Studies on Modification of Some Flammability Characteristics by Plasma. II. Polyester Fabric*

G. AKOVALI† and F. TAKROURI

Department of Chemistry and Macromolecular Research Division,
Middle East Technical University, 06531 Ankara, Turkey

SYNOPSIS

Cold plasma treatment of polyester fabric in the presence of several volatile monomers containing expected flame retardant elements was made and some of the flammability characteristics of the plasma/monomer-treated fabric were studied. The plasma treatment on the fabric caused a slight decrease in both oxygen index values and burning rates. It is believed that crosslinking outweighs the effect of grafted elements. The results of wettability and TGA tests as well as SEM data are included.

INTRODUCTION

The introduction of flame resistancy to polyester [poly(ethylene terephthalate)] has been an active object of research for years.[1-3] Polyester is already a multibillion pound per year polymer, a result of its widespread use mainly as a fiber in household items and clothing. On the other hand, international statistics of fire deaths still continue to show two deaths per 100,000 people in the western hemisphere,[4] which are mainly due to "room burns"; hence, the flame retardancy of polyester fabrics is still an important issue.

A polymer is considered flammable as long as its oxygen index value (OI) is equal to or smaller than 26.[5] The (OI) value of virgin polyester is 20 and it is classified as a "group 1" substance with a "relatively flame retardant structure."[6] This group of polymers is known to form "char" on burning, which is believed to be responsible for the generally low flammability characteristics.[7,8]

It is well known that during burning heat generated in the flame is transferred back to the polymer surface producing volatile fragments which diffuse into the flame region and react there by chain processes, producing heat and promoting a continuous cycle. Flame retardants are believed to interrupt this cycle either in the solid or in the vapor phases (or in both). In the first, promoted crosslinking at the surface results in a char which insulates the bulk from the heat of the flame zone preventing further pyrolysis, while, in the second, volatile free radicals directly inhibit the reaction.

Conventionally to protect a polyester fabric against fire with an effective flame retardant, considerable quantities of the latter is necessary. To achieve this, direct blending of a retardant with the polymer is usually done, which frequently causes a considerable change in the mechanical properties of the bulk material. In addition, it was even shown that polyester may become more sensitive to degradation in the presence of the usual flame retardants.[2] Hence, effective modification of fiber surfaces while leaving the bulk of the material unchanged by use of plasma seems to be an attractive and promising method.

In plasma, the effects of treatment are usually confined to a surface layer of 1–10 μm in depth and the effects at the outermost layer are strongest. The radicals generated by plasma can be used to produce grafts and crosslinks at the surface layer. In fact, the chlorination of polyester fabrics induced by γ-rays to decrease its flammability[9] and grafting several nonvolatile monomers onto different fabrics (like wool, rayon) by exposing the impregnated fabrics to cold plasma were reported,[10,11] with the formation of easily extractable homopolymers[10] and

* Part I: Studies on PAN Fiber, *J. Appl. Polym. Sci.*, to appear.
† To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 42, 2717–2725 (1991)
 CCC 0021-8995/91/102717-09$04.00

