

Eco-friendly Flame Retardant (FR) Pet Fibers Through P – N Synergism

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ABSTRACT

Polyester forms a major constituent among the synthetic fiber industry. It is the most popular synthetic fiber because of its high strength and esthetic appeal. Polyester being highly crystalline, hydrophobic and devoid of reactive groups, it is difficult to introduce reactive phosphorus into the fiber structure through chemical reactions with the phosphorus compounds. Fairly large quantities of the FR chemicals have to be incorporated to achieve self-extinguishing behavior. Although not all Flame Retardant (FR) chemicals are hazardous, it is advisable from an ecological point of view to introduce minimum quantities of FR substances in the fiber structure. The present Paper tries to address the said problems in a small way, so that the PET fiber could be better acceptable. Therefore, graft copolymerization of nitrogenous vinyl monomers has been carried out on the fiber followed by its reaction with phosphorus chemicals, thereby incorporating reactive phosphorus in the grafted substrate. It has been shown that a very small amount of the FR chemical could impart fire resistance of very high order to polyester. Self-extinguishing characteristic was achieved for poly (ethylene terephthalate) fibers with acrylamide-grafted-phosphorylated (AM-g-P) PET fibers containing just 0.189% phosphorus on-weight-of-fiber (owf). Similar results were obtained for methacrylamide-grafted-phosphorylated (MAM-g-P) polyester fibers at the 0.77% phosphorus content level. Efficiency of phosphorus in presence of nitrogen that was achieved was at 263% for acrylamide (AM) system, while it was -12% for acrylonitrile (AN-phosphorus combination). This is attributed to P-N synergism in case of the FR polyester system when the nitrogen is in the amido form present in AM and MAM monomers.

INTRODUCTION

The pioneering research work by Houtz and Adkins [1, 2], and Flory [3, 4] in mid 1930s opened up

tremendous possibilities of polymer modifications through graft copolymerization reactions using vinyl monomers in presence of suitable catalysts. Paul J. Flory, the Nobel Laureate, developed mathematical models that explained growing molecular size and molecular weight of a polymer chain due to chemical attachment of a growing polymer chain of the same or other type of polymers during graft copolymerization reactions. These models can be validated experimentally using techniques such as viscometry. The reasons for such a large volume of research work that has been carried out in the last few decades in fiber grafting is perhaps the realization that it may well be possible to effect desirable physical and chemical modifications in the fiber properties through the grafting technique. Graft copolymerization reactions usually leave the main polymer (fiber) unchanged; affect only the surface, without altering most of its basic desired properties. Even a fairly extensive graft add-on does not destroy the essential properties of substrates. Several research papers published on this subject have demonstrated such systems [5-12].

It is a common knowledge that considerable loss of life and properties occur due to burning of textile fabrics. Out of these, a significant portion of casualties consists of women and children due to accidental burning of their cloths. In 1953, the U. S. Government adopted Standards for flammability of apparel fabrics. Subsequently, in 1967, new and stricter Federal Laws were passed that set different standards for sleepwear fabrics, carpets and mattresses [13]. Recently, CPSC open flame standard was issued on March 15, 2006. The rule became effective on July 1, 2007. Mattresses sold in the United States must be in compliance with the Standard. The mattress must burn slowly and the flash over must not occur in 30 minutes, permitting the occupants to safely escape the fire (CA AB 603). The present-day polyester standards take into account

even the environment protection aspects, apart from the concerns about life and property issues.

In the past, Sb has been a workhorse of FR systems. Antimony alone does not act as FR chemical, but when present in some formulations with other substances, synergistically enhances the effectiveness of halogen FRs. Sb being a heavy metal, no longer finds favor, from the environmental point of view. Recently, catalytic systems for synthesis of polyester, which are based on Sb have even been modified to give eco-friendly catalysts that are used in transesterification of PET, in which metals like tin and titanium replace antimony.

The traditional FR chemicals are based on elements such as phosphorus, nitrogen, halogen or water of dehydration. Phosphorus-containing compounds have been proved to be highly effective in conferring flame-retardancy to highly oxygenated polymers. But the best results would be achieved if the FR formulation were relatively water-insoluble long chain polymeric phosphorus compound. Synergism between two or more elements as well as their compounds becomes imperative since the high doses of these substances are undesired due to emission of non-eco-friendly toxic gases during the burning process. It is, therefore, necessary that the least amount of FR chemical present in the substrate must be found that give desired FR properties, while simultaneously protecting the environment.

ADVANSA (formerly DuPontSA) have recently developed Dacron 483, a new flame retardant poly (ethylene terephthalate) fiber [14]. A French company has manufactured non-toxic fireproofing products for upholstered furniture coating [15]. Recently, Hebeish [16] and co-workers have observed P – N synergistic influence in the case of FR cotton fabrics.

