Studies on Flame Retardancy of Polyacrylonitrile Fiber Treated by Flame-Retardant Monomers in Cold Plasma

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Synopsis

Plasma polymer hexamethyldisiloxane, ethyldichlorophosphate and tris(butoxyethyl) phosphate modified polyacrylonitrile fibers were examined by FTIR, XRF, and SEM and the extend of flame retardancy introduced were checked. Certain levels of concentrations of flame-retardant elements grafted or coated at the fiber surface during plasma treatment are believed to overcome some negative effects of a number of reactions that usually are concurrent with plasma polymerization, such as crosslinking.

INTRODUCTION

Flame resistance of polyacrylonitrile (PAN) fiber can be achieved by several methods such as copolymerization or blending as well as by treatment with flame retardant finishes.[1,2] However, most of these methods, except the latter one, cause a considerable change in physical and chemical properties of fibers at the end since up to 60 to 70% overall uptake of flame retardants are usually needed. In addition, surface finishes are known as not being permanent and can be lost considerably after each washing.

As already known, it is possible to modify surface properties of polymeric substrates without altering their bulk properties, mainly by using plasma polymerization technique. The effects of plasma treatment are confined to a layer of 1 to 10 μm in depth and it is mostly limited to the surface.[3] Since flammability is controlled mainly by surface properties, modification of substrate surfaces and proper grafting of flame-retardant groups would alter flammability without affecting bulk properties. Although the overall uptake of flame-retardant groups would be in considerably small quantities in this case, still their concentration at the thin surface layer could be concentrated enough to cause appreciable modifications in the flammability characteristics.

EXPERIMENTAL

Materials

All of the monomers were of pure grade and used without further purification. Polyacrylonitrile (PAN) fiber was also a commercial product (a product of

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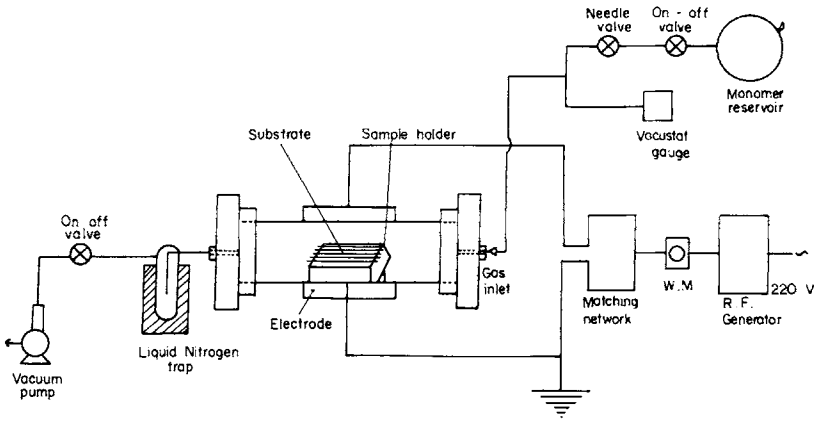

Fig. 1. Schematic diagram of plasma apparatus.

Yalova Elyaf) and it was used as received. Fibers were kept in a vacuum oven for 24 h at 25°C to stabilize their moisture contents.

Plasma Treatment

Plasma polymerizations were carried out with use of a 13.56 MHz rf source. A reactor was built with a Pyrex tube, with two parallel copper electrodes located externally (Fig. 1).

Liquid monomers were degassed before plasma treatment. The pressure of the system was decreased to about 0.1 mm Hg before the initiation of glow discharge. Since, tris(butoxyethyl) phosphate had a very high boiling point it was used by the impregnating spray method and hence applied onto the fiber directly. In this case, the glow discharge was applied after impregnation of monomer. Unpolymerized monomer was cleaned out with acetonitrile after