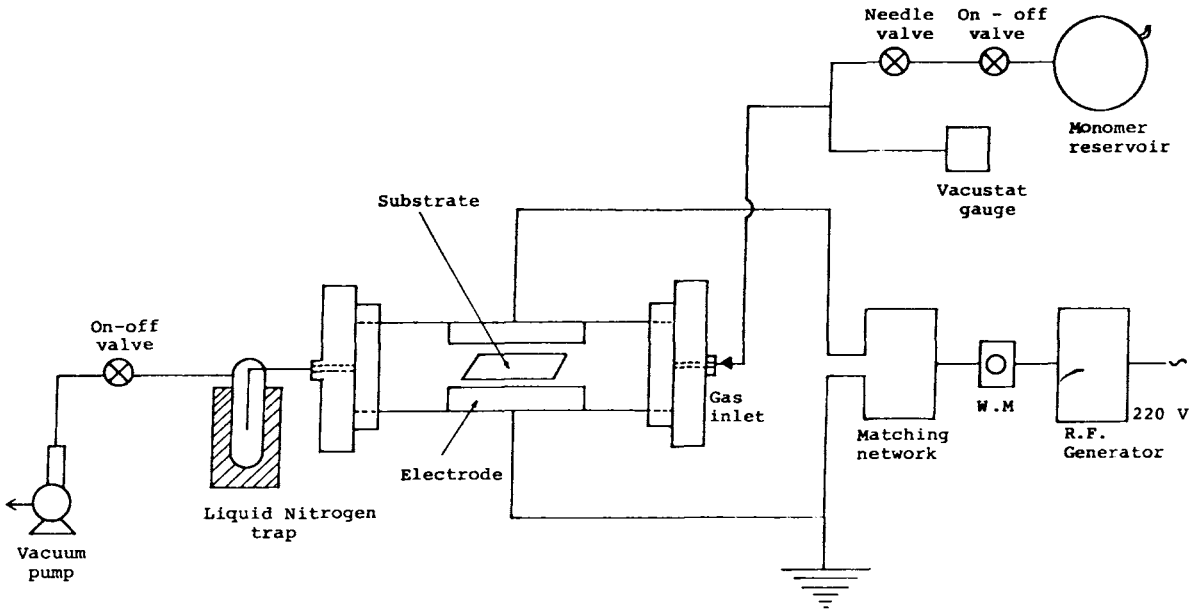


Figure 1 Schematic diagram of plasma apparatus.

burned spots due to the high intensities used. In another study, radiation fixation of flame retardants on polyester/cotton blend fabrics was also reported.[1]

This study, which is the second in a series of flame retardance work in progress, presents results of studies on surface modification of a polyester fabric by use of plasma and proper monomers at mild intensities to gain more information about the subject.

EXPERIMENTAL

Polyester fabric (woven) used was a product of Bossa, Turkey (type 4/1 satin, containing 24/30 filaments with 100/2 × 167 dtex, spun and batch dyed prewashed and with antistatic treatment). It was used as received. Since flammability of fabrics is known to increase as their area/volume ratio increases and it is highly sensitive even to a slight alteration in the fiber content as well as handling-preparation procedure of the sample, its moisture content, and ambient humidity, samples were carefully prepared from the same lot for all experiments and all were pretreated in a vacuum oven at 50°C for 25 h prior to treatment and testing.

The volatile monomers with expected flame retardant elements used were: pure grade hexamethyldisiloxane (HMDS), 1,1,2-trichloroethane, trichloroethylene, tetrachloroethylene, and allylamine. All were used without purification.

A capacitively coupled rf plasma system (Tegal)

Table I OI Values of Several Plasma/ Monomer-Treated Polyester Samples and Conditions of Treatment

Monomer	Power (W)	Plasma Duration (min)	OI
None	Untreated polyester		22.2
Plasma in vacuum only	20	60	20.0
HMDS	20	60	19.5
Tetrachloroethylene	20	60	21.8
Plasma in vacuum only	30	10	21.1
1,1,2-Trichloroethane	30	10	21.4
Trichloroethylene	30	10	21.1
Allylamine	30	10	21.1
Plasma in vacuum only	40	5	22.2
Trichloroethylene	40	5	22.2

Table II Burning Rates in Air of Plasma/ 1,1,2-Trichloroethane-Treated Polyester Fabric

Power (W)	Duration of Plasma Exposure (min)	Rate of Burning in Air (cm/min)
20	60	3.0
20	30	2.6
20	15	2.7
30	10	Self-extinction
30	15	3.6
40	5	Self-extinction
40	10	3.4

operating at 13.6 MHz was used. The tubular reactor used was 4.6 cm in diameter and a pair of external copper electrodes, each 15 cm long, were located on it (Fig. 1).

The monomer to be used was degassed first and then its vapor was fed into the reactor under vacuum, passing over the samples located on the lower electrode until reaching a stable pressure, which was kept for at least 15 min more before the discharge was applied.

For the percent crosslinked calculation, preweighed untreated and plasma treated polyester fabric specimens were dissolved in *O*-chlorophenol separately and from the undissolved part, weight percent of the crosslinked portion was calculated.

Oxygen index (OI) test[12] and rate of burning were carried out with a home made system (Fig. 2). The specimen (12 × 4.6 cm) was clamped vertically in a U-shaped holder in the approximate center of the column with the top of the specimen being 10 cm below the upper edge of the column. A propane ignitor was used. To measure the rate of burning, two lines, 2 cm and 11 cm from the upper end of the specimen holder, were marked and the time of burning between these two lines was followed. The flow of gases was set so that the desired concentration of oxygen was flowing through the column for at least 30 s before ignition. The entire top of the specimen was ignited so that the specimen was well lit. OI was taken to be the value of oxygen concentration that will just sustain the combustion for which a change of 0.3% or less would make the difference between the burning of the entire length of the sample and the extinction.

