

2) Molecular Dynamics Simulations of the Thermal Degradation of Nano-Confined Polypropylene

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Summary

Recent work conducted in this laboratory has demonstrated that nanocomposites consisting of polymer and montmorillonite clay exhibit a significant reduction in flammability, as compared to immiscible mixtures of these components, even in compositions that contain as little as 3 to 5% clay. This increase in fire resistance is not achieved at the expense of compromising other physical properties. Indeed, in most cases, a dramatic improvement in the important thermal and mechanical properties is also observed. Furthermore, the cost of producing these nanocomposites from the

constituent polymer and clay are expected to be almost negligible. Although research in this area is just getting underway, preliminary results suggest that it is possible to make nanocomposites from a wide range of commodity polymers, thereby opening the way for the development of an entirely new generation of low cost, ultra fire resistant, high performance materials.

Experimental measurements have indicated that the rate of mass loss from polymer/clay nanocomposites exposed to fire-like heat fluxes is significantly reduced from the values observed for the immiscible composites containing the same amounts of polymer and clay, while

the enthalpies of combustion are almost identical. This suggests that source of the disparity in flammability performances of the materials is due to differences in condensed phase decomposition processes and not to a gas phase effect.

The purpose of the investigation that is summarized in this paper was to identify the operant mechanisms of this increase in thermal stability and fire resistance. The strategy adopted for this purpose was to investigate the decomposition of polymer/clay nanocomposites using a computational model, hereafter referred to as MD_REACT, that was developed at this laboratory to study the thermal reactivity of polymers. The basis

MD_REACT is molecular dynamics. This technique involves solving Hamilton's equations of motion for each of the $3N$ molecular degrees of freedom. The simulations are initiated by providing kinetic energy to the atoms from a random velocity distribution. The resulting distortions from the equilibrium geometry are opposed by a force commensurate with the gradient of a potential energy function, which is parameterized for a class of chemically related molecules. The unique capability of MD_REACT is that it allows for the formation of new bonds from free radical fragments generated when bonds in the polymer break and, thereby, accounts for the chemical reactions that play a major role in the thermal degradation process. The most important of these are random scission, beta-scission, hydrogen transfer, chain stripping, cyclization, crosslinking and radical recombination reactions.

The simulated thermal degradation experiments were performed using models of polypropylene/graphite, rather than polypropylene/clay nanocomposites. In making this decision, we were motivated by the considerable body of experience and high level of confidence that we have acquired in using force fields to model hydrocarbon polymers and surfaces. The substitution of montmorillonite clay for graphite would have required that we use an untested force field that would introduce additional uncertainties into the calculations. A series of nanocomposite structures with the polypropylene intercalated between graphite layers separated by a variable distance, b , was obtained by annealing the model polymer and graphite inside of a unit cell with the following dimensions: $a = 10.0$, $c = 3.0$ and $b = (2.5, 2.8, 3.0, 3.2$ and $5.0)$ nm. The same models of the polymer and graphite were used in all of the structures. That is, only the distance between the graphite sheets and, consequently, the density of the composite was allowed to change from one simulation to the next. The average rate of mass loss was determined by tabulating

the mass of the polymer fragments diffusing outside of the central unit cell as a function of time obtained from 3 independent calculations corresponding to different realizations of the initial momentum distribution for the specified temperature of 873 K. The rates of mass loss from the nanocomposites were compared to the values for immiscible polymer/clay composites with the same density, which were obtained simply by turning off the nonbonding interactions between the polymer and the graphite.

The average rate of mass loss from both the immiscible polymer/clay composites and the nanocomposites indicated that there is clearly an optimal polymer density that occurs when the distance of separation between the graphite layers is about 3.0 nm. At lower densities, the interactions with the polymer melt do not provide sufficient resistance to prevent the rapid diffusion of fragments to the gas phase, whereas the Van der Waals repulsions between the atoms destabilize the polymer when the density is too high. The consequences of the repulsive nature of the forces, that predominate when the polymer chains are crowded into the small volume bounded by the graphite sheets, is so pervasive that we could not even locate a stable conformation for a layered nanocomposite structure with b less than 2.5 nm using the simulated annealing procedure described in the full paper. Presumably, the intercalated structure becomes unstable when the repulsive forces between the atoms that make-up the nano-confined polymer exceed the attractive forces between the layers. The clay then delaminates to form a hybrid structure where the layers are individually dispersed throughout the polymer matrix.