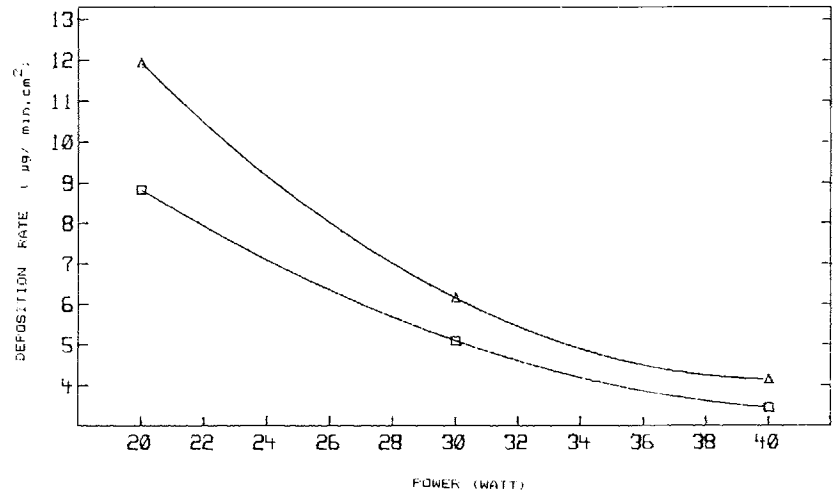

Fig. 2. Deposition rate of EDCP vs. plasma power: (△) 20 min; (□) 40 min.

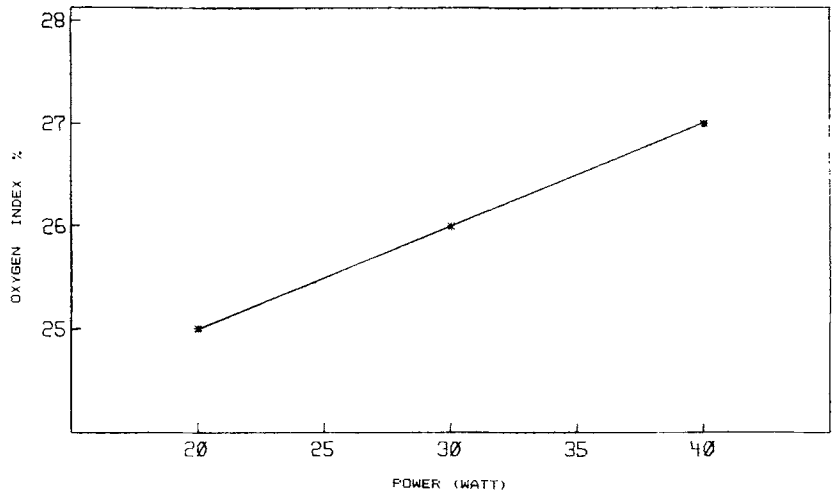

Fig. 3. OI vs. rf power for plasma-treated PAN fiber with EDCP.

plasma treatment by taking the benefit of the fact that it was a solvent of the monomer and a nonsolvent for both the substrate and polymer formed at the surface.

Oxygen Index (O.I.) Testing System

The oxygen index method was originally developed for evaluating the flammability of self-supporting bulk polymer.[4] A special fiber sample holder was used in this work.[5] Reproducible results were obtained with the helix shaped sample holder.

Others

In order to analyze the polymer which was formed at the fiber surface after plasma treatment, depositions were also carried out on a NaCl crystal. Elemental analysis of phosphorus for plasma-treated samples was made by X-ray fluorescence spectrometer (Model 56-5). The surface morphology of the untreated and plasma-treated samples were examined by scanning electron microscope. Wettability test was also made by using a cathetometer.

RESULTS AND DISCUSSION

In plasma polymerization, polymer which is deposited on the surface of PAN fiber need not necessarily be grafted as the deposition may also occur without formation of any chemical bond between the PAN backbone and the deposited polymer molecules.