The surface morphology of untreated and plasma-treated samples was examined by scanning electron

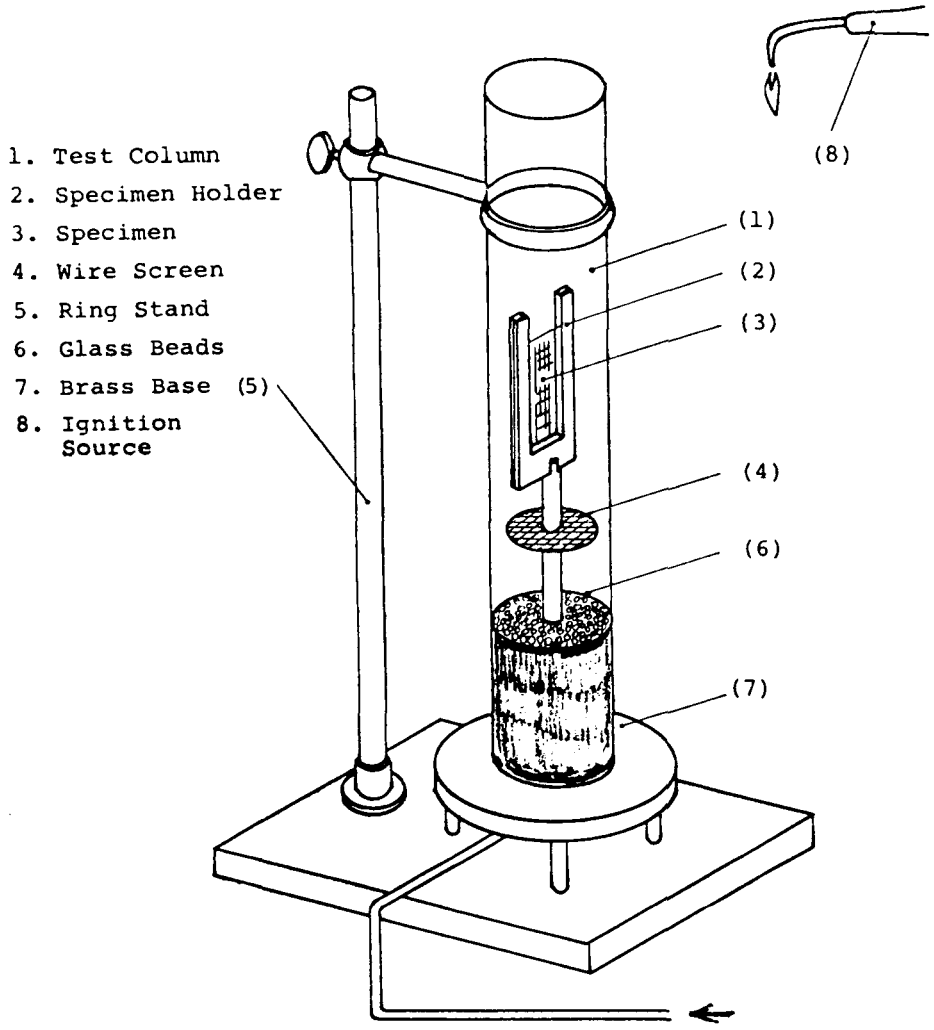


Figure 2 Diagram of the apparatus used in the oxygen index test.

Table III Burning Rates in Air of Plasma/ Trichloroethylene-Treated Polyester Fabric

Power (W)	Duration of Plasma Exposure (min)	Rate of Burning in Air (cm/min)
10	10	3.5
10	20	3.3
10	30	2.9
10	40	2.1
20	10	3.2
30	10	2.7

microscope performed with a Cambridge stereoscan 54-10 SEM. The thermogravimetric analysis (TGA) was performed with a DuPont TGA Model 1090. Wettability tests were carried out by means of a home-made system coupled to a tensometer (Kruss).

RESULTS AND DISCUSSION

Plasma modification of polyester fabric was carried out under a variety of selected processing conditions (Table I). The conditions were those which yield the highest polymer depositions in plasma (e.g., Ref. 13). The OI values for all plasma-treated samples were found to be somewhat less than that of virgin material (Table I). It is interesting to see that, although flammabilities were increased in all plasma-treated samples, the burning rates were decreased considerably. Figures 3–5 present the dependency of burning rates to oxygen concentrations, which is seen to be linear with different slopes and intercepts for different samples.[14] Obviously, the rate of burn-

Table IV Burning Rates in Air of Polyester Fabric Plasma-Treated with Different Monomers and Combination of Monomers (30 W, 10 min)

Monomer	Rate of Burning in Air (cm/min)
Trichloroethylene	2.7
Tetrachloroethylene	2.8
Allylamine	2.4
N_2	3.2
PCl_3	2.6
N_2 + trichloroethylene mixture	2.6
PCl_3 + allylamine mixture	2.7
Trichloroethylene + allylamine mixture	2.6