The use of phosphorus compounds as fire retardants for polymers dates back to the days of Gay Lussac (1820). The study of organic phosphorus compounds as reactive “carriers” of the fire retardant elements has been pursued for over a century now. The first patent was granted in 1735. Phosphorus-based flame-retardants meet most of the FR requirements of textile industry [17]. Flame-retardants break the burning cycle of textile. Phosphorus-based FR products work mainly in the condensed phase, promoting the formation of a carbon char and reducing flammable by-products. However, the hypothesis that the effectiveness of phosphorus compounds as fire retardants may depend upon the

mode of bonding and the amount of phosphorus in the treated substrate was reported perhaps for the first time by Tesoro [18] in the Technical Conference of Fiber Society held at Philadelphia, Pa, USA on Oct 10, 1969, and at the Synergism During Fire Retardation in Case of Cotton Fibers at a Conference held at University of Utah in 1970 [19] followed by Barker [20] at the 1973 Symposium on Textile Preparation and Finishing held at Zurich, Switzerland on March 23, 1973.

Aims and Goals of the Present Investigation

The present investigation is intended to seek self-extinguishing behavior of polyester fibers through a suitable FR treatment. It is also the intention to check other desired properties such as moisture absorbance as well as dyeability with cationic and other ionic dyestuffs because of commercial importance of these properties.

In the present investigation, an experimental design has been planned that would possibly develop a novel process to make the polymer self-extinguishing and fire retardant. It is previously known that phosphorus in combination with nitrogen (P-N bond) exhibits synergistic behavior during chemical modification of cotton cellulose to impart fire resistant properties. It was also reported that not all P-N systems exhibit synergism [21]. Polyester being devoid of reactive groups, they are being incorporated through graft copolymerization reactions with two different types of groups of vinyl monomers - one that are N-deficient, like acrylic acid (AA) and methacrylic acid (MAA), and the other N-containing ones like acrylonitrile (AN), acrylamide (AM), and methacrylamide (MAm). Chemical initiation technique was planned to effect grafting reactions followed by reaction with FR chemical (phosphorus oxychloride) to incorporate reactive phosphorus in the polymer matrix. The grafted polyester obtained in these experiments is expected to be fully phosphorylated. Each grafted polyester sample that would be prepared in triplicate will be tested pre- and post-phosphorylation reaction for the burning test. The burn characteristics that are desired include self-extinguishing behavior accompanied by the prevention of the after-glow phenomena. Experimental design with N-deficient vinyl monomers is expected to throw some light on whether presence of nitrogen is beneficial or not in imparting FR properties to the grafted polyester. Assuming that the answer is affirmative, then the further experiments are designed to get an answer whether nitrogen shows synergism, irrespective of its source, or whether a particular type of nitrogen is

avored in the FR systems. For this purpose amido nitrogen (from AM and MAM) and nitrile nitrogen (from AN) have been selected. The ultimate experimental design is expected, if feasible, to develop an eco-friendly FR polyester that would contain the least possible amount of FR chemical and also exhibit, if possible, some new desirable properties like hydrophilicity and deability with cationic and other ionic dyes, which are less energy intensive as compared to disperse dyes.

MATERIALS AND METHODS

Materials

Terene polyester fibers (ICI, UK) were purified with methanol in Soxhlet extraction unit for 8 h, dried at room temperature and finally stored in P₂O₅ desiccators. Since fabric construction, particularly weight per unit area, type of weave, and other such factors profoundly influence the amount of chemicals required to meet given flame retardancy specifications, use of fibers is preferred in such situations. In the present investigation, therefore, polyester in the fiber form has been used. There is also a ease of maneuverability of making variety of items out of the FR polyester in the fiber form Vinyl monomers –Acrylic Acid (AA), Methacrylic Acid (MAA), Methacrylamide (MAM), Acrylamide (AM), Acrylonitrile (AN) – and other chemicals like phosphorus oxy-chloride, pyridine (retarder) and non-ionic detergent poly (oxy ethylene) alkyl ether (scavenger) & cetyl trimethyl ammonium bromide (CTMB) (scavenger) and cetyl pyridinium bromide (scavenger) were of Chemically Pure (C. P.) grade. 0.02 Molar concentration of the retarder/scavenger was used in the grafting bath. Benzoyal peroxide was used as a catalyst that was dissolved in benzene to give solutions of 1.2 mg/ml for AA & AM, 0.9 mg/ml for MAA and 0.4 mg/ml for MAM & AN. Different monomer concentration ranges (1-25% v/v AA, AAm, AN; 1-8% v/v MAA; 0.5-4.25% v/v MAM) were used for grafting one-gm dry fiber samples. The anionic dyes used were Sandocryl Blue B3G (C.I. Basic Blue 3), which is a cationic dye and Nylosan Blue E2GL (C.I. Acid Blue 40), an acid dye. These dyes were purified as per their respective standard methods of purification