In this study, three different types of flame-retardant monomers were attempted. The first monomer used was hexamethyldisiloxane (HMDS). Silicones are particularly heat- and oxidant-resistant materials and they have been used as flame retardant coatings.[6] HMDS was used at various plasma powers and exposure time levels. The oxygen indices (OI) for all plasma-treated PAN fibers

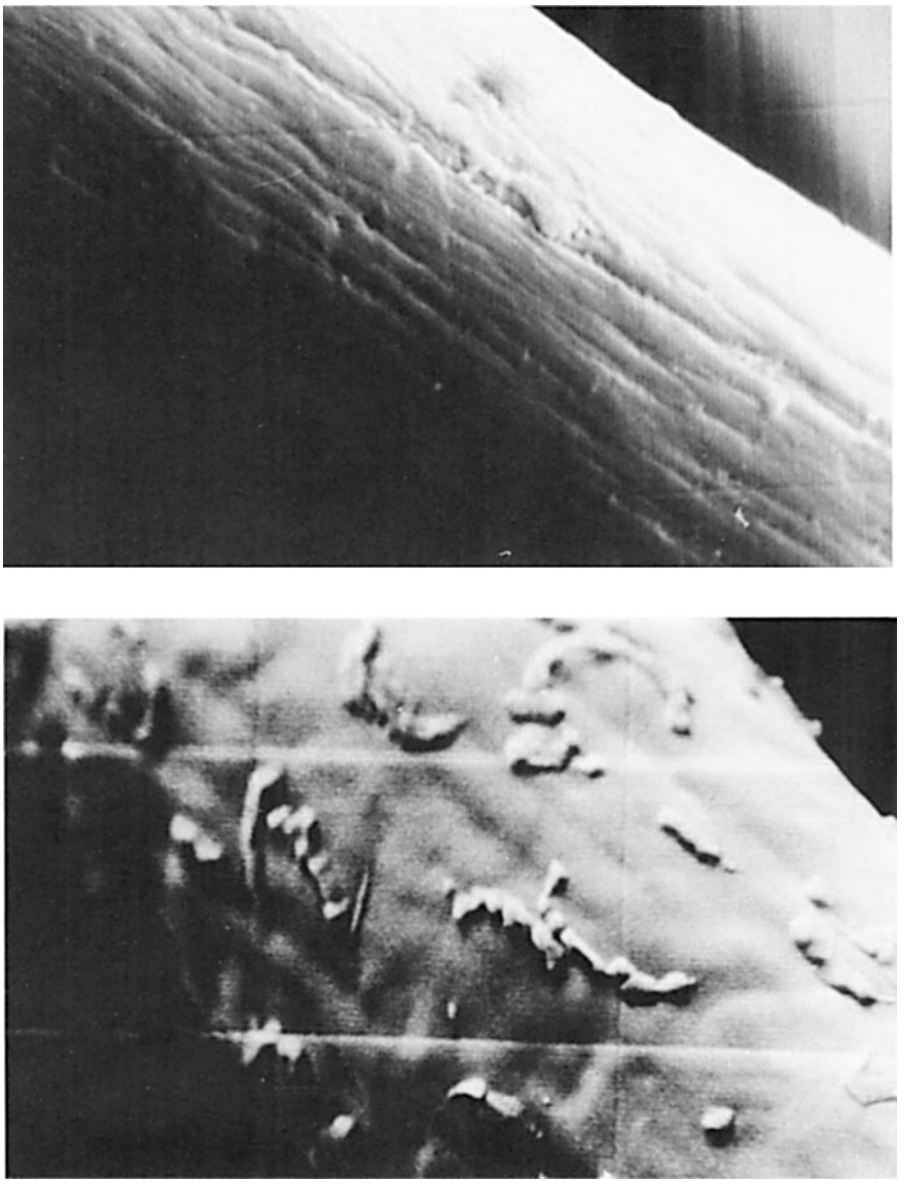

Fig. 4. (a) Scanning Electron Micrograph (SEM) of untreated PAN fiber ×1600; (b) SEM of plasma-treated fiber with EDCP (40 W and 40 min) ×1600; (c) SEM of plasma-treated fiber with TBEP (40 W and 40 min) ×1600; and (d) SEM of plasma-treated fiber with argon (40 W and 40 min) ×800.

with HMDS were less than that of the untreated one. Although HMDS gives its highest yield at 20 W for 60 min, OI of PAN fiber which was treated under this condition were also less than untreated one.[7] In other words, HMDS causes an increase in the flammability of PAN after plasma treatment. In another study from our laboratories, the flammability of a polyester fabric was also found to be increased with HMDS after its treatment in cold plasma alone.[8]

