

Photoaddition of Fluoroolefins on Aromatic Polyamide

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Synopsis

A photografting method has been developed to surface treat aromatic polyamide fabrics in the presence of fluoroolefin vapors. The new fabrics are more flame resistant in oxygen-enriched environment than untreated commercial aramid fabrics. The photoaddition reaction of haloolefins has been shown to irreversibly modify the fabrics, which were analyzed by water wettability, scanning electron microscopy, x-ray analysis, and ^{19}F nuclear magnetic resonance spectroscopy.

INTRODUCTION

The objective of this work is to chemically modify commercial aromatic polyamide for providing flame-resistant fibrous materials in an oxygen-enriched environment. Such fibrous products are aimed for applications in space and deep-sea vehicles. Organic fibrous products, which possess highly aromatic backbone, are known to exhibit outstanding flame resistance.¹ Nomex, which is a high-temperature aromatic polyamide manufactured by du Pont, is self-extinguishing in air but burns in atmospheres with an elevated partial pressure of oxygen (e.g., 31/69 O_2/N_2 at 10 psia).

Prior work with Nomex fabric shows that improvement of flame resistance is feasible through chemical modification as phosphorylation² and halogenation.³ However, such treatments strongly color the fibrous products and also degrade the aromatic polyamide.

This paper describes a photoaddition reaction of fluoroolefins to modify aromatic polyamide without the apparent change of physical properties and appearance of the fibrous material.

EXPERIMENTAL

Materials

Aromatic polyamide (Nomex HT-10-41, woven fabric, natural color) was purchased from Stern and Stern Textiles; tetrafluoroethylene and bromotrifluoroethylene were obtained from PCR; and nitrogen (99.999%), special gas mixture of 31% oxygen and 69% nitrogen, and fluorotrichloromethane were obtained from Matheson Gas. The fabric and reagents were used as received. The vapors of fluoroolefins were checked by infrared analysis.

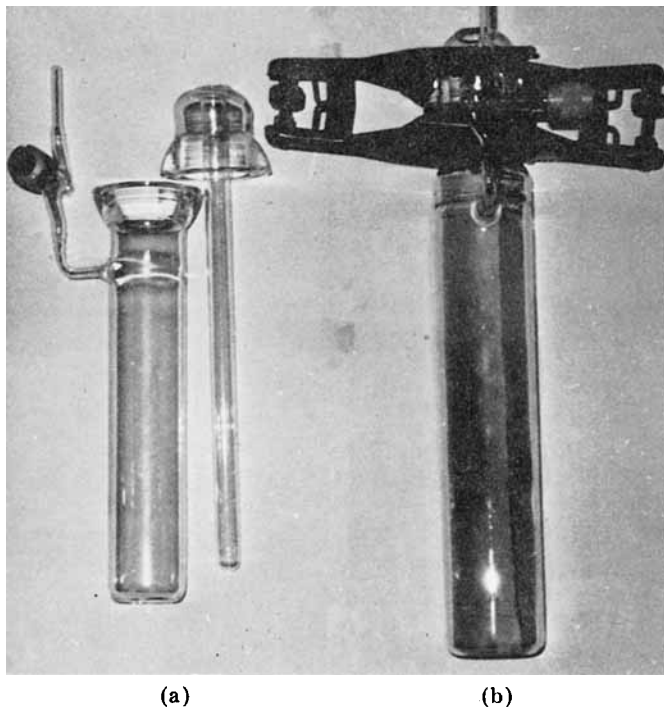


Fig. 1. Reaction vessel: (a) an opened cylindrical Pyrex reactor with side arm and valve for attachment to the manifold (to the left) and quartz sleeve (to the right); (b) a closed reaction vessel with the fabric mounted around the centered quartz tube.

Apparatus

A copper vacuum manifold was used for transferring fluoroolefin vapors from the storage cylinder to a piece of fabric specimen hanging in a reaction vessel (Fig. 1). The cylindrical Pyrex reaction vessel consists of a centered quartz sleeve for receiving a 11-in. Pen Ray mercury-arc lamp (Ultraviolet Products). Pressures were measured with a Heise gauge, and the reaction temperature was maintained by heating tape or infrared lamps.

Figure 2 shows the flammability test apparatus. The ignitor (Type B, Clenweld Products) was held in position by a coiled Nichrome ignition wire (1 ohm/in.). The sample (2.5 × 5 in.) was mounted vertically between the stainless steel sample holders, leaving 2 × 5 in. of exposed surface. The vertical flame test⁴ uses a mixture of 31% oxygen and 69% nitrogen at 10 psia.

