

Radiation Grafting of Flame Retardant to Polyester/Cotton Blend

Young Kun Kong, Hun Sun Chang, Jong Kwang Lee and Jai Ho Choi

Korea Atomic Energy Research Institute.

(Received September 22, 1979)

Abstract

The grafting studies were concentrated on working out the methodology for radiation of flame retardants to polyester/cotton (65/35) blend fabric.

The Fyrol 76 was used as a flame retardant in developing methodology for localizing flame retardants on the surface of the blend fabric.

By judicious control of the swelling conditions, time of contact with the monomer, and dose rate, locating the graft in the fiber became possible. The yield of the graft polymerization was depended upon the total dose and the preswelling conditions.

Oxygen Index was used to evaluate the effect of the location of Fyrol 76 and other flame retardants within the surface upon the flame retardance efficiencies.

To get a better flame retardance efficiency by the localized grafting of Fyrol 76 to polyester/cotton blend fabric, a technique of one step processing at room temperature was developed substituting the ordinary two-step processing at high temperature.

요 약

고선량을 전자가속기를 이용하여 폴리에스터/면 혼방직포에 난연제 (Fyrol 76)를 그래프트 중합반응시키는 방법의 개선을 시도하였다. 폴리에스터/면 (65/35) 혼방직포에 고착시킨 난연제는 Fyrol 76을 사용하였다.

팽윤조건과 단위체와 접촉시간 및선량을 등을 적절히 조절하므로써 섬유에 난연제를 그래프트 반응시킬 수 있었으며, 그래프트 중합반응의 수율은 방사선 선량과 선팽윤(先膨潤) 조건에 좌우되었다. 난연제로 처리한 혼방직포의 난연성 효과는 산소 지수로 측정하였다.

폴리에스터/면 혼방직포에 난연제를 그래프트 중합반응시키는 방법으로 종래에는 고온에서 두 단계를 거쳐 실시하는 것이었으나 본 연구를 통하여 실온에서 단 단계로 처리토록 하는 방법을 개선하였다.

Introduction

The possibilities of using radiation as a catalyst for chemical reactions on textiles have intrigued researchers in this field for about 20 years, but practical applications

have been elusive. The use of cobalt-60 isotope for radiation source in the early part of sixties was the primary limitation, but much interesting and useful works were carried out. The radiation processing of textiles has been reviewed in detail by Gilbert and Stannett¹⁾, Rutherford²⁾, and by

many other researchers. The introduction of high intensity electron accelerators in the mid-sixties lead to a further increase in interest and commercial processes for permanent press and crease recovery. Another barrier was the lack of chemicals available that were suitable for high rates of polymerization. The research on textile radiation processing in the late sixties and early seventies relied almost on the versatile N-methylol acryamide, which has a high degree of polymerization and has cellulose reactivity through the methylol group. Recently the research aims have also been shifted somewhat to fibers themselves and on imparting crease resistance. More recently, the emphasis has been on fire retardancy and a number of other textile finishing operations such as coating, printing and grafting. Some textile applications have already been published. Fabric coating³⁾, flocking⁴⁾, bonding of nonwoven fabric⁵⁾, pigment prints⁶⁾, and fixation of flame retardants^{7,8,9,10,11,12,13,14)} are some of the most promising applications. The grafting studies were concentrated on working out the methodology^{7, 8, 9, 10)} for radiation fixation of flame retardants to polyester and polyester/cotton (50/50) blend.

In general, grafting to fibers superimposed the properties of the grafted polymer onto the fiber without disturbing the properties of parent fiber such as its mechanical strength. However, the grafting of massive amounts can produce new types of fiber where the properties of the side chains predominate.

Good examples are the formation of highly elastic fiber^{15,16,17)} or super-absorbent fibers¹⁸⁾. Such properties can be imparted at more modest degrees of grafting if the structural order of the fiber, such as crystallinity, is

destroyed and reformed at a lower level after grafting^{19,20)}.

In this paper flame retardants were combined to polyester/cotton blend through radiation-induced free radical. Flame retardants contain phosphorus and halogen components. Effect of dose rate and preswelling agent on the radiation grafting of flame retardant onto polyester/cotton blend fabric were discussed. To evaluate the flame retardant effect, Oxygen values were determined.