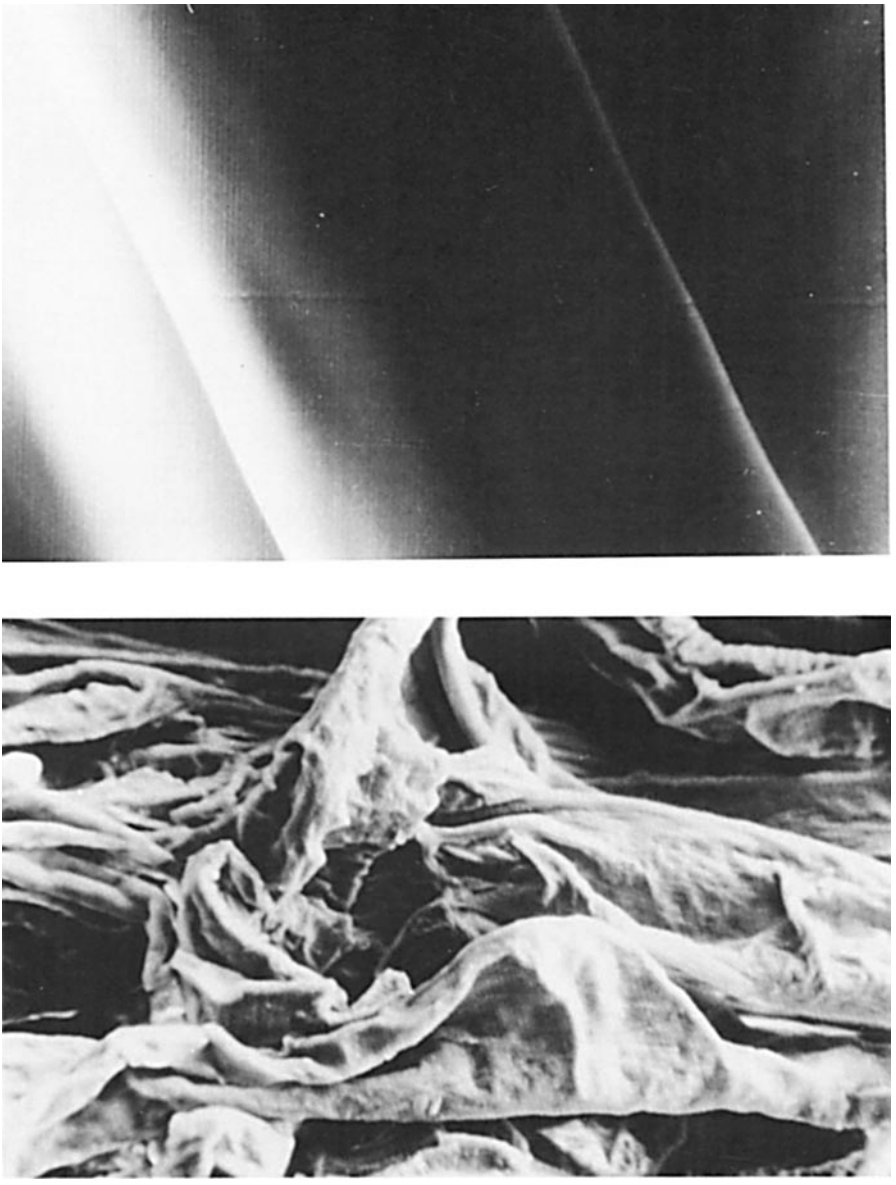

Fig. 4. *(Continued from the previous page.)*

While the number of reactions that are usually concurrent with plasma polymerization such as crosslinking can give an explanation to increase in the flammability of plasma-treated specimens with HMDS, it can also be expected that oxygen content of the surface may also be increased by HMDS treatment and may cause an increase in the flammability characteristics of PAN fiber.