METHODS

Graft-Copolymerization of Polyester

The graft copolymerization reaction on polyester was carried out at 100°C using different monomer concentrations, catalyst and the retarder/scavenger. Afterwards, the fibrous material was washed with

boiling water 10 times with vigorous stirring in order to remove the homopolymer completely, except in case of the AN graft copolymers. They were treated with hot dimethyl formamide (DMF) for 6 h in order to remove homopolymers, followed by washing in hot boiling water for 4 h and drying at 100°C for 2 h and then cooled in P₂O₅ desiccators. The repeating washing-drying-weighing cycles were carried out till constant weight of the substrate was obtained. The graft add-on was determined gravimetrically as follows:

If,

W1 = weight of the control (PET fibers)

W2 = weight of grafted PET fibers,

Then,

$$\text{Graft Add-on (\%)} = 100 \times (W2 - W1) / W1$$

During the chemical initiation method of grafting of different monomers on to Poly (ethylene terephthalate) fibers, the fibers were treated with the respective monomer solutions containing initiator like benzoyl peroxide. On heating, the benzoyl peroxide decomposes to give a free radical, which abstracts a H atom from another chain. The free radical thus formed on the solid reacts with the monomer molecules to form a chain on the backbone. This chain propagates till its termination in the bath at a later stage. Thus the graft is incorporated in the poly (ethylene terephthalate) chain molecule. In this process, the free radical from benzoyl peroxide can also directly react with the monomer and cause homopolymerisation, which is undesired in the graft-copolymerization reactions. The homopolymer formation was suppressed by the addition of scavengers, like pyridine and cetyl pyridinium bromide, in the reaction mixture.

Phosphorylation of Grafted Polyester Fibers

Phosphorylation of grafted PET fibers was carried out by treatment with stoichiometrically calculated phosphorus oxychloride in dry benzene along with 2% pyridine as a catalyst in reflux condenser for 1 – 6 h at 60 – 110°C. After completion of the reaction, samples were refluxed with benzene for 4 h, dried at room temperature and stored in P₂O₅ desiccators. Quantitative estimation of phosphorus content of the substrates was carried out using Barnhart's [22] method that was suitably modified for the fibrous substrate. Grafted polyester fibers were phosphorylated using phosphorus oxychloride as the FR chemical. Thus, phosphorus was incorporated in the fiber structure through the graft-copolymer that determines the amount of phosphorus content of the particular sample of modified substrate. Essentially,

the grafted samples are fully phosphorylated and there is quantitative interdependence between graft-content and the quantity of phosphorus present in such a sample.

Phosphorylation of Un-grafted Polyester Fibers

Phosphorylation of un-grafted polyester fibers was carried out by the same method as has been described above for the grafted ones but without using any monomer in the treatment bath.

Determination of Phosphorus Content of Phosphorylated Polyester

The method followed was Kjeldahl digestion followed by colorimetric analysis of the phosphomolybdate complex [22].

Calculations of Change of Rate of Burning of FR Polyester and Efficiency of Phosphorus

The change in Rate of Burning (increase/(-)decrease) was calculated for both grafted and grafted-phosphorylated PET fibers with respect to the control in terms of graft content and phosphorus content of the substrates.

Similarly, Efficiency (positive/(--) negative) of phosphorus for each monomer was calculated in terms of quantity of phosphorus required to achieve a given level of fire resistant property such as self-extinguishments of the polyester samples.

Infra Red (I. R.) Spectroscopic Analysis of Grafted Polyester Fibers

Infrared analysis of substrates was carried out using Perkin-Elmer Infrared 457 Spectrophotometer by the standard KBr – pellet technique.