Analytical Instruments and Sample Preparations

For IR transmission analysis, a strip of fabric was ground into 40 mesh, mixed with KBr, and pressed into a pellet. A fabric sample for attenuated total reflectance (ATR) IR used a Wilkes double-beam ATR attachment at a 45° angle of incidence in direct contact with a KRS-5 reflector plate (52.5 × 20 × 2 mm). Both IR transmission and ATR spectra were recorded on a Perkin-Elmer Model 467 spectrometer.

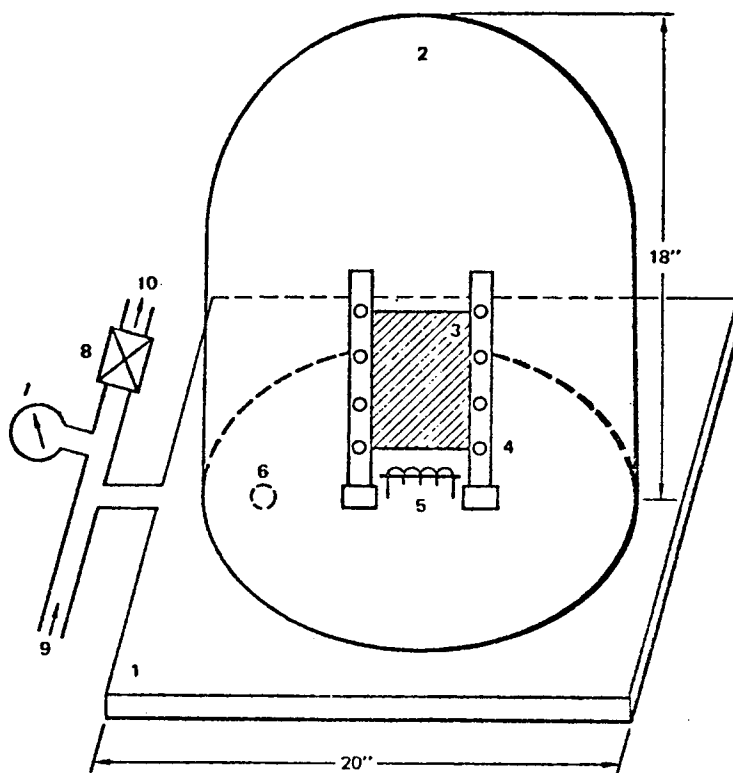


Fig. 2. Flammability test apparatus: (1) metal base plate; (2) bell jar (2 cu ft); (3) sample; (4) sample holders; (5) ignition wire and ignitor; (6) vacuum and gas inlet; (7) vacuum gauge; (8) valve to vacuum; (9) gas inlet; (10) to vacuum pump.

A Cambridge Mark IIA Stereoscan scanning electron microscope (SEM) equipped with an EDAX 505 energy dispersive x-ray probe was used for the photomicrographs and x-ray analysis. The SEM fabric samples were chilled and cut in liquid nitrogen for a clearer end view at the interphase and were subsequently deposited with a thin layer of gold-palladium. An antistatic solution (Ernest F. Fullam, Inc.) was added on the SEM fabric samples right before examination for improved resolution of the photomicrographs.

The ^{19}F NMR spectrum was measured by a Varian XL-100 spectrometer operating at 94.1 MHz. A piece of 4×9 in. (3.6 g) treated Nomex fabric was shredded into individual fibers and dissolved in 4 ml concentrated sulfuric acid with added deuterated water for the internal lock. The viscous solution was poured into a 12 mm O.D. NMR tube. Fluorotrichloromethane was used as an external standard.

Procedure

The fabric sample was mounted around the centered quartz tube (at 0 to 1 cm from the surface) in the photografting reaction vessel [Fig. 1(b)]. The side arm was attached to the copper manifold and evacuated. A measured amount of

