DEVELOPMENT OF A CONTINUOUS FLOW FLAME TEST EXTRUDER FOR HIGHT-THROUGHPUT FORMULATION AND SCREENING OF FLAME RETARDANTS AND MORE FIRE RESISTANT MATERIALS

by

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ABSTRACT

The purpose of this paper is to initiate discussion on the viability of using a high-throughput approach, based on the combinatorial methodology that has been successfully employed in the pharmaceutical industry, to formulate and screen new flame retardants and more fire resistant materials. The basis of our concept is the development of a new processing capability that will enable variable composition samples to be extruded, analyzed, and burned on the same device. This extension of existing technology will permit researchers to screen hundreds of potentially effective fire retardant formulations in the same time it now takes to perform flammability tests on a single sample. The potential application of this approach to determine optimal levels of polymer, organically treated clay, flame retardant synergists, and other additives in polymer-clay nanocomposites is also considered.

INTRODUCTION

The materials industry is under increasing pressure to produce better products at lower cost in less time. Now, more than ever before, the profitability of a new material is determined by the time required to bring it from the laboratory to the marketplace. While it is in the interest of public safety that efforts directed at reducing flammability continue to be a critical component of this effort, there are no guarantees that innovation cycle times can be sufficiently reduced using current research tools to respond to the competitive pressures of the global marketplace. In the final analysis, the continued success of the flame retardant industry may hinge on the availability of new and more efficient research and development (R&D) techniques.

Traditionally, new treatments to reduce flammability have been developed by a laborious trial-and-error process consisting of three independent steps: sample preparation; characterization; and flammability testing. The purpose of the investigation outlined in this paper is to examine the feasibility of using combinatorial methods to formulate and screen new flame retardants and more fire resistant materials. Here the adjective "combinatorial" is used in the generic sense to denote a research strategy in which experiments are conducted in parallel on a library of compounds or materials as opposed to the conventional practice of preparing and testing a single candidate at a time [1,2]. For the remainder of this proposal, we use the term "high-throughput," in preference to combinatorial because it emphasizes the

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objective of the approach, which is invariant, rather than the methodology, which is in a state of flux as the field expands to encompass new and more diverse applications.

The motivation for examining the feasibility of employing high-throughput experimentation in materials R&D is the successful track-record compiled by the pharmaceutical industry in applying these techniques in the drug discovery process. On the basis of this experience, we think that it is reasonable to expect that the introduction of high-throughput experimentation will result in a similar dramatic improvement in the efficiency of R&D efforts directed at reducing materials flammability. An added benefit of this approach is that its use will facilitate the process of determining the optimal level of additives that are required to ensure good mechanical properties as well.

The idea of applying high-throughput experimentation in materials research has stimulated intense interest here at NIST and in other government and private sector laboratories throughout the world [4]. A new high technology industry, consisting of a multitude of small U.S. companies is beginning to take shape. At the same time, large multinational companies are working at a feverish pace to gain expertise in adapting this technology to aid in the discovery of new materials for the biotechnology, telecommunications, and electronics industries. This paper, however, is among the first to call attention to the potential benefits of employing high-throughput experimentation to facilitate the discovery of new flame retardants and more fire resistant materials.

In what follows, we will present an overview of our plans for the development of a new processing capability that will enable variable composition samples to be extruded, analyzed, and burned on the same device. This extension of existing technology will permit researchers to screen hundreds of potentially effective fire retardant formulations in the same time it now takes to perform flammability tests on a single sample.

OVERVIEW OF THE PROPOSED RESEARCH

The basis of our approach to the high-throughput formulation and screening of more fire resistant materials is the device, hereafter referred to as the continuous flow flame test extruder (CFFTE), conceptualized in figure 1. There are three essential components: a computer-assisted gravimetric feeder that can be programmed to change the relative concentrations of the additives as a function of time; a series of in-line sensors that can measure the concentrations and degree of dispersion of additives in the output stream; and a flammabilty test apparatus capable of providing a realistic assessment of the inherent flammability of the extruded polymer in real-time. Once a prototype of the basic device is operational, the next step forward will be to incorporate an intelligent process controller with the capability to adjust the input stream based on the results of online flammability testing. This will facilitate the formulation of optimal compositions with respect to fire resistance and other measured properties.

The construction of a prototype CFFTE and the subsequent validation of the high-throughput flammability test will require a multi-year research effort. The immediate objective is to provide a detailed proof of concept that will consist of independent demonstrations of the feasibility of each of the following component processes.

1. **The extrusion of multi-component samples with continuously varying compositions by computer-controlled gravimetric feeding.**

A computer-controlled gravimetric feeder will be installed on our extruder and tested by blending a polymer resin with a variety of inorganic additives. The limitations of computer-controlled mixing, with respect to the number of additives, the range of compositions, and reproducibility, will be assessed by comparing the results obtained from chemical gas analyses of the extruded material with the expected (programmed) sample compositions.

2. **Online analysis of the extruded material by fiber-optically coupled Fourier Transform Infrared (FTIR) spectrometry and continuous static light scattering.**

The signal-to-noise levels of mid-infrared (MIR) spectra of thin film samples produced on the extruder will be determined as a function of scan time. The accuracy of the on-line characterizations will be assessed by comparing results obtained from the quantitative analyses of MIR spectra, which will be acquired at times comparable to the output of the extruder, to the values obtained from the chemical analyses of representative samples of the extruded material. Similar studies will be conducted to determine the reliability of continuous static light scattering methods in assessing the dispersion of the additives in the extruded resin. In the application to polymer-clay nanocomposites described in the following section of this paper, we will also use x-ray diffraction (XRD) transmission electron microscopy (TEM) to verify the dispersion of the polymer and clay.