Flammability Test of FR Polyester Fibers

The flammability test of phosphorylated samples was conducted by the standard Vertical Burning Test method [23] the details of which are as follows. The flammability of prepared samples was tested by vertical burning test for fibers. This test has achieved wide acceptance for determining the fire resistance (both flame and glow resistance) of textiles. The test is most suited for determining self-extinguishing nature of fibers and particularly the synthetic ones like polyester. In this modified test, a constant weight of polyester fiber (150 mg) was taken and a 7-Inch vertical strip was prepared. They were conditioned at $20 \pm 2^\circ\text{C}$ under $65 \pm 2\%$ relative humidity (RH) for 8 to 10 hours. Uniformity of the strip was maintained by considerable care. The samples were mounted on a suitable clamp and the lower edge ignited by a standard flame in a wooden chamber under the most

natural atmospheric conditions with adequate ventilation system inside the chamber. The bottom edge of the strip is exposed to a standard flame for exactly 12 sec under controlled conditions. At the end of the 12-sec period, the flame is removed and time of flaming and afterglow determined. Length of the char produced by the combined flaming and afterglow is measured from the lower edge of the sample to the uppermost point of the char area. The rate of burning was then calculated. Each sample was tested in triplicate. The data obtained was satisfactorily reproducible.

Differential Thermal Analysis (DTA) of FR Polyester Fibers

Differential Thermal Analysis (DTA) of samples was carried out on AMINCO Modular Thermograv, USA apparatus. The fiber sample was cut in powder form. A sample of about 100 mg was heated at a rate of $6^\circ\text{C}/\text{min}$ from room temperature (25°C) to 450°C . Temperature differential was kept at $0.5^\circ\text{C}/\text{Inch}$. Calcined aluminum oxide, a thermally inert substance, was used as the reference. The temperature difference (ΔT) between the reference and the sample was continuously recorded as a function of sample temperature plotted against T in the thermogram.

Dyeing of FR Polyester Fibers with Cationic and Acid Dyes

The grafted PET fibers along with the control were dyed with cationic dyes (on AA-, MAA- and AN-grafted PET before and after phosphorylation) as well as acid dyes (on MAM- and AM-grafted PET) by standard methods. The dye content of the dyed samples was determined spectrophotometrically using standard methods. Typical data on dye content of have been given in Table VIII (cationic dye) and Table IX (acid dye).

Moisture Regain of FR Polyester Fibers

Moisture content of the samples was determined by the standard oven drying method.

RESULTS AND DISCUSSION

The free radicals produced on the PET backbone polymer molecule can attach the growing chain through Chain Transfer reaction in the chemical initiation technique as postulated by Paul J. Flory and Harman Mark. The present paper has used the well-established tool of graft copolymerization reaction to introduce P – N bond in the PET molecule as a result of grafting reactions. Nitrogen was incorporated in the substrate in two different forms, viz. nitrile nitrogen (through AN grafting) and amido nitrogen

(through AM and MAm grafting). It was followed by phosphorylation with phosphorus oxychloride.

Extent of Graft Add-on in Polyester Fibers

Although the aim is to restrict the polymer modification to the minimum in achieving FR polyester fibers, the experimental design has allowed higher levels of grafting purely from academic point of view and also to complete picture. From the commercial point of view, it is understood that, any process that consumes least possible amount of chemicals and other resources like energy, time, etc, would be welcome.

Summary of Samples Tested

Table I summarizes the number of polyester samples prepared and analyzed for different properties in this work.

I.R. Analysis of AM-g-P Polyester Fibers

Typical Infra Red spectra of the grafted poly (ethylene terephthalate) fibers and that of the control have been shown in *Figure 1*. A prominent peak in the region of 3500 – 3400 cm⁻¹ for the control that has been affected due to grafting (AM-g), is fully wiped out in the AM-g-P sample due to the phosphorylation of the grafted polymer. This peak is affected because of the N – H bonding first and subsequently due to P – N single stretching. Similar results were obtained in case of other monomers studied in this investigation.

TABLE I. Summary of Polyester Samples That Were Grafted, Phosphorylated and Rendered Cationic & Acid Dyeable, and Moisture Absorbent

Monomer Graft Content (%) Phosphorus Content (%)	Number of Polyester Samples Tested							
	Grafted	Phosphorylated	Cationic Dyed		Acid Dye Dyed		Moisture Absorbent	
	g	g-P	g	g-P	g	g-P	g	g-P
AA (0 to 45.84% Graft, 0.14 to 1.33% P)	10	10	6	6	-	-	6	6
MAA (0 to 96% Graft, 0.14 to 2.31% P)	11	11	6	6	-	-	6	6
MAm (0 to 60% Graft, 0.14 to 1.97% P)	9	9	-	-	6	6	6	6
AN (0 to 38% Graft, 0.14 to 0.81% P)	6	6	6	6	-	-	6	6
AM (0 to 8.8% Graft, 0.14 to 0.326% P)	7	7	-	-	7	7	7	7

g, Grafted; g-P, Grafted and Phosphorylated; P, Phosphorus. Each sample was made and tested in triplicate.

