

Surface-Active Flame Retardants

Wei Chen, Padma Rajagopalan, David Long and Thomas J. McCarthy
Polymer Science and Engineering Department
University of Massachusetts Amherst, MA 01003

Research Objective: To find a general approach to enhance the efficiency of flame retardant additives in polymer materials by using surface free energy minimization. Surface-active agents are adsorbed or attached to solid flame retardants. Under appropriate conditions (heating or fire) we want the flame retardants to spontaneously concentrate at the exterior of the polymer object.

Approach: The interfacial properties of a material depend primarily on the surface structure and chemical composition of the outermost surface layer. . We believe that ignition is controlled primarily by interfacial properties. Solid polymers have nonequilibrium structures with chains rotating and reorienting, and exhibit a range of relaxations and transitions in response to time, temperature, and other environmental changes. Surface reconstruction has been reported in the literature extensively from both theoretical and experimental point of views. In general, reconstruction tends to concentrate to the surface the component of lower surface energy. Our approach is to prepare flame retardants that have been modified to exhibit low surface energies. Thermal annealing of the samples is carried out and the excess surface concentration of flame retardant (over the bulk composition) is determined by quantitative X-ray photoelectron spectroscopy. Our initial studies (now complete and published) involved fullerene as a model flame retardant. Current studies involve the preparation of surface-active palladium nanoclusters that are dehydrogenation catalysts – we anticipate that these will promote char formation.

Accomplishment Description: Adsorption/migration of a perfluorohexylated- C_{60} ($C_{60}(C_6F_{13})_5$) from the bulk of a polymer matrix (polystyrene) to the polymer/air interface has been demonstrated as a tool for surface modification as well as a method to increase the efficiency of polymer additives including flame retardants. We view C_{60} as a model flame retardant. Surface activity of $C_{60}(C_6F_{13})_5$ was evaluated as a function of bulk concentration, annealing temperature, and annealing time. $C_{60}(C_6F_{13})_5$ is extremely surface-active in the polystyrene matrix, occupies ~90% of the outermost ~40 Å (XPS sampling depth), and renders a surface that is similar in wettability to a monolayer containing CF_3 groups (hexadecane contact angle data). Surface reconstruction studies were carried out by either spin-casting or the transfer of a free standing (solid) polystyrene film onto the composite materials (the surface-active agent and polystyrene) and subsequent thermal annealing. Both approaches show similar results: migration of perfluorohexylated- C_{60} from the bulk to the surface is driven by surface free energy minimization and is a function of annealing temperature, annealing time, and molecular weight of the polymer matrix. Peel tests indicate that the composite materials have good mechanical integrity. Figures 1 and 2 indicate the high affinity of the model flame retardant to the surface. Less than 1 weight percent is required to saturate the surface.

Significance: The potential for amplification of the effects of flame retardants by over an order of magnitude through surface activity will have profound significance on applications of polymers where fire is a possible environmental component.

Expected Results: The research with fullerenes must be regarded as impractical. If we can achieve the same surface activity with proven flame retardants we will make superior flame retardant materials.

References:

Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) **1999**, 40(1), 228 (P. Rajagopalan and T.J. McCarthy) “Metal-Polymer Composites in Supercritical Fluid Carbon Dioxide”

Macromolecules **1999**, 32, 2342 (W. Chen and T.J. McCarthy) “Adsorption/Migration of a Perfluorohexylated Fullerene from the Bulk to the Polymer/Air surface”

Point of Contact: Dr. Richard E. Lyon, AAR-422, FAA William J. Hughes Technical Center, Atlantic City International Airport, NJ 08405, (609) 485-6076, FAX: (609) 485-6909, email: rlyon@admin.tc.faa.gov.

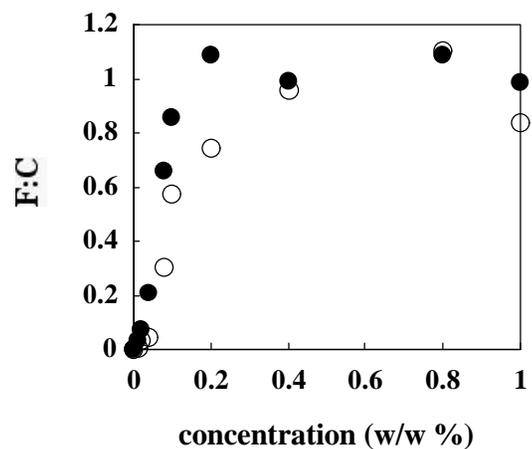


Figure 1. Adsorption isotherm (F:C) of $C_{60}(C_6F_{13})_5$ in a polystyrene matrix; 15° (●) and 75° (○) take-off angle data.

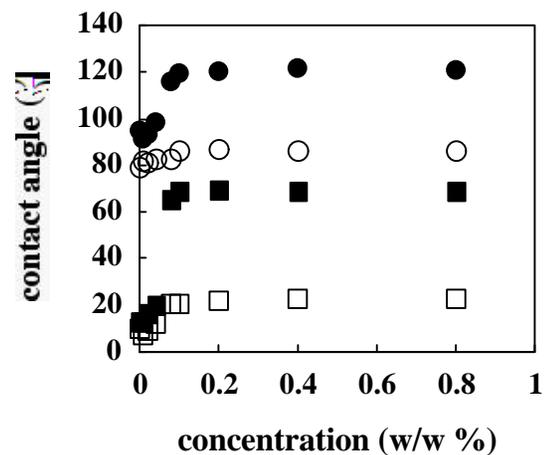


Figure 2. Adsorption isotherm (contact angles) of $C_{60}(C_6F_{13})_5$ in a polystyrene matrix; advancing water contact angles (●); receding water contact angles (○); advancing hexadecane contact angles (■); receding hexadecane contact angles (□).