3. **Continuous flammability assessments by heat release rate (HHR) measurements on the extruded material.**

The optimal conditions for a continuous flow flammability test will be determined by performing HRR measurements on extruded material as a function of the mass and shape of the sample and comparing the results to those obtained from standard flammability tests which are routinely performed in this laboratory.

The second and third phases of this project, consisting of the construction of the prototype CFFTE and the development, validation and benchmarking of the flammability test method, will be undertaken as soon as we establish the long-range viability of the approach in phase 1. We hope to be able to pursue this work in cooperation with representatives of the materials industry in the context of a consortium.

POTENTIAL APPLICATIONS TO POLYMER-CLAY NANOCOMPOSITES

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 [5,6]. This favorable result 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 of these materials is also observed [7,8].

The preparation of these materials typically requires an organic treatment consisting of the introduction of a compatibilizer, such as an alkylammonium compound, that renders the polymer miscible with the clay. Although the peak HRR obtained from cone calorimeter flammability measurements performed on polymer-clay nanocomposites is usually far less than the value obtained for the untreated polymer, a tendency to early ignition has been observed in some cases [6]. This phenomenon has been attributed to the organic treatment, which involves the introduction of compounds that are known to have lower thermal stability than the polymer itself. Based on these observations, we suspect that there is an optimal concentration of compatibilizer, below which there is inadequate dispersion of the polymer and clay, and above which there is a propensity to early ignition. Thus, one of our first applications for the combinatorial approach described above will be to determine the levels of polymer, organically treated clay, flame retardant synergists, and other additives that maximize mechanical properties while minimizing the flammability of polymer-clay nanocomposites.

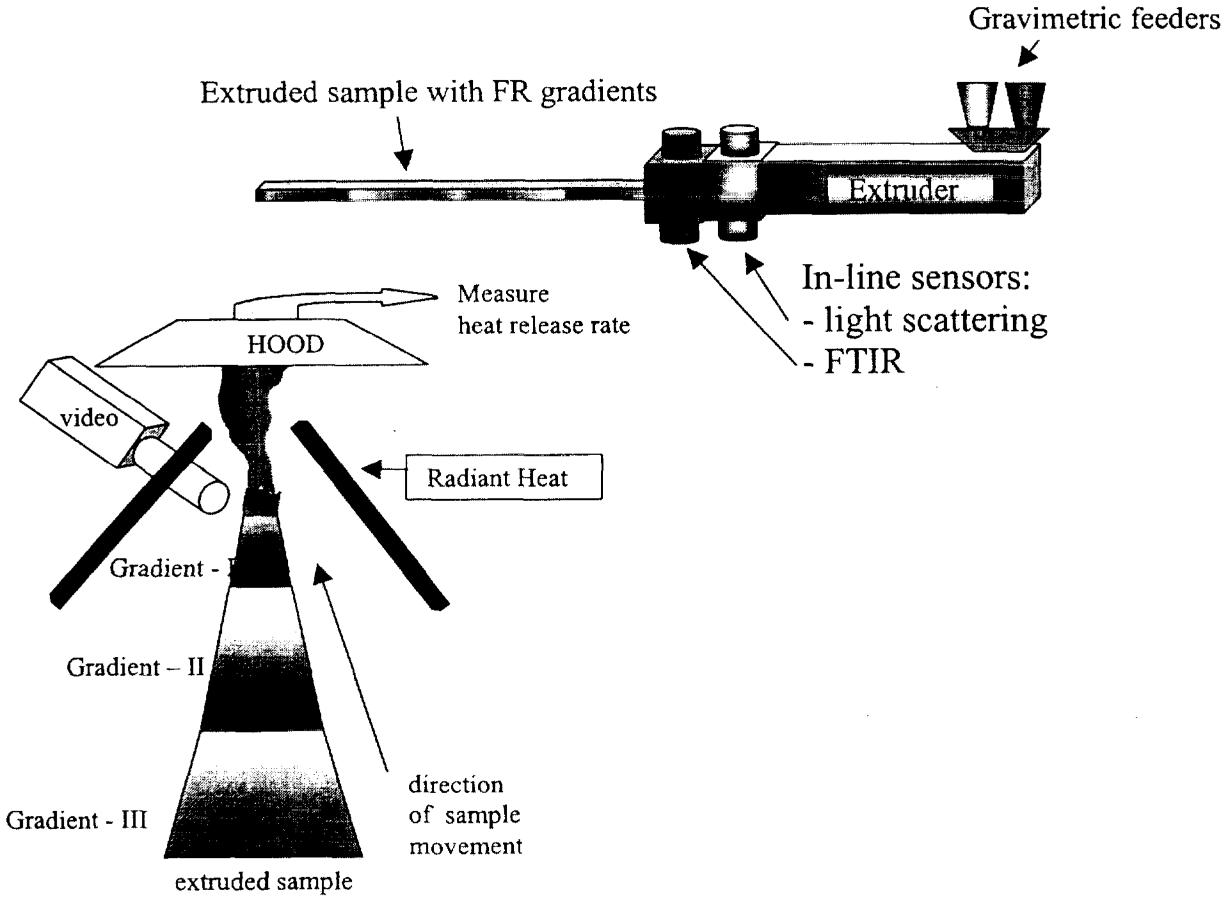

Figure 1. Conceptualization of the Continuous Flow Flame Test Extruder.

SUMMARY AND CONCLUSIONS

In this paper we have outlined a plan of research to establish the technical basis for a new processing capability that will enable variable composition samples to be extruded, analyzed, and burned on the same device. This extension of existing technology will permit researchers to screen hundreds of potentially effective fire retardant formulations in the same time it now takes to perform flammability tests on a single sample. The long-range goal of this research is to introduce assembly-line efficiency into the development of a new generation of more fire resistant materials.

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