Experimental

1. Materials

Polyester/cotton (65/35) blend fabric samples were purified by treating with the mixture of 1% sodium carbonate solution and 0.3% Tween 80 solution (surfactant) at 80°C for 2 hours. Acrylic acid was purified by vacuum distillation²¹⁾ (20mmHg, 56°C) and used immediately after distilling or stored below 0°C. All preswellnig agents such as 1,2-dichloroethane, chlorobenzene, chloroform, carbon tetrachloride, N,N-dimethylformamide were obtained from the Merck Co. and were not purified further. Fyrol 76, trimethylol propane triacrylate, bromine and Moropol 1000 (softner) were E. P. reagent grade and were not purified further either.

2. Localized Grafting

The two important variables used to achieve localized grafting are diffusion of the monomer to the active sites and dose rate. Since the monomer must diffuse into the fiber from the outside, the diffusion control also leads to control of the location of the graft.

Preswelling of the fiber not only increases the rate of diffusion of the monomer into the fiber but also may result in a higher initial monomer concentration in the fiber.

By judicious control of the swelling conditions, the time of contact between the fiber and the monomer, and the dose rate, it becomes possible to locate the graft at various depths in the fiber. In this paper, the PET/COT (65/35) blend was preswollen in carbon tetrachloride, at 60°C, 2hrs, and then placed in the mixed solution containing flame retardant. Subsequently the treated sample was padded and was irradiated with electron beams.

3. Grafting Techniques

An electron accelerator (High Voltage Engineering Corporation) with a maximum beam current of 25 mA and operated at 390,000V was used in this work. This equipment utilized a vertical beam (X-scan 12%, Y-scan 70%). The samples were laid on a conveyor, so that the samples were irradiated by the suitable doses.

Most of work was done with samples 5×10cm in size, and conducted on preswollen fabric. Irradiations were carried out in nitrogen or air-filled polyethylene-bags. The beam current and conveyor speed were varied from 0 to 15mA and 9.4 to 29.2cm/sec, respectively. The dose obtained with those variations was a linear function of the ratio of beam current to conveyor speed as previously established²². The operation current-speed curve was used to calculate delivered dose for all experiments.

The treated samples (5×10cm) were pre-swollen in carbon tetrachloride (7-20hr at 30°-70°C) and then impregnated in a 22% flame retardant mixture solution. The

mixture solution contained 2% of Moropol 1,000 (softner) and N-methylol acrylamide. Following the swelling procedure, the samples were removed from the solution, padded 100% of pick up percent, and then placed in polyethylene bag under nitrogen or air, weighed and irradiated.

In the case of grafting under high dose rate (Mrad/sec) of electron beams, instead of two step processing at high temperature, one step processing at room temperature was modified for localized grafting of Fyrol 76 upon polyester/cotton blend fabric.

4. Oxygen Index

Since the samples in the initial phase of this work were in the form of fabrics, it was necessary to develop a modified technique for measuring the Oxygen Index (OI) of these materials. The development of the sample holder and the procedure for measuring the OI has been described²³. The procedure permitted not only the determination of the OI values, but also an estimation of the char yield as the material burned in the tester.

This procedure was also applied to the evaluation of the various grafted fabric samples.

5. Differential Thermal Analysis

The DTA instrument used in this work was a Setaram (Lyon, France). The decomposition point was taken as the temperature which curve goes through the maximum of the peak.

10mg of sample was capped in a platinum cup and the other platinum cup which is packed with Al₂O₃ was used for reference.

The analyses were conducted in a atmo-

sphere at a programmed heating rate of 5°C/min.

Results and Discussion

1. Effect of Dose

When Fyrol 76 was grafted onto PET/COT (65/35) blend fabric at room temperature, the percent graft and conversion increased with dose (see Table 1, Table 2).

It is shown in Table 1 that the percent graft was 2.6% at 0.5 Mrad and 17.1% at 10.4 Mrad. Such results suggested that while macro radicals of PET/COT blend (65/35) was produced by the amount of the dose, most of macro radicals were combined with the monomer radicals and macro

radicals were partially crosslinked.

As can be seen from the Table 1 the first ten cycles laundry were sufficient to remove a small portion of the flame retardant in some cases.

It is interpreted that the flame retardant was diffused into the core of the swollen fabric and core grafting was occurred, so that the chemical bonding between fabric and flame retardant was not easily destroyed by the washing. It is seen from the results that the higher the total dose, the higher the grafting efficiency.

Effect of radiation dose on the grafting of Fyrol 76 onto polyester/cotton blend fabric (65/35) at room temperature is shown Table 2.