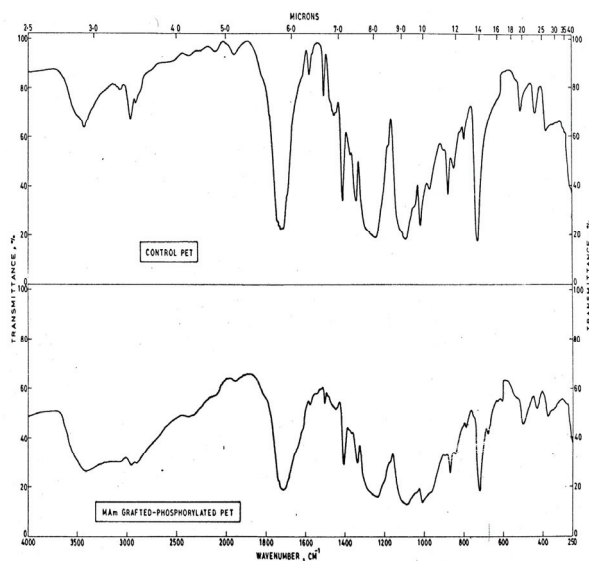


FIGURE 1. Infrared spectra of control and MAM-grafted polyester fibers

Preliminary Investigation on FR Polyester Fibers

Phosphorus-nitrogen assisted fire retardant chemicals and finishing processes for cotton cellulose have been reported extensively in the literature. Importance of halides in these reactions has also been described. P-N synergism in case of fire retardant (FR) cotton is well known. However, very little is known about FR polyester fibers. Similarly, not much is reported whether P-N synergistic possibilities exist in case of this synthetic fiber. Keeping these points in mind, two nitrogen containing monomers – acrylonitrile and acrylamide – were selected for the preliminary investigation of FR reactions on poly (ethylene terephthalate) fibers using phosphorus oxychloride as the FR chemical. Encouraged by the initial results, three more monomers were carefully selected for detailed investigations. The additional monomers selected were acrylic acid (AA), methacrylic acid (MAA) and methacrylamide (MAM). The first two are nitrogen-deficient monomers while the third one contains N in its molecule.

Acrylonitrile (AN)- and Acrylamide (AM)-g-P Polyester Fibers

Table II gives the data regarding AN- and AM-graft contents of polyester and its effect on rate of burning. The results indicate that polyester fiber burns at a higher rate as a result of the graft-copolymerization reaction with AN, and the rate of burning is directly proportional to the graft content of the substrate. Thus, when the AN-graft was increased from 7.1% to 38%, the rate of burning also increased from 0.472 Inch/sec to 0.667 Inch/sec.

TABLE II. Relation Between AN- and AM-Graft Add-On and Rate of Burning of Grafted Polyester

Monomer: AN		Monomer: AM	
Graft Add-On (%)	Rate of Burning (Inch/Sec)	Graft Add-On (%)	Rate of Burning (Inch/Sec)
7.1	0.472	5.2	0.432
12.2	0.510	6.2	0.440
19.0	0.540	7.2	0.450
25.2	0.610	8.8	0.461
30.0	0.630	-	-
38.0	0.667	-	-

This may be due to the possible changes in the decomposition products of AN-grafted polyester fibers that could be in the form of combustible gases, generation of which would be in proportion to the amount of graft-content of the fiber. Yet another factor that might be playing an important role in enhancing the rate of burning is the heat of combustion. As the AN graft increases, the amount of formation of combustible fuel also increases leading to the generation of greater amount of heat that has the cascading effect on the rate and extent of burning. The other important point regarding burning of AN-grafted polyester fiber that was noted was the ease of ignition, the ignition time being just 1-2 sec as compared to 2-4 sec required for the control (polyester).

The results given in Table III show that, phosphorylation of AN-grafted fibers do reduce the rate of burning, but only marginally. The polyester sample having 38% AN-graft and the corresponding phosphorus content of as high as 0.81% burns at the same rate as the sample of 12.2% AN-graft that is devoid of phosphorus. This observation suggests the possibility of lack of proper and effective P-N bond formation in the fibers, since N in the form of nitrile group is unlikely to react with phosphorus oxychloride under the given reaction conditions.

As regards the AM-grafted polyester, the results indicate that the rate of burning remains almost static and seems to be independent of graft-content in the range from 0 to 8.8% graft (Table II). It is known that aliphatic polyamide, in presence of sufficient oxygen, undergoes rapid oxidation leading to the formation of carbon dioxide, carbon monoxide, water and low molecular weight hydrocarbons. The decomposition products seem to balance themselves in such a way that the flammability of the substrate is unaffected in spite of increasing amounts of graft that was incorporated in the fiber structure.