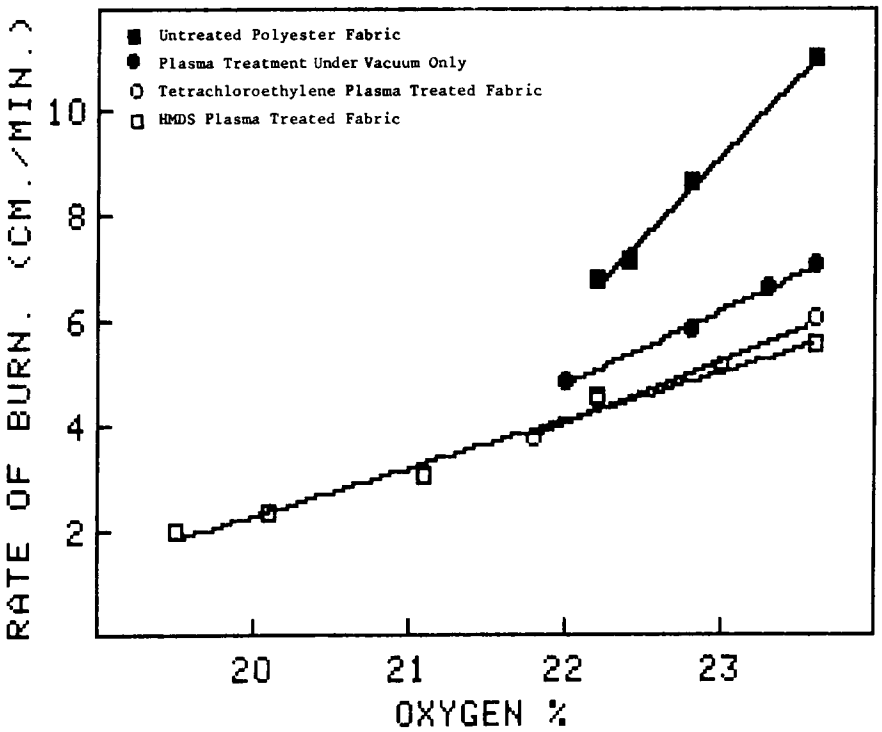


Figure 3 Rate of burning as a function of environmental oxygen concentration for untreated polyester fabric and plasma-treated fabric at 20 W, 60 min.

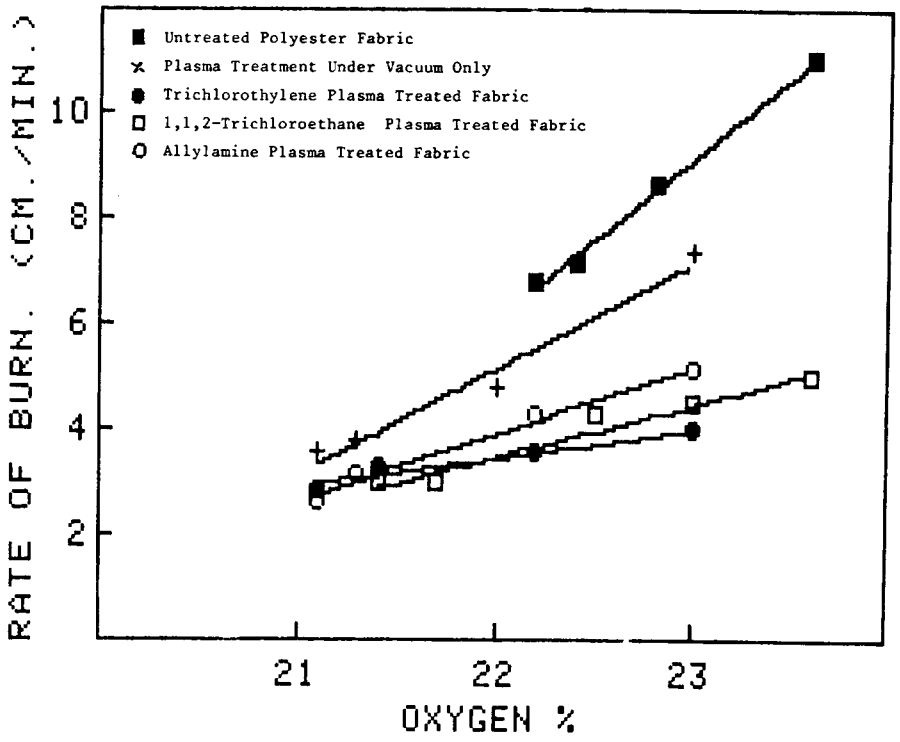


Figure 4 Rate of burning as a function of environmental oxygen concentration for untreated polyester fabric and plasma-treated fabric at 30 W, 10 min.