As shown in Table 2, the percent graft

Table 1. Effect of Radiation Dose on the Grafting of Flame Retardant onto Polyester/Cotton Blend Fabric, at 15°C

Total dose, Mrad	Pick up of monomer, %	Conversion, %	Apparent graft, %	Graft efficiency, %	After 10 home wash cycles
					Apparent graft, %
0.5	36.4	9.6	2.6	27.1	2.8
1.0	35.9	12.8	4.6	36.0	4.2
2.2	36.0	21.7	9.5	43.8	7.3
3.2	36.7	20.5	8.4	41.0	6.2
7.5	36.2	30.2	13.5	44.7	9.1
10.4	36.7	36.3	17.1	47.1	11.6

Preswelling: 1,2-Dichloroethane, 60°C, 1hr.

Impregnation: 30°C, 2hr.

Monomer Mixture: Water/Moropol 1000/Fyrol 76/MAM (60%)=50/4/22/24 (w/w).

Table 2. Effect of Radiation Dose on the Grafting of Fyrol 76 onto Polyester/Cotton Blend Fabric (65/35) at 15°C.

Total dose, Mrad	Pick up of monomer, %	Conversion, %	Apparent graft, %	Graft efficiency, %	After 10 home wash cycles
					Apparent graft, %
0.5	37.1	10.4	3.7	35.5	3.8
1.0	35.4	12.9	5.6	43.4	5.0
2.2	36.2	20.8	9.1	43.7	8.0
3.2	35.6	19.9	7.3	36.7	7.3
7.5	38.0	29.7	11.6	39.1	9.8

Preswelling: Chloroform, 60°C, 1hr.

Impregnation: 30°C, 2hr.

Monmer Mixture: Water/Moropol 1000/Fyrol 76/MAM (60%)=50/4/22/24 (w/w).

was increased with the radiation dose.

The general graft mechanism discussed above may contribute to further advancement in a new technology for the graft of flame retardants and the new technology for the process may bring about a new point of view in the study of solvation of polymers.

Table 3 illustrates the effect of radiation dose on the grafting of trimethylol propane triacrylate onto polyester/cotton blend fabric, which is treated with the mixed solution of 10% Br₂ and 15% KBr. It was found from the results that the percent graft was increased with increasing dose, but content of bromine in the polyester/cotton blend fabric was decreased with increasing dose.

It is considered that the double bonds of trimethylol propane triacrylate which is grafted onto the blend fabric are decreased with increasing dose and then bromination reaction which can be occurred through the substitution reaction is occurred in the undestroyed double bonds.

2. Effect of Oxygen on Grafting

When graft copolymerization was induced by γ -ray of low dose rate in the atmosphere, the graft copolymerization was influenced by the oxygen²⁴⁾.

The treated samples were irradiated with electron beams in nitrogen or ambient air to examine the effect of oxygen at high dose rate. The data are shown in Table 4.

The percent graft onto polyester/cotton blend fabric in air was almost equal to the percent of grafting in nitrogen.

It is considered from such a result that oxygen has no sufficient time to attack the propagating radicals because of the short irradiation time at high dose rate.

Table 3. Effect of Radiation Dose on the Grafting of Trimethylol Propane Triacrylate onto Polyester/Cotton Blend Fabric at 15°C,

Total dose, Mrad	Pick up of monomer, %	Conversion, %	Apparent graft, %	% of Bromine content after bromination
0.5	51.7	38.8	35.3	15.2
1.0	52.2	46.8	42.4	13.1
2.2	49.4	43.4	41.4	9.6
3.2	52.4	47.6	45.9	9.9
5.2	51.9	50.6	49.3	8.6
7.5	51.5	50.4	48.8	7.9

Preswelling: 1,2-Dichloroethane, 69°C, 1hr.

Impregnation: 30°C, 2hr.

Monomer Mixture: Trimethylol Propane Triacrylate/CH₃OH=60/40 (v/v).

Table 4. Effect of Oxygen on Grafting

Total Dose	Graft %	
	*N ₂	**Air
1.0 Mrad	5.6	4.8
2.2 Mrad	14.7	13.1
4.4 Mrad	19.5	17.6

* N₂: Nitrogen Atmosphere

** Air: Atmosphere

Preswelling: 1,2-Dichloroethane, 70°C, 1hr.

Impregnation: 30°C, 3hr.

Monomer Mixture: Water/Moropol 1000/Fyrol 76/MAM (60%)=50/4/22/24 (w/w).

Experiment Temperature: 25°C

Being clear that there was little effect of oxygen at high dose rate used, it is thought that grafting reaction under the atmospheric condition can be conducted in mass production system.

3. Effect of Preswelling Agents

The studies with many different polymer-monomer grafting systems demonstrated the great importance of the swelling in radiation grafting.