Ethyldichlorophosphate (EDCP) was used to see the effect of chloride and phosphorus together on the flammability of PAN fiber. Deposition rates of EDCP vs. rf power at two different time levels are shown in (Fig. 2). It was

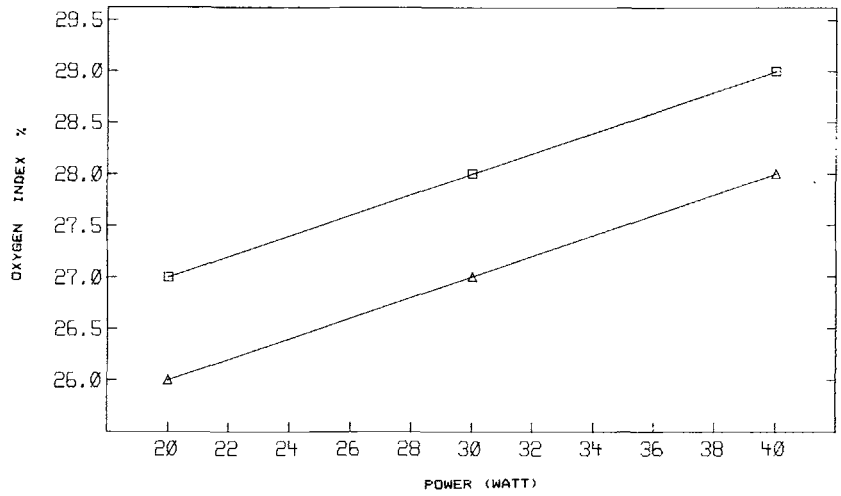

Fig. 5. OI vs. plasma power for treated PAN fiber with TBEP at 30 (△) and 40 (□) min.

observed that, deposition rate of this monomer was inversely proportional with power and exposure time of plasma. Decrease in deposition rate with increasing rf power shows that depolymerization and/or polymer chain scission increases at high powers. Furthermore, flame-retardant effect of EDCP increases when rf power is increased as shown in (Fig. 3).

As it was stated in literature, there may be a synergistic effect for chloride and phosphorus elements if they are used together.[4] However, it is necessary to achieve an optimum ratio between these two elements at the fiber surface to see a synergistic effect. It may be concluded that this optimum ratio could not be reached at a high deposition rate of EDCP (i.e., low rf power and low exposure-time level).

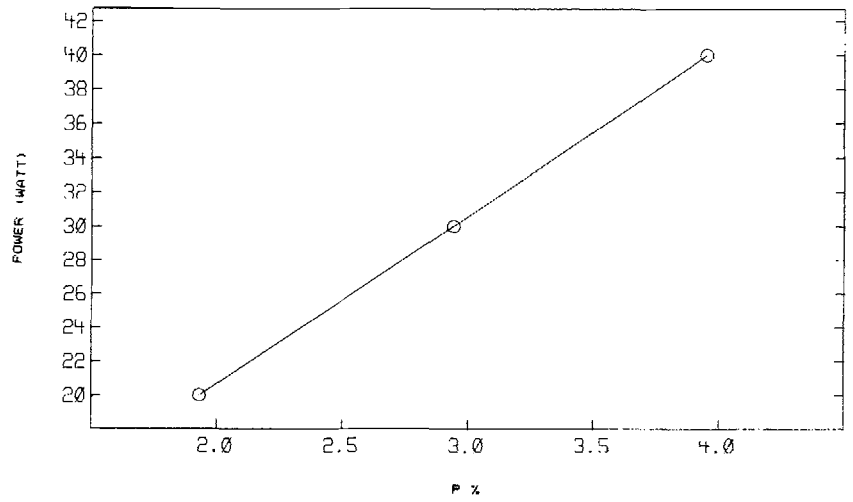

Fig. 6. Plasma power vs. P % content at the fiber surface plasma treated with TBEP.

