Because of this, a great deal of research has been carried out with the aim of improving the flame resistance and thermal stability of TPU.

There are three prerequisites for continual material combustion in a fire,^{3,4} at least one of which must be negated to achieve flame retardance. First, combustible vapors must be released from the degraded polymer. Second, the presence of oxygen is required for the combustible vapors to burn. Third, there must be enough heat to maintain the temperature of the material above its ignition point. If one of the above three conditions is absent, the fire will self-extinguish. Based on these concepts, various fire-resistant plastics have been produced by adding halogenated additives as flame retardants into the polymer matrix. These halogenated flame retardants can release toxic gases in a fire, however, causing serious air pollution.⁵

Halogen-free inorganic fillers have therefore been extensively researched as novel flame retardants and, in recent years, have been gradually used as a substitute for halogenated additives.^{1,4} The inorganic fillers used for this purpose mainly include aluminum hydroxides, graphene oxides, and nanoparticles. Of these, aluminum hydroxides undergo an endothermic decomposition process during combustion and release water that cools the condensed phase and dilutes the oxygen concentration around the surface.⁶ In contrast, graphene oxides display intumescent behaviors at high temperatures that result in the formation of a porous structure that can provide effective insulation for heat radiation from the outside in, and ultimately stop the fire from spreading.⁷

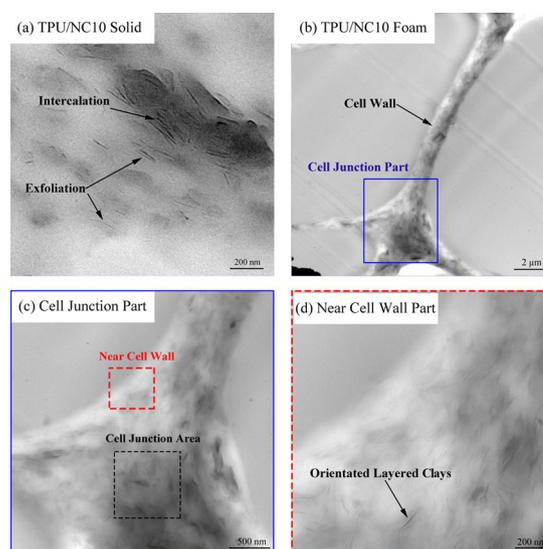


Figure 1. Tunneling electron micrographs of our flame-retardant composites (i.e., thermoplastic polyurethane/nanoclay, TPU/NC) showing the nanoclay dispersion morphology for transverse sections of (a) solid and (b) foam with nanoclay loadings of 10wt% (TPU/NC10). (c) Magnification of the multicell junction in the foam composite, shown as a blue square in (b). (d) Magnification of the area near the cell wall in the foam composite, shown as a red square in (c).

Finally, nanoparticles—such as nanoclays and sepiolite nanorods—have been extensively studied for use in flame retardants.^{1,3,7} Their flame-retardant mechanism is related to the ability of nanoparticles to generate a condensed carbonized layer at the material surface, thus providing an effective barrier property and leading to a decrease in heat release and combustible-vapor diffusion.

We have demonstrated that layered nanoclay has a synergistic effect for improving the flame retardance of microcellular foams. The advantages of this synergy mainly manifest in three ways. First,

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nanoclay additives orientated along cell walls can improve material barrier effects against the further diffusion of oxygen or heat in the foams (i.e., thermal shielding) and thus protect the sub-layer from burning.⁸ Second, the additives dispersed in the cell walls also act as mechanical performance enhancers, reinforcing the stiffness of the foams. Finally, nanoclay acts as a bubble-nucleating agent, thus leading to a significant increase in the number of cells and a more homogeneous distribution of cell sizes, which can increase the formation rate of carbonized char. Therefore, nanoclay with a lamellar structure can significantly increase the thermal-shielding effect and cell uniformity of foams.