Diffusion in radiation grafting process plays a dual role: i) it controls the chain growth via diffusion of monomer to the

Table 5. Relationship of Preswelling Agent, Preswelling Temperature and Time on Grafting,

Preswelling agent Preswelling condition	Graft %					
	1,2-Dichloroethane	Bromobenzene	Chloroform	Carbon tetrachloride	Dimethylformamide	n-Butanol
30°C, 20hr	1.1	1.4	0.7	1.8	1.2	1.2
50°C, 20hr	1.8	1.0	1.8	1.0	1.7	1.0
70°C, 4hr	0.5	0.9	0.1	1.0	0.5	0.6
70°C, 7hr	2.2	1.6	1.7	2.9	1.7	2.8

Irradiation Dose : 7.5 Mrad

growing chain end, and ii) it controls termination via diffusion (combination) of two polymeric systems. Another consequence of diffusion control is that the grafting often tends to be concentrated in the surface regions, particularly in poorly swollen systems, or in systems with high dose rates. The swelling behavior of polyester/cotton blend in different solvents was an important factor.

A series of experiments was conducted using different preswelling agents to explore their effect upon grafting yield. The preswelling agents, their δ values, preswelling time, preswelling temperature, and grafting yield are illustrated in Table 5 and Table 6.

As shown in Table 5, the percent graft was increased with increasing temperature and time. It is supposed that the grafting yield with these preswelling agents is due to their efficient induction of crystallinity and density changes in the amorphous regions of polyester/cotton blend.

Of the preswelling agent used, carbon tetrachloride was proved the best swelling agent for grafting in Fyrol 76.

By comparing Table 1 with Table 5, when Fyrol 76 with N-methylol acrylamide was grafted, the percent graft was 13.5% and when only Fyrol 76 used, the percent graft was 2.9%.

Thus it is found that using N-methylol acrylamide is efficient for this proceeding.

Table 6. Effect of Preswelling Agent on Grafting Yield

Preswelling Agent	Boiling point, °C	Solubility parameter δ	Grafting yield, %
Ethylene	84	9.8	2.2
n-Butanol	117	10.6	2.8
Chloroform	61	9.3	1.7
Dimethyl formamide	153	10.6	1.7
Carbon tetrachloride	77	8.5	2.9
Bromobenzene	152	9.9	1.6

For the experiment, instead of two step processing at high temperature, one step processing at room temperature has been developed for the grafting of Fyrol 76 on 65/35 PET/COT blend fabric.

4. Oxygen Index versus Graft Yield of Flame Retardant

Data on grafted Fyrol 76, grafting yield versus OI is depicted in Figure 1. The initial rapid increase in OI with percent grafting yield start to slow down after about 10% Fyrol 76. The results would seem to indicate that the maximum OI achievable with Fyrol 76 on 65/35 PET/COT blend is in the vicinity of 29.

5. Thermal Stability versus Flame Retardance

The thermogram of blend fabric treated with Fyrol 76 is shown in Fig. 2.

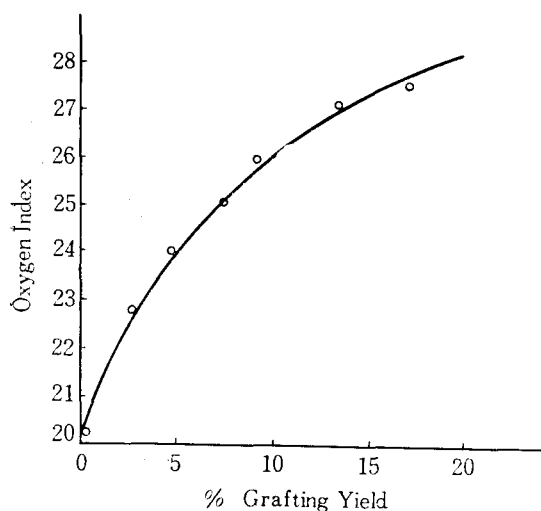


Fig. 1. Oxygen Index vs. Fyrol 76 percent Grafting Yield

Thermal behaviors of copolymers of PET/COT blend fabric treated with Fyrol 76 were examined by differential thermal analysis and are shown in Fig. 2.

As the copolymer contained more Fyrol 76, its decomposition temperature increased accordingly.

It's glass transition temperature was ranging from 86°C to 150°C.

Conclusion

To get a better flame retardance efficiency by the localized grafting of Fyrol 76 onto polyester/cotton blend fabric, a technique of one step processing at room temperature was developed substituting the ordinary two-step processing at high temperature. So we can save the energy, time and labor by using one step processing and make mass production possible.