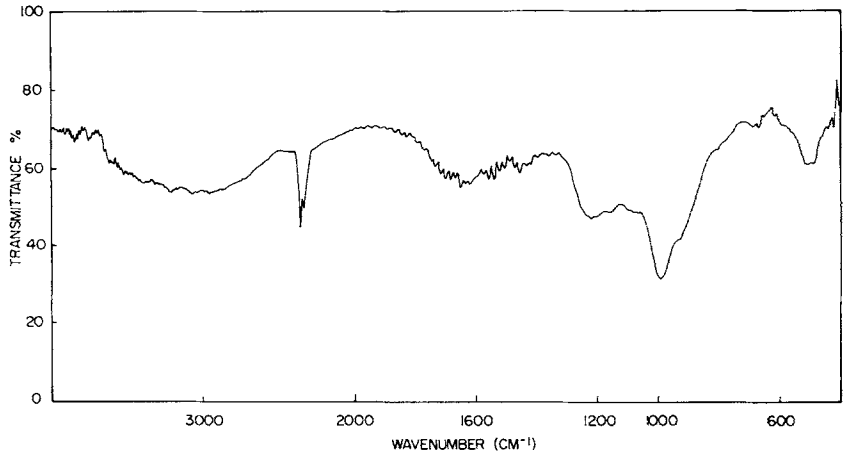

Fig. 7. FTIR Spectrum of plasma-treated EDCP (40 W and 40 min).

The SEM data of the untreated and plasma-treated sample with EDCP are shown in [Fig. 4(a–b)]. These data may bring additional proof for the deposition of polymer under plasma condition and it is easy to see appreciable changes in the morphology of PAN surface. Hence, one may conclude that, EDCP-treated fiber shows an improved flame retardancy even at 0.55% average uptake of retarding elements.

TBEP is one of the flame-retardant monomers used extensively for PAN fiber by conventional "blending" technique. Here, it was used at different plasma conditions. O.I. observed vs. plasma powers applied at 30 min and 40 min were shown in (Fig. 5). The highest O.I. value for treated PAN fiber was obtained at 40 W for 40 min in this work. It is easily observed that there is a linear relationship between OI values and rf power, which means that if power and exposure time to plasma increase, the flammability of treated PAN fiber decreases.

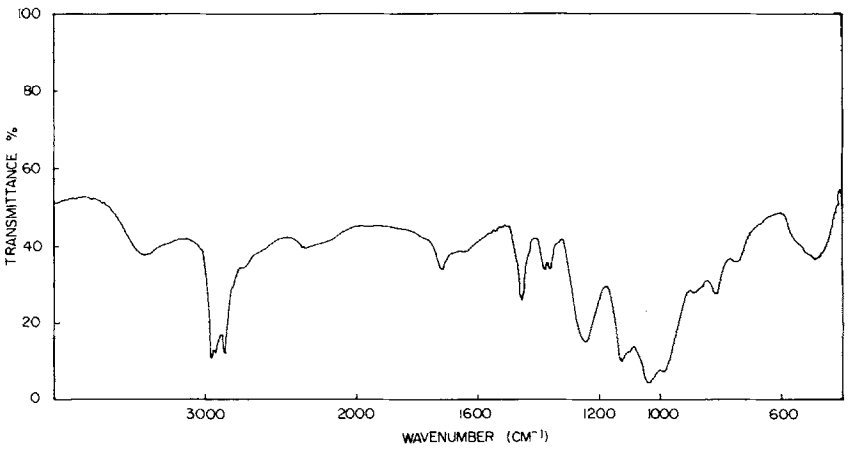

Fig. 8. FTIR spectrum of plasma-treated TBEP (40 W and 40 min).