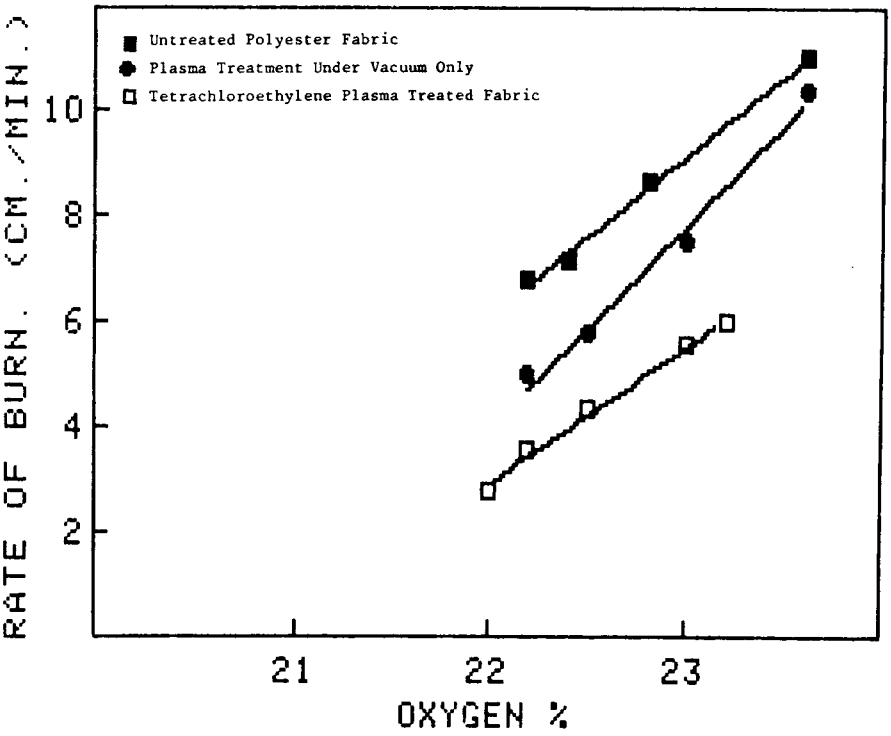


Figure 5 Rate of burning as a function of environmental oxygen concentration for untreated polyester fabric and plasma-treated fabric at 40 W, 5 min.

Table V Wettability Tests for Untreated and Plasma-Treated[a] Polyester Fabric

	Untreated	Plasma in Vacuum	Tetrachloroethylene Plasma
Average height (water, mm)	1.45	2.11	1.89
Contact angle ($\theta°$)	56.7	40.7	46.2

[a] Plasma treatment: 20 W and 60 min.

ing depends on the oxygen concentrations and this dependency is found to be more pronounced for the untreated sample. Even plasma treatment carried out in vacuum only is found to be effective in altering this dependency, and the alteration observed is more significant for all monomers tested.

The interrelation between the burning characteristics and the plasma conditions can also be seen from the burning rates (in air) of different treated samples (Tables II, III, and IV). The contact angles for plasma treated fabric were found to be lower than those of untreated fabric (Table V), showing that

Table VI Thermogravimetric Analysis (TGA) Results for Untreated and Plasma-Treated Polyester Fabric in Oxygen and Nitrogen Atmosphere

		First Break		Second Break		
Sample	ATM[a]	Average Temp (°C)	Weight Cont. (%)	Average Temp (°C)	Weight Cont. (%)	Char Residue (%)
Untreated polyester fabric	O_2	436.3	78.45	547.5	13.71	3.38
	N_2	453.2	91.70	—	—	8.32
Plasma treated in vacuum only (20 W, 60 min)	O_2	440.5	78.14	586.0	14.93	3.05
	N_2	459.0	79.42	—	—	20.52
Tetrachloroethylene/ plasma-treated fabric (20 W, 60 min)	O_2	439.3	79.67	554.3	17.15	2.73
	N_2	458.6	75.27	—	—	24.70
HMDS/plasma-treated fabric (20 W, 60 min)	O_2	444.2	58.32	552.6	8.23	31.31
	N_2	441.9	81.98	—	—	18.06
Plasma-treated in vacuum only (30 W, 10 min)	O_2	440.7	73.38	530.5	12.36	9.75
	N_2	445.2	82.32	—	—	17.59
Allylamine/plasma-treated (30 W, 10 min)	O_2	439.5	74.47	528.6	17.29	4.46
	N_2	453.1	82.19	—	—	17.79
Plasma-treated in vacuum only (40 W, 5 min)	O_2	440.5	78.72	545.0	14.50	1.82
	N_2	469.8	84.87	—	—	15.13
Tetrachloroethylene/ plasma-treated (40 W, 5 min)	O_2	441.4	76.43	550.9	14.27	3.54
	N_2	459.8	81.16	—	—	18.87
Chlorobenzene/ plasma-treated (20 W, 15 min)	O_2	439.7	71.65	567.6	17.52	6.77
	N_2	447.5	79.30	—	—	20.63

[a] TGA in oxygen or nitrogen atmosphere.

