Real-Time Measurements of Condensed-Phase Spectra in Burning Polymers

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INTRODUCTION

A major goal of the research conducted in this laboratory is to provide the polymer industry with the technical understanding and measurement tools that are needed to develop a new generation of fire-resistant materials. In the pursuit of this goal, we have examined the feasibility of using mid-infrared (MIR) transmitting fibers coupled to a Fourier transform infrared (FT-IR) spectrometer to monitor changes in the condensed-phase spectra of burning polymers.

The potential of using MIR transmitting optical fibers for making concentration measurements in fire-like environments was demonstrated in recent papers that reported real-time concentration measurements of N_2O produced in the thermal decomposition of an RDX (hexahydro-1,3,5-tri-nitro-1,3,5-triazine) gun propellant[1,2] and fuel/air ratios in an automobile cylinder.[3] Although these particular measurements were made with bandpass filters, applications where MIR transmitting fibers were used to-

gether with an FT-IR spectrometer to investigate thermally induced changes in polymeric materials over more extensive spectral windows have also been reported in the literature. These studies include papers where the extent of cure in a thermoset composite,[4] the composition of ethylene/propylene copolymers,[5] and the formation of a polyurethane foam[6] were examined.

The use of MIR transmitting fibers in conjunction with otherwise conventional FT-IR spectrometers has opened new possibilities for scientists to monitor chemical and physical processes as they are taking place. In this note, we present *in situ* spectra of nylon-6 and a nylon-6/clay nancomposite that were obtained while these materials were burning during rate-of-heat release (rhr) measurements conducted on the cone calorimeter.[7] The rhr is an intrinsic indicator of materials flammability that can be estimated by measuring the rate of oxygen consumption during burning. Nanocomposites, such as the nylon-6/clay hybrid considered in this investigation, are characterized by the molecular level incorporation of an inorganic additive (commonly alumino silicate clays) into an organic polymer. These materials can have unique properties compared to conventional filled polymer systems.[8,9] Indeed, research conducted by Gilman et al. has demonstrated a significant reduction in flammability in a series of polymer nanocomposites, as compared to immiscible mixtures of the same components, even at compositions that contain as little as 2–5% clay.[10,11] The motivation for monitoring spectral changes occurring during rhr measurements on these materials is to gain insights into the nature of the condensed-phase chemistry that is most responsible for the heat release in nylon-6 and, thereby, to facilitate identification of the source of the reduction in the flammability of the nanocomposite.

EXPERIMENTAL

The fiber-optic setup used in the experiments consisted of a sapphire probe (300 μm in diameter and 10 cm in length) that was mounted on a steel rod and connected at both ends to zirconium fluoride (ZrF) cables. These cables were connected to focusing optics, consisting of a pair of off-axis parabolic mirrors, that launch an evanescent wave at the source and capture it at the detector. A reflectance spectrum results from the attenuation of the evanescent wave due to absorption of the polymer (and its degradation products) in the immediate vicinity of the probe. Disk-shaped samples (approximately 7.5 cm in diameter) of the polymers were placed on top of the probe, which fit snugly into a groove that had been previously milled to facilitate a good contact between the polymer melt and the optical fiber. Although the sapphire probe can withstand temperatures up to 2000 °C, the ZrF cables are sensitive to heat and had to be protected by water-cooled jackets constructed by winding plastic tubing around a copper pipe. As an added protection, these jackets were also wrapped in aluminum foil.

Condensed-phase absorbance spectra of nylon-6 and a nanocomposite of nylon-6 and montmorillonite clay were acquired by using a Midac Illuminator spectrometer† dur-

FIG. 1. Experimental setup showing the sapphire reflectance probe imbedded in burning nylon-6. The sapphire probe is connected at either end to zirconium fluoride cables, which are interfaced through focusing lenses to the source and detector of an FT-IR spectrometer.
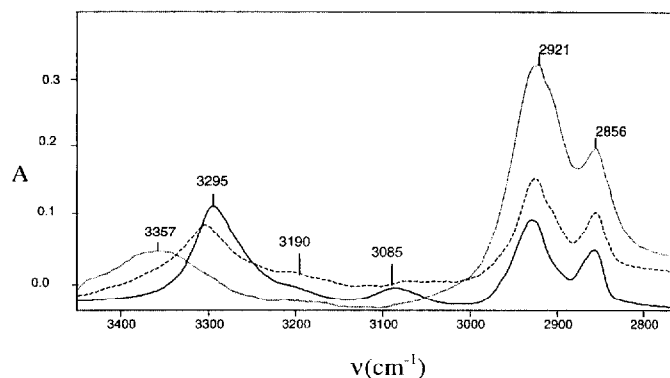

FIG. 2. The spectra obtained from nylon-6 just before ignition (dashed line) and in the vicinity of the peak rhr (dotted line) compared to a spectrum measured at room temperature (solid line).

ing flammability measurements on the cone calorimeter. The nylon-6 and nylon-6/clay nanocomposite (mass fraction clay, 5%) were obtained from UBE industries and used as received. The samples were exposed to a radiant heat flux of 35 kW/m² and ignited when there was sufficient volatilization to sustain gas-phase combustion. Spectra were measured continuously until the flames self-extinguished, which was about 15 min (from the time the samples were exposed to the radiant heat) for the pure polymer and almost twice as long for the nanocomposite. A photograph showing the probe assembly and the burning polymer during an experiment is presented in Fig. 1.