TABLE III. Relation Between Phosphorus-Treated-AN-Grafted Polyester and Rate of Burning

AN Graft Add-on (%)	Phosphorus (%)	Rate of Burning (Inch/sec)
7.1	0.21	0.44
12.2	0.36	0.43
19.0	0.57	0.46
25.2	0.69	0.47
30.0	0.77	0.50
38.0	0.81	0.51

Table IV describes the data of AM-grafted-phosphorylated polyester fibers. It can be seen that there is very significant reduction in the rate of burning as a result of incorporation of phosphorus in the fiber structure. Graft content as low as 5.2% containing just 0.189% phosphorus could impart self-extinguish property to the substrate. The rate of burning at this level and beyond was negligible (which was almost zero with some amount of incineration of the sample). The excellent fire retardancy that was witnessed in the AM-g-P polyester fibers suggest the existence of highly effective P-N bond in the fiber structure, which is formed as a result of chemical reaction between the polyacryamide (PAM) and the FR chemical phosphorus oxychloride.

TABLE IV. Relation Between Phosphorus-Treated-AM-Grafted Polyester and Rate of Burning

AM-Graft Add-On (%)	Phosphorus (%)	Rate of Burning (Inch/Sec)
1.50	0.075	0.30
2.43	0.131	0.16
3.10	0.155	0.10
5.20	0.189	Negligible*
6.20	0.215	Negligible*
7.20	0.256	Negligible*
8.80	0.326	Negligible*

* Resistant to burning; shrinkage and char formation occur.

TABLE V. DTA Analysis (°C) of AN- and AM-Grafted Phosphorylated Polyester Fibers

PET	M.P	Cryst. Peak	Oxd. Peak	Decom Peak	Endotherm	Exotherm
Control	258	100	300	430	258 & 430	300
AN-Grafted (30%g)	255	-	292	337 (Smaller)	120(Smaller) & 317	-
AN-g-P (30%g, 0.77% P)	-	-	-	337 (Larger, Sharper)	120 (Larger), 298 (Larger, Sharper) & 400 (Larger, Sharper)	-
AM-Grafted (5.2%g)	258	100	-	417 (Smaller)	350 (Smaller)	392 (Larger)
AM-g-P (5.2%g, 0.189% P)	258	100	292	417 Larger, (Sharper)	318 (Smaller)	352 (Smaller)

In Table V, Differential Thermal Analysis (DTA) data of the control as well as that of AN- and AM-grafted polyester fibers subjected to pre-phosphorylation and post-phosphorylation treatments have been summarized. The DTA curves give solid phase reactions that occur when the samples are heated, reflecting the changes that occur at the molecular level.

DTA Analysis of the Control (Polyester)

The DTA curve details for the control have been given in Table V. The pyrolysis of polyester fibers begins at room temperature (25°C), which starts rising giving a prominent exothermic peak at 100°C. This peak may be due to the possible changes being effected in the fiber structure leading to crystallization. On further heating, not many prominent changes occur in the fiber structure up to its melting point (M. P.) at about 258°C giving a prominent endothermic peak at that temperature. Beyond this temperature, oxidation reactions set in since the heating is carried out in air. A very prominent exothermic peak in the region of 300°C occurs which is assigned to the formation of oxidation products of polyester fibers. Finally, an endothermic peak at about 430°C is obtained which may be due to depolymerization and decomposition products of PET that act as “heat sink” for the flame.

DTA Analysis of AN-g-P and AM-g-P Polyester Fibers

An endothermic peak in the region of 258-260°C in case of polyester fibers is assigned to melting; this peak is shifted to 255°C in case of AN-grafted polyester, showing that melting of this sample occurs at lower temperature as compared to the control. This may be due to a change in chemical nature as well as more open physical structure of fibers that were rendered as a result of AN- grafting. An exothermic peak at 100°C is the crystallization peak.

This peak is totally absent in the AN-grafted sample, indicating that the sample has poor heat resistance. A new characteristic peak, an exothermic one that occurs for AN-grafted fiber, is totally absent in case of the control. This may be due to the formation of combustible gases in AN-grafted fibers leading to faster burning of substrates.

In case of AN-g-P polyester sample also, the crystallization peak is missing showing that the phosphorylation of the AN-grafted polyester fibers has not helped in raising the heat resistance capacity of the substrate. DTA results further reveal that, in spite of phosphorylation reaction, there is no change in the decomposition products of polyacrylonitrile (PAN) that can be seen from the exothermic peak at 337°C that is present in both the cases.