Of the preswelling agent used, carbon tetrachloride was proved the best swelling agent for grafting in Fyrol 76.

The glass transition temperature of PET/COT blend fabric treated with Fyrol 76

was changed from 86°C to 150°C and the Oxygen Index of that PET/COT blend fabric was 29.

It is considered that the PET/COT blend fabric treated with Fyrol 76 has the desirable thermal stability.

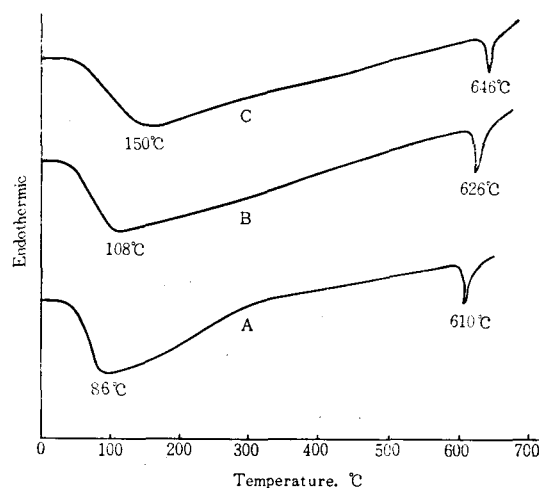


Fig. 2. Thermogram of Blend Fabric Treated with Fyrol 76

References

1. R.D. Gilbert and V. Stannett, *Isotop. Radiat. Technol.*, **4**, 403 (1967)
2. H. Rutherford, *Textile Chemist and Colorist*, **6** (11), 237 (1974)
3. A. Lerner, *J. Coated Fabrics*, **6**, 20-27 (1976)
4. A.D. Fussa, S. V. Nablo and L. A. Johnson, AATCC Flock Technology Symposium, N.Y., N.Y., December 4-5 (1974)
5. J. W. Vogler, M. H. II Mohamed, and W. K. Walsh, *TAPPI*, **58** (9), (1975)
6. W.K. Walsh and E. Bittencourt., Book Pap Int. Tech. Conf. Am. Assoc. Text. Chem. Color 281-290 (1976)
7. W.K. Walsh, E. Bittencourt, L.B. Miles, and H. A. Rutherford., *J. Macromol. Sci-Chem.*, **A10** (4), 695-707 (1976)
8. R. Liepins, J.R. Surles, N. Morosoff, and V. T. Stannett., *J. Appl. Polym. Sci.*, **21**, 2529-

- 2550 (1977)
9. V. Stannett, W.K. Walsh, E. Bittencourt, R. Liepines, and J. R. Surles., *J. Appl. Polym. Sci.*, Appl. Polym. Symposium **31**, 201-227 (1977)
10. R. Liepins, J. R. Surles, N. Morosoff, V. T. Stannett, and R. H. Barker., *Radiat. Phys. Chem.*, **9**, 465-474 (1977)
11. E. Bittencourt, J. Ennis, and W. K. Walsh, *Am. Dyest. Rep.*, **67** (19), 32-28 (1978)
12. *U.S. Pat.* 4,076,650 (1978)
13. *U.S. Pat.* 4,066, 812 (1978)
14. A. Wilson, *J. Coated Fabric.*, **7**, 233-239 (1978)
15. J.L. Williams, and V. Stannett., *Text. Res. J.*, **38**, 1065 (1968)
16. J. L. Williams, K. K. Woods, V. Stannett, S. B. Sell, and V. Stannett, *Int. J. Appl. Radiat. Isotope*, **26**, 159 (1975)
17. J.L. Williams, V. Stannett, L.G. Rolden, S.B. Sell, and C.V. Stevens, *Int. J. Appl. Radiat. Isotope*, **26**, 169 (1975)
18. P. K. Chatterjee and R. F. Schwenker, *U. S. Pat.* 3,889,678 (1975)
19. J. L. Williams and V. Stannett, *J. Polym. Sci., B*, **10**, 665 (1972)
20. J. L. Williams, and V. Stannett, *U.S. Pat.*, 3,814,676 (1974)
21. P. Y. M. Huang and B. Immergut, *J. Polym. Sci., Part A* **1**, 1257-1297 (1963)
22. Y.K. Kong, H.S. Chong, C.K. Lee, and J. H. Choi, *J. Kor. Nucl. Soc.*, **10**(4), 195-201 (1978)
23. ASTM: D 2863-76
24. A. Chapiro, *J. Polym. Sci. Symposium*, No. **50**, 181-188 (1975)