Computer Modeling of Polymer Degradation

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Research Objective: To develop a computer model for the prediction of flammability performance and the molecular level design of new fire resistant materials for use in aircraft cabins.

Approach: Research conducted in this laboratory has focused on the application of molecular modeling techniques to identify factors that affect the thermal degradation chemistry of polymers in ways that result in a reduction in their flammability. This effort has culminated in the development of a novel computer program, hereafter called MD_REACT. The basis of this model is molecular dynamics (MD), which involves solving equations of motion for the 3N (where N is the number of atoms in the polymer) degrees of freedom associated with the model polymer. The forces are obtained as the negative gradient of a potential energy function (sometimes referred to as the forcefield) which describes the variation of the molecular energy with changes in the internal degrees of freedom (i.e., bond distances and angles). This potential energy function is parameterized on the basis of quantum mechanical calculations on smaller model compounds and experimental data. The feature that distinguishes MD_REACT from other MD codes is that it allows for the formation of new bonds from free radical fragments that are 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 motivation behind the development of MD_REACT was to create a versatile model that could be used to study thermal degradation at a molecular level in a wide range of polymers. The strategy employed to accomplish this objective was to interface our program for performing reactive dynamics on simple vinyl polymers with Discover 95, a commercially available MD code offered by Molecular Simulations, Inc. (MSI)

Accomplishment Description:

The predictive capability of MD_REACT was tested by comparing computed rate constants to experimental values for molecular systems ranging from small gas phase radicals to polymers. In all cases, there is reasonable agreement between the computed and experimental results, with a maximum error of about a factor of 4 over the temperature range of interest for burning polymers (500 K - 1000 K). In a recent paper presented at the International Aircraft Fire and Cabin Safety Research Conference, the Ahrrenius constants for the global rate-of-mass from burning polypropylene, that were obtained from simulations performed with MD_REACT, were

compared to experimental values. The activation energy, E_a = 238 (32 kJ/mol and pre-exponential factor, A = (5.3 (0.2) x 1012 s-1, compare favorably to the experimental values, obtained from thermalgravimetric analysis, which are 220 kJ/mol and 1.9x1013 s-1, respectively. Additional simulations were performed as part of a survey of the effect of fire retardant additives on the thermal degradation of polypropylene. Included in this survey were blends of polypropylene with silica gel, representative bromine-containing fire retardants, and a polymer layered nanocomposite. The results of the simulations are consistent with experimental findings and, at the same time, provide new insights into the mechanisms by which these additives affect a reduction in the flammability of the polymer.

Significance: MD_REACT is a useful tool for the prediction of flammability performance and the molecular level design of new and more fire resistant aircraft materials.

Expected Results: The focus this year will be on obtaining time and temperature dependent molecular weight distributions in order to better understand the mechanism by which volatile gases (fuel) are transported through the polymer melt and into the gas phase.

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[1]Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. This

in no way implies endorsement or recommendation by NIST. MD_REACT is presently available as a part of MSI's Polymer 9.0/4.00 software release.