In case of AM-g-P sample, both the melting point peak at 258°C and the crystallization peak at 100°C persist. The presence of characteristic exothermic peak at 292°C and endothermic peak at 417°C (which is absent in AM-g sample as well as in the control) indicates the possible changes that occur in the decomposition products of PAM. These changes lead to the possible condensed phase reactions. The endothermic peak at 350°C was completely wiped out and the exothermic one at 393°C was considerably reduced in its size as a result of POCl₃ treatment of the AM-grafted polyester fibers. It can be said that, the changes might be primarily occurring in the condensed phase (i. e. promoting char formation) and hence reducing the concentration of combustible carbon-containing volatiles in the gaseous phase. This possibly disrupts propagation of the flame and virtually stops the combustion process.

The presence of chlorine in phosphorus oxychloride might also be playing an important role in the dehydration reaction, which ultimately causes the char formation.

All these factors contribute in rendering the AM-g-POCl₃-treated polyester fibers self-extinguishing in nature. The effectiveness of fire retardant system containing acrylamide-phosphorus over the acrylonitrile-phosphorus combination suggests the possibility of P-N synergism in case of the former, making significant contribution to set up an eco-friendly and efficient FR polyester. The present work reveals that poly (ethylene terephthalate) fibers could be effectively made fire resistant through grafting with acrylamide followed by treatment with phosphorus oxychloride.

Another important point of AM-g-P system to be noted is that, due to synergistic effect, much lesser amount of phosphorus is required to impart the given level of fire retardancy to the polyester fibers as compared to any other known method of FR treatment. This is important ecologically as well as commercially.

AA- & MAA-g-P Polyester Fibers

The results of *Figures 2–5* show that the rate of burning decreased from 0.69 Inch/sec for the ungrafted PET containing 0.14% P to 0.25 and 0.19 Inch/sec for the 45.2% AA and 96% MAA-g PET containing 1.53% and 2.31% P, respectively. It is possible that the residual homopolymer could also account for these improvements in flame resistance like in case of MAM-g (i.e. before FR chemicals were introduced in the fiber). Some others, on the other hand, enhanced burning (e.g. AA-g & AN-g), while AM- & MAA-g showed no influence on FR properties of polyester. However, even such high levels of AA- and MAA-grafts could not reach self-extinguishing level perhaps due to the formation of C – O – P bond, which is devoid of N.

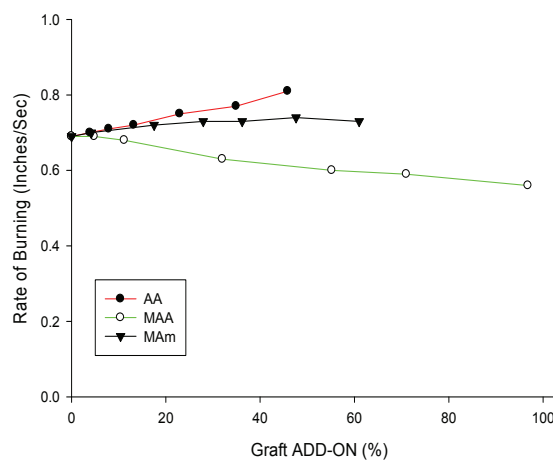


FIGURE 2. Relation between AA-, MAA- and MAM-graft add-on and rate of burning of grafted polyester fibers

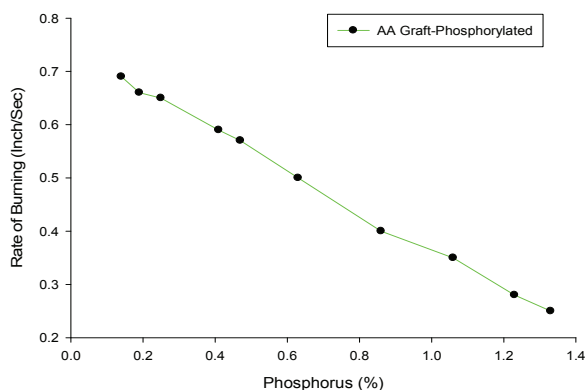


FIGURE 3. Relation between phosphorus content and rate of burning of AA-grafted-phosphorylated polyester fibers (graft content: 0 to 45.84%)

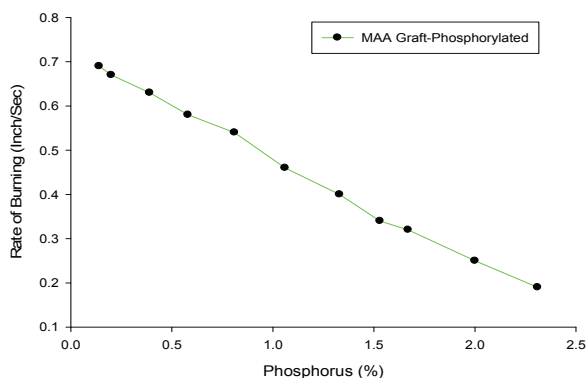


FIGURE 4. Relation between phosphorus content and rate of burning of MAA-grafted-phosphorylated polyester fibers (graft content: 0 to 96%)