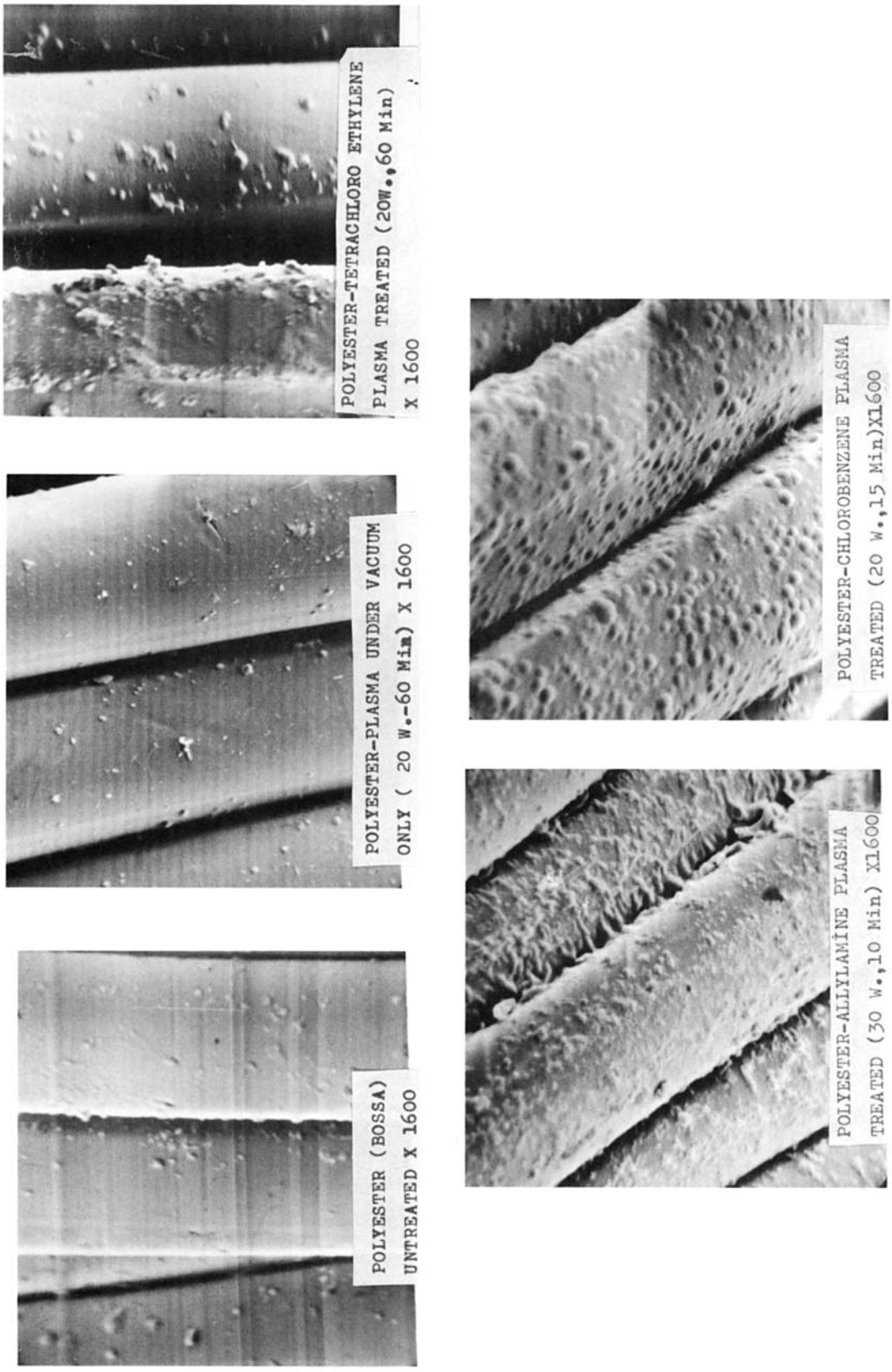
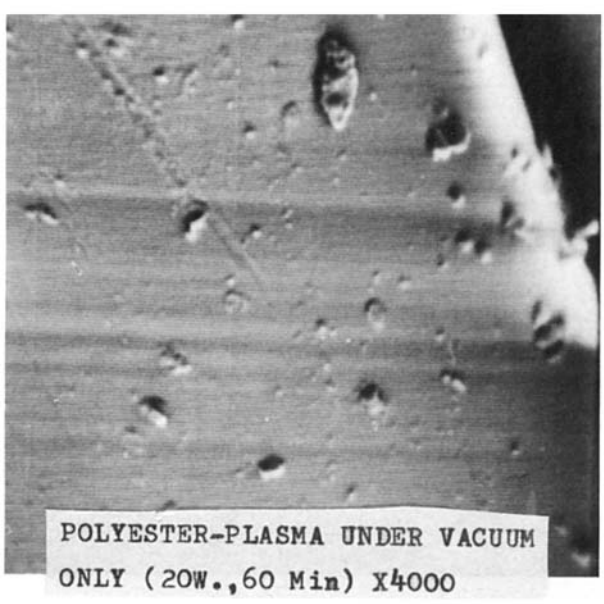