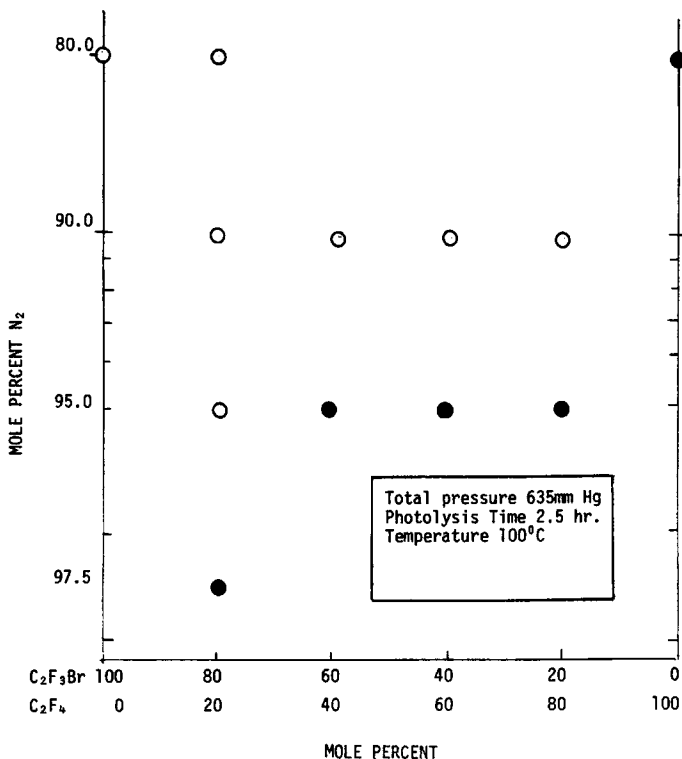


Fig. 3. Effect of fluoroolefin composition on flammability characteristics of photografted Nomex fabrics: (○) self-extinguishing; (●) burned.

gaseous fluoroolefins as neat or premixed fluoroolefins at specified ratio was introduced alternately for improved mixing with anhydrous nitrogen to a specified pressure, temperature, and photolysis time. The amounts of volatile reagents were determined by *P-V-T* measurements assuming ideal gas behavior.

At the end of the irradiation time, the reaction vessel was evacuated and air was introduced. The photografted fabric sample was washed with fluorotrichloromethane and dried under vacuum.

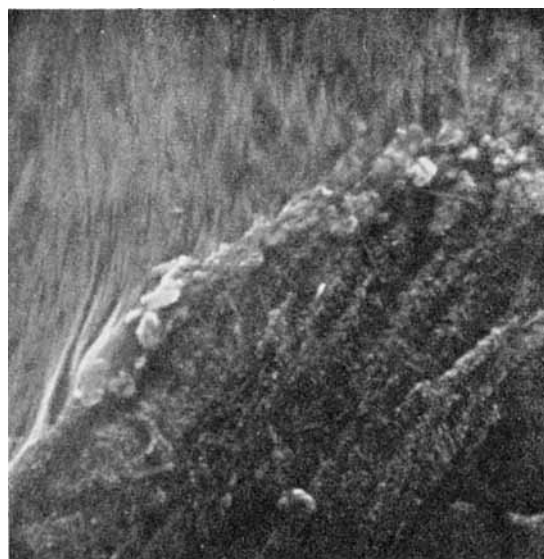
RESULTS AND DISCUSSION

The vertical flame test (Fig. 2) in a mixture of 31% oxygen and 69% nitrogen at 10 psia was used to show the difference of flammability characteristics of some photografted Nomex fabrics which were treated by varied fluoroolefin compositions in the presence of nitrogen. Figure 3 summarizes the results using one exposure to a medium-pressure mercury arc lamp (see under Apparatus). The photoaddition reaction of fluoroolefins chemically modified the aromatic polyamide surface and thus upgraded not only the flame resistant properties but also acid resistance.

An increase in light energy of the process shortens the fabric treatment time under photolysis, but high-energy ultraviolet source darkens the Nomex fabric rapidly.



(a)



(b)

Fig. 4. Edge views (cut in liquid nitrogen) of treated Nomex fibers: (a) 12,000 \times , angle 75 $^\circ$, 20 kV; (b) after soaking in 70% H₂SO₄ for 80 sec, 11,000 \times , angle 30 $^\circ$, 20 kV.

In Figure 3, all samples are photografted and water nonwetttable regardless of their flammability characteristics. The water-nonwettability characteristic readily distinguishes them from the untreated samples. However, the IR spectroscopy (transmission and ATR) failed to show any significant difference between the treated and untreated samples. The absence of C—F bonds by ATR measurements for difluorocarbene-modified fiber surfaces has been previously reported.⁵ The lack of IR absorption for C—F bonds suggests the monomolecular-like character of the modified surface.

Figure 4 shows the edge views of treated Nomex fiber before (a) and after (b)

soaking in 70% sulfuric acid for 80 sec. The SEM photomicrographs illustrate the ease of aromatic polyamide fiber to be strongly etched by the concentrated acid, while the surface of the treated fiber is affected at a substantially decreased rate.

The x-ray probe attached to the SEM is not a sensitive elemental analysis for the light elements,⁶ but the presence of bromine on the photografted fabric shows a strong signal. Thus, several treated samples by varied ratios of tetrafluoroethylene and bromotrifluoroethylene were subjected to a gold evaporation process in the same vacuum chamber. Then the gold content of the various samples was assumed as identical and used as the standard. The higher ratios of C₂F₃Br to C₂F₄ in the premixed vapor composition show a corresponding higher bromine content on the treated sample.

The ¹⁹FNMR spectrum shows the two major narrow absorptions, $\phi = 144$ and 170 ppm, from CFCI₃ at the relative intensities of 2:1. The spectrum rules out any significant quantity of the homopolymer⁷ and confirms the presence of chemically bonded fluorocarbon-modified Nomex surface.

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