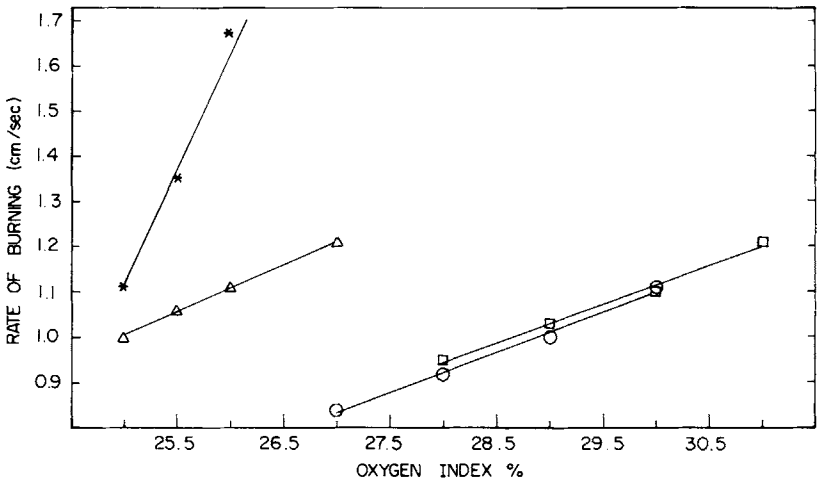

Fig. 9. Burning rates of untreated and plasma-treated PAN fiber vs. their OI: (△) untreated; (*) plasma treated with argon; (□) plasma treated with TBEP; (○) plasma treated with EDCP.

XRF data show that, % P content at the fiber surface may increase linearly with increasing plasma power as it is shown in (Fig. 6). Thus flammability of PAN fiber decreases with % P content increase at the surface.

FTIR spectra of plasma polymerized EDCP and TBEP at 40 W for 40 min are shown in Figures 7 and 8.

SEM shows that plasma-treated fiber with TBEP monomer has a smoother surface than that of the untreated one as it was shown in [Fig. 4(c)].

Plasma treatment was also made under vacuum only to see the effect of crosslinking on PAN fiber by using argon as a carrier gas. Argon plasma-treated PAN fiber was dissolved in DMF then dried in vacuum oven at 50°C. SEM of this residue implies some changes occurred at the fiber surface after plasma treatment as shown in Figure 4(d).

The burning rates of Argon plasma-treated and untreated fibers were also compared. Burning rate of the first is found to increase rapidly with respect to that of untreated one, although OI of it remained almost unchanged. This result can be explained easily by the effect of introduced crosslinking. Crosslinks at the surface of fiber are believed to hold the burned and nonburned parts together and thus help to keep most of the heat in the preflame layer of burning which is evolved during combustion and inhibit dripping of the burning material. Therefore, flame can spread easily through the core of fiber downward without spending much heat to preheating of the preflame zone.

Burning rates of PAN fiber, plasma-treated with argon, as well as with monomers EDCP and TBEP all at 40 W for 40 min vs. their oxygen indices are shown in (Fig. 9). Although OI of TBEP and EDCP plasma-treated fibers were increased, their burning rates were decreased a little bit with respect to untreated fiber. In this case, one can think of the existence of two effects which are most probably operating in opposite directions. First, there is the negative effect of crosslinking and then there is also positive effects of flame retardant compounds (coated or grafted at the fiber surface) on the burning rate and OI value of plasma-treated fibers. It may be concluded that the positive effects of flame retardants can overcome the negative effect of crosslinking in our case.

A wettability test was made to see changes on the surface characteristics of treated PAN. The contact angles obtained for the untreated and for plasma-treated fibers (with argon and TBEP) at 40 W for 40 min were found as 57, 78, and 61°C respectively. Surface modification of polymers by plasma with conventional monomers were made before and resulting surfaces were generally found to be more hydrophilic.[9] In our study, it is interesting to see the large difference between contact angles of untreated and argon plasma-treated PAN fiber. This difference may be explained by removal of hydrophilic–CN groups contained in PAN backbone during plasma treatment, thus decrease of wettability results.

CONCLUSIONS

The plasma-treated PAN fibers with TBEP showed an increase in OI value of the fiber changing the character of PAN from a "slowly burning material" to "self-extinguishing." XRF results showed that, if percent phosphorus content on the fiber surface increases, flammability decreases as expected.

Studies with EDCP showed a good flame resistance, although there are small quantities of overall uptake on fiber surface by weight.

Burning rates of plasma-treated fiber with argon are much higher than for the untreated sample while their OI values remain almost unchanged.

There are small changes in burning rates of the samples treated with EDCP and TBEP, although high oxygen index values were found for these samples. It is expected that under the conditions studied concentrations of flame-retardant elements that are attached to the fiber surface during plasma polymerization do overcome the negative effects of crosslinking.

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