The stabilization of the polymer is most pronounced in the $b = 3.0$ nm nanocomposite and approaches zero at $b = 5.0$ nm, when the graphite layers are too far apart for there to be a significant interaction between

them. At these large distances of separation, the interactions are almost exclusively between the polymer and the graphite, which should approximate what occurs in the delaminated nanocomposites where the graphite layers are individually dispersed in the polymer matrix. The reduction in the average rate of mass loss from the $b = (2.8, 3.0$ and $3.2)$ nm nanocomposites, with respect to the immiscible composites, is consistent with the results obtained from radiative gasification measurements made on intercalated nanocomposites. These experiments were performed under conditions that were designed to emulate fire conditions by providing heat fluxes to the surface of the sample that are comparable to those that would be experienced in an actual fire.

The observation that the thermal stability of the polymer increases when it is intercalated but is not affected by the presence of the graphite when the layers delaminate is consistent with thermogravimetric data that indicate that intercalated nanocomposites are more thermally stable than delaminated nanocomposites. The fact that the delaminated nylon-6/clay nanocomposites exhibit a reduction in flammability comparable to what is observed for the intercalated nanocomposites, even though derivative thermogravimetric results indicate that polymers are not stabilized when present in delaminated nanocomposites, suggests the possibility that the clay layers reorganize after some of the polymer is gasified. That is, the nanocomposite undergoes a phase change from a delaminated to an intercalated structure in response to the change in composition brought about by the thermal degradation of the polymer. The result is an intercalated nanocomposite which is, presumably, stabilized by the mechanism discussed in the preceding paragraphs. This hypothesis is supported by transmission electron microscopy (TEM) of the char that remained after burning samples of the delaminated

nylon-6/clay nanocomposites under a thermal flux of 35 kW/m² on the cone calorimeter. The TEM images clearly reveal an organized layered structure that was not present prior to combustion.

The nature of the stabilization effect is revealed in the computer animations of the trajectories corresponding to the nanocomposites and immiscible composites. In general, the polymers in the $b = (2.8, 3.0 \text{ and } 3.2) \text{ nm}$ nanocomposites lost fewer fragments and retained their shape longer than the polymers in the immiscible composites. The most obvious difference was that the fragments generated by the degradation of the model polymer in the nanocomposites had a pronounced tendency to collide with the graphite and bounce back into the central unit cell where they could undergo recombination reactions with other

free radical polymer fragments, rather than escape from the melt as combustible fuel. This effect is evident in Figure 1 which depicts the last frames from the computer animations of the trajectories of the $b = 3.0 \text{ nm}$ nanocomposite and the immiscible composite with the same

density. Notice that the fragments only escape from the sides of the nanocomposite (right) because of repulsive interactions with the graphite that bounds the polymer from above (not pictured) and below, whereas they leave the immiscible composite from all directions (left).

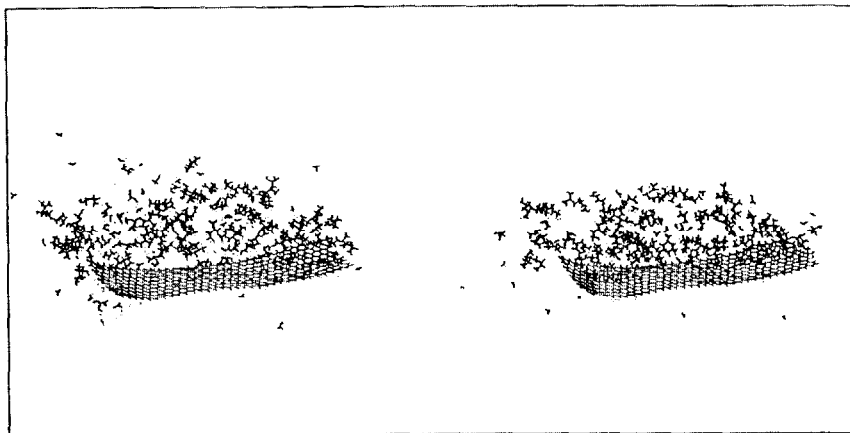


Figure 1. The last frames from the animated trajectories of the $b = 3.0 \text{ nm}$ nanocomposite (right) and the immiscible composite with the same density (left).