In our study, we used a flexible elastomer-thermoplastic polyurethane (Elastollan[®] 1180A10) as the matrix material. We prepared the microcellular TPU foams using the microcellular injection foaming process (with supercritical carbon dioxide as the physical blowing agent), and organically modified the nanoclay particles (Cloisite[®] 30B) with ammonium quaternary salt. We also developed TPU/nanoclay (TPUNC) composites in a solid form, for comparison, using the same injection conditions without blowing agents. A previous study reported that organically modified layered clays have strong interactions with the polymer matrix due to their functional group polarity.² This gives rise to a preference of the nanoclay layers to orientate tangentially to the cell walls during bubble growth. In fact, the barrier effect of nanoclay additives can also improve the cell growth stability of foams by generating a uniform cell structure.

We investigated the dispersion morphology of nanoclay within our TPU samples (foams and solids) using a tunneling electron

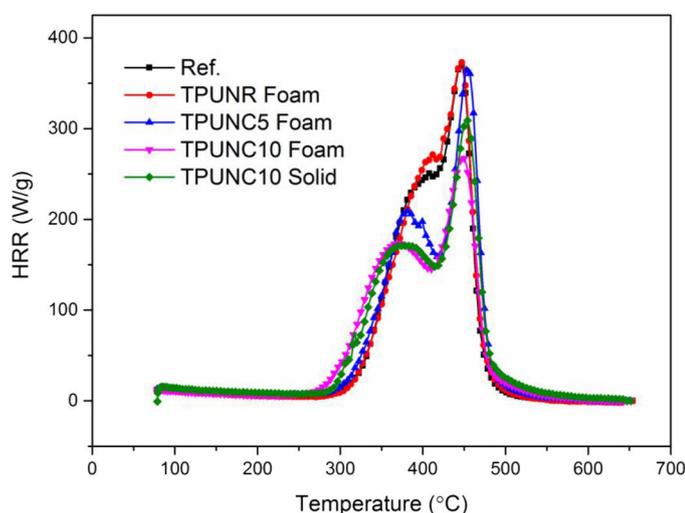


Figure 2. The heat release rate (HRR) curves of raw TPU pellets (Ref.), unfilled neat TPU resin (TPUR), and our TPU nanocomposites (at nanoclay loadings of 5 and 10wt%). TPUNC5: TPU with 5wt% nanoclay.

microscope (see Figure 1). In solids, the nanoclay layers aggregate—see Figure 1(a)—but this phenomenon does not occur in foams due to the influence of the microcellular injection foaming process. Magnifications of the junction of the three touching cells—see Figure 1(b) and (c)—show that the layered clays were randomly dispersed in the central zone. However, they generated an oriented structure near the cell walls—see Figure 1(d)—thus showing the advantages of the barrier effect that the nanoclay introduces. We attribute the fully dispersed structure of the nanoclay in the foams to the stronger diffusion capability of the physical blowing agent among the nanoclay layers.

The curves of the heat release rate (HRR, a measure of the material's flammability) versus heating temperature (measured by microscale combustion calorimetry) for TPUNC composites and neat TPU are plotted in Figure 2. Our results show that the HRR of the TPUNC foam with a nanoclay loading of 10wt% decreased by 36.3% in comparison with the foam comprised of unfilled neat TPU resin. We suggest that there are two contributions to this result. First, the carbonized residue generated by the nanoclay has a remarkable thermal-shielding effect. Second, the modified cell structure improved the formation rate of the condensed phase of the foams.

In summary, we were able to significantly enhance the flame retardance of microcellular TPU nanocomposites by inducing nanoclay layers to generate an orientated dispersion in cell walls, thus forming thermal-shielding layers. We achieved the best results for TPUNC foam composites with loadings of 10wt% nanoclay. We have also demonstrated the multifunctional role of nanoclay in obtaining composites with a combination of useful properties, i.e., that are lightweight ($0.2\text{g}/\text{cm}^3$), have high thermal stability, and achieve a high char residue. Our study provides substantial motivation for the continued development of lightweight, high-performance, and flame-resistant foams produced by a technique suitable for mass production (i.e., microcellular injection foaming) to reduce the environmental impact of chemical-reaction foaming. In our next steps, we intend to fabricate material systems with other combinations of flame retardants and material modifiers to further enhance the flame-resistant potential of TPU.

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