The spectral window of the measurements was limited to the region extending from about 2250 cm⁻¹ to 4000 cm⁻¹ due to the transmission properties of the fiber optics. This frequency range encompasses absorption due to C–H, N–H, and O–H stretching modes that are active in the amines, amides, and carboxylic acids known to be produced in the thermal decomposition of nylon polymers.[12] Each spectrum was signal averaged by coadding 256 scans over the specified frequency range. This condition corresponds to a time resolution of about 30 s per spectrum at a frequency resolution of 4 cm⁻¹. The uncertainty in the peak positions is approximately ±6 cm⁻¹. This estimate was obtained by comparing the measured peak positions, which were determined as the midpoints between the corresponding P and R branches in the asymmetric stretches in CO_2 (2346 cm⁻¹) and H_2O (3790 cm⁻¹), with the values obtained by Chu et al., who reported a standard uncertainty of only 0.0042 cm⁻¹ in the wavenumber precision of their measurements.[13]

RESULTS AND DISCUSSION

The spectra obtained early in the cone calorimeter experiment (i.e., before ignition) and in the vicinity of the peak rhr are compared to a spectrum of nylon-6 measured by using a diamond reflectance probe at room temperature in Fig. 2. These spectra are similar, but not identical, to spectra obtained from solid residues collected at various stages in the thermal decomposition of nylon-6 carried out on a thermogravimetric analyzer.[14] The spectrum

measured before ignition closely resembles the reference spectrum of nylon-6 except for an apparent broadening of the peak centered at 3295 cm⁻¹, which is probably an effect of the elevated temperature. The reference spectrum was measured at about 25 °C, whereas the temperature of the melt at this point in the cone calorimeter experiment was probably in excess of 300 °C. The unresolved absorbance in the region between 3050 and 3200 cm⁻¹, which is evident in both the reference spectrum and in the spectrum prior to ignition, is probably due to the monomer (ε-caprolactam) and its cyclic oligomers, which have peaks centered at about 3055 and 3185 cm⁻¹. There is also an overtone of the amide II band in the spectrum of nylon-6 at about 3085 cm⁻¹ that is sensitive to the conformation of the polymer chains.[15]

There are some obvious differences between the spectrum obtained in the vicinity of the peak in the rhr and the spectrum measured before ignition. In particular, there is a shift in the center of the N–H stretching vibration from about 3300 cm⁻¹ to 3357 cm⁻¹. This observation is consistent with spectral features that have been attributed to conformational changes resulting in the disruption of hydrogen bonds.[6] In this case, the hydrogen bonds involve the carbonyl oxygen and amide hydrogen on adjacent anti-parallel chains.[16] There is also a shoulder extending from about 3400 cm⁻¹ to 3450 cm⁻¹ that may be due to the formation of carboxylic end-groups resulting from the hydrolysis of peptide bonds in the interior of the polymer chains.

The spectra obtained from nylon-6 and the nylon-6/clay nanocomposite, which were both measured about 4 min into the burn (after ignition but before the peak rhr), are compared in Fig. 3. The spectrum from the nanocomposite, although noisier, presumably because the melt did not adhere as well to the sapphire probe, exhibits features similar to those observed in the spectrum of the pure polymer. This observation is consistent with previous results from computer simulations[17] and electron microscopy,[18] which indicate that the same products are produced during the thermal degradation of both materials, but, in the case of the nanocomposite, they become trapped in a char-like residue. This hypothesis will be examined further in future experiments, where both the condensed- and gas-phase spectra corresponding to ny-
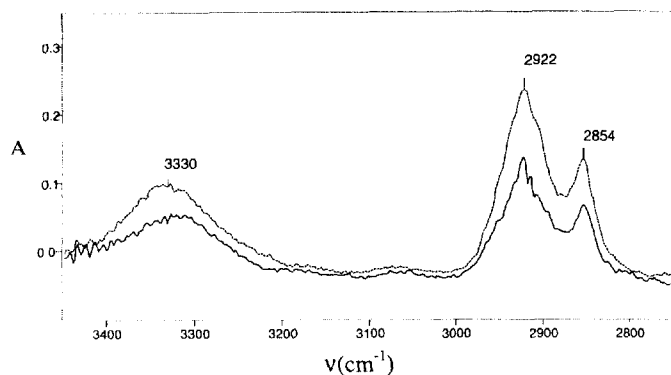
FIG. 3. The spectrum from nylon-6 (dashed line), which was measured just after ignition, compared to the spectrum of nylon-6/clay nanocomposite (solid line) measured about the same time into the burn.

lon-6 and the nylon-6/clay nanocomposite will be monitored at critical points along their rhr curves.

CONCLUSION

Changes in the condensed phase MIR spectra of nylon-6 and a nylon-6/clay nanocomposite were monitored in real time during flammability measurements conducted on the cone calorimeter. The spectra obtained during the burning process were of sufficiently high quality to show the progression of the material in contact with the probe from molten polymer to thermal degradation products. The spectral features are consistent with the evolution of formation of ε-caprolactam as a result of depolymerization reactions. On the basis of these results, we have concluded that the use of MIR fiber optics in conjunction with an FT-IR spectrometer to monitor changes in the condensed-phase chemistry of burning polymers is both feasible and useful. In the future, we hope to use this tool to identify major degradation products of burning polymers and thereby to elucidate the chemistry responsible for the heat release at critical points along the corresponding rhr curves.

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