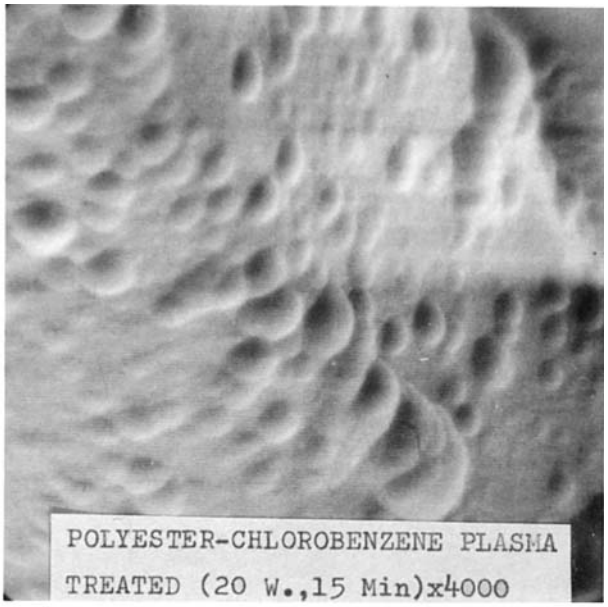
Figure 6 SEM pictures of plasma treated and untreated polyester samples (×1600).

the plasma treated fabric is more wettable than the untreated one.

Figures 6 and 7 present the SEM pictures of various samples prepared. The untreated sample and plasma treated samples in vacuum show similar surface texture, while tetrachloroethylene, allylamine, and chlorobenzene plasma produces "snow or flakelike precipitates" at the surface and their surface texture seem different from each other (Fig. 6). A similar result can be observed (Fig. 7) for HMDS and chlorobenzene-plasma-treated surfaces in SEM pictures with higher magnifications.

From the results obtained, it may be concluded that two factors mainly affect the flammability behavior of plasma-treated polyester fabric. The first is related to the amount of polymer deposited or grafted on the surface. The second is related to the effect of a number of reactions usually concurrent with the plasma polymerization process such as crosslinking, unsaturation, and oxidation.





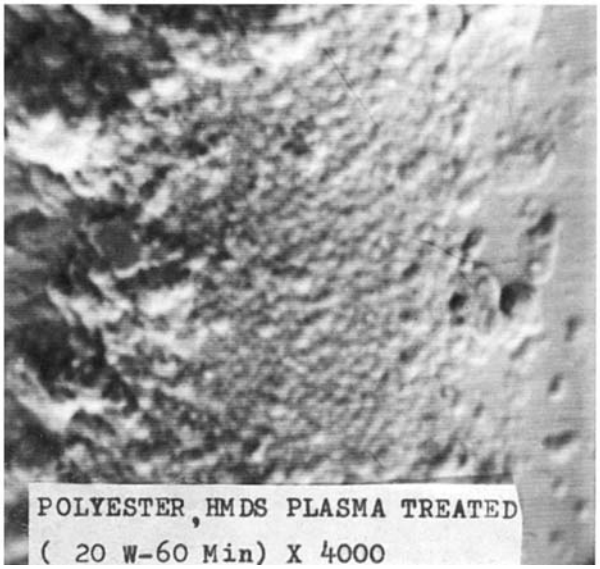


Figure 7 SEM pictures of plasma-treated polyester samples (×4000).

For the first factor, most probably the amount of the uptake of flame retarding species at the fabric surface was not high enough to show any appreciable improvement. In the case of tetrachloroethylene plasma treatment at (20 W, 60 min) the average uptake was about 1% by weight, whereas crosslinking as the second factor is expected to change the main characteristic of the burning behavior, namely, the softening of the material under the influence of heat which was followed by dripping and escaping of molten parts from the system. This behavior was noted to decrease or even disappear for the plasma-crosslinked samples. Lack of dripping of molten parts will prevent heat loss from the vicinity of the burning region and hence a decrease in OI values for plasma-treated samples is expected. Similar behavior was reported for polyester–cotton blend, which was found to be more flammable than polyester alone. Nonmelting cotton fibers in the blend form a carbonaceous gridwork during combustion supporting the molten fiber and prevent dripping off, and this behavior was termed as "scaffolding effect."[15]

Since grafting of flame-retarding species will act to increase the OI value and crosslinking will tend to decrease it, the results obtained in this work clearly show that the effect of crosslinks at the surface outweighs the effect of grafted elements for the samples prepared and tested.

The TGA test was used as a tool to check the extent of crosslinking of the fabric as it is expected that the crosslinking process enhances the char formation. The results are presented in Table VI. The char residues of plasma-treated fabrics were more than those of untreated, especially if TGA results in nitrogen atmosphere are considered. Since it was not possible to observe a relationship between the decrease in oxygen indices and the increase in char residues, it was not possible to obtain any solid explanation from the TGA results and some additional data are needed, which is expected from a research in progress.

Another indication for crosslinking was shown by solubility tests where untreated, plasma-treated (in vacuum only), and tetrachloroethylene/plasma-treated samples (20 W, 60 min) were dissolved in *o*-chlorophenol separately. The percent weight of the undissolved part was 1.1% for the untreated sample whereas the corresponding values were 2.2 and 2.5% for plasma/vacuum- and plasma/tetrachloroethylene-treated samples, respectively.

The results and comments presented here show the complexity of the problem as many factors and parameters affect plasma treatment of polyester fabric. But it is possible to conclude that plasma treatment can alter the flammability behavior of polyester fabric and the final result is related to plasma condition and to the kind of flame retardant. As the percent uptake is usually small, the flame retardant must be effective enough even at low levels of uptake. Otherwise, the negative effects of crosslinking from plasma can overcome and cover the expected positive effects of flame retardant groups and hence flammability of the polyester fabric may not change much or it may even increase.

This work was supported both by METU Research Fund (ODTU-AFP 89.01.03.01) and by Tübitak (through TUMKA unit). Kind cooperation of Bossa for the generous supply of polyester fabric is also gratefully acknowledged.

REFERENCES

1. R. Liepins, C. Jarvis, S. Amufiogu, and R. Barker, -AFP-SME Technical Paper FC76-522.
2. J. L. Hechtand and W. E. Garrison, *Polym. Plast. Technol. Eng.*, **18**(1), 109 (1982).
3. *Flame Retardant Polymeric Materials*, M. Levin and E. M. Pearce, Eds., Plenum, New York, 1975, Vols. 1 and 2.
4. Editorial, *Urethanes Technol.*, (Feb./Mar.), (1988).
5. D. W. Krevelen, *Polymer*, **16**, 625 (1975).
6. G. L. Nelson, P. L. Kinson, and C. B. Quinn, *Annu. Rev. Mater. Sci.*, **4**, 391 (1974).
7. R. C. Nametz, *Ind. Eng. Chem.*, **62**(3), 41 (1970).
8. K. M. Gibov, L. N. Shapovalova, and B. A. Zhubanov, *Fire Mater.*, **10**, 133 (1986).
9. *Chem. Abstr.*, 89.7499r (1978).
10. A. Pavlath and K. S. Lee, *J. Macromol. Sci. Chem.*, **A10**, 619 (1976).
11. C. I. Simionescu, F. Denes, M. M. Macovanu, G. Cazau, M. Totolin, S. Perea, and D. Balour, *Cellulose Chem. Technol.*, **14**, 869 (1980).
12. ASTM-D.2863, *Annual Book of ASTM Standards*, Part 33-752, 1980.
13. G. Akovalí and N. Hasírcí, *J. Appl. Polym. Sci.*, **29**, 2617 (1984).
14. B. Miller, B. C. Gaswami, and R. Turner, *Text. Res. J.*, **43**, 61 (1984).
15. Y. P. Khanna and E. M. Pearce, *Flame Retardant Polymeric Materials*, Plenum, New York, 1978, Vol. 1.

Accepted July 20, 1990