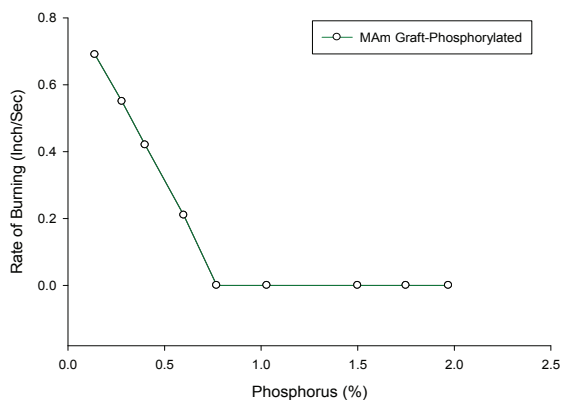
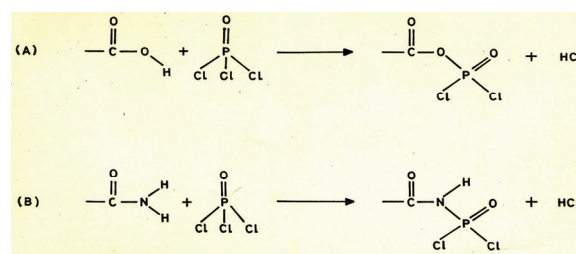


FIGURE 5. Relation between phosphorus content and rate of burning of MAM-grafted-phosphorylated polyester fibers (graft content: 0 to 60%)

MAM-g-P Polyester Fibers

In case of MAM (like AM), the rate of burning was rapidly brought down to 0.21 Inch/sec and to the self-extinguishing level for 18.6% and 27.4% MAM grafts containing as low as 0.44% and 0.77% P, respectively. Furthermore, at 60% MAM graft corresponding to 1.97% P, the FR polyester does not burn at all even when it is kept in contact with the flame for a long period of time (It, however, incinerates). These results indicate the possibility of P – N synergism between N of MAM (as well as AM, as has been discussed before) and P of phosphorus oxychloride. Mechanisms of these reactions are given in the Mechanism Chart (Figure 6). It is possible that the reactions might not be proceeding exactly as shown in this figure. The role played by halides (in this present work, it is Cl) cannot be ignored even if its influence might be marginal. As a result of the continuous burning reactions, branching takes place forming different intermediate products containing the quenchers as also the promoters of the flame. The halogenated and fully phosphorylated polyester shows that various oxides that are formed quench flames of the fibers by the volatilizing phenomenon near the flame point to give halides, which oxidize to solid particles, thereby destroying the branching intermediates of the substrate. While recognizing the role played by the halide in enhancing the FR characteristic of phosphorus to some extent, it is the P-N synergism, which is a major factor that is responsible in achieving such a high degree of fire retardancy reported in the present investigation.

MECHANISM CHART



REACTION MECHANISM OF PHOSPHORUS OXYCHLORIDE WITH THE FUNCTIONAL GROUPS: (A) CARBOXYL FOR AA- AND MAA- (B) AMIDO FOR MAM- GRAFTED PET FIBERS

FIGURE 6. Reaction mechanism of phosphorus oxychloride with the functional groups: (a) carboxyl for AA- and MAA- and (b) amido for MAM-grafted polyester fibers

DTA of AA-, MAA- and MAM-g-P Polyester Fibers

The DTA curves give solid-phase reactions, which occur when the sample is heated, revealing changes

at the molecular level, so that the structure of the sample is reflected in the thermograms. These results have been given in typical thermogram curves for MAm-g-P samples in *Figure 7* and the evidence for the P-N synergism in *Figure 8*. DTA data for all the above three monomer samples, however, are summarized in *Table VI*.

DTA of AA-g and AA-g-P PET

The DTA data for AA-g PET (45.2% graft) before phosphorylation and post phosphorylation (AA-g-P, 1.53% P content) reveal that the grafting seems to increase the M. P. of the substrate to a little higher level at 260°C from 258°C for the control (*Table VI*). There is additional endothermic peak at 315°C, which may be due to melting of AA graft material in the molten polyester. This is followed by a very broad exotherm in the region of 350-425°C, which may be due to the oxidation products of polyester and AA graft. The final heat sink reaction is shifted to lower temperature at 390-395°C from the 430°C peak for the control polyester. These changes seem to be due to the presence of phosphorus that shows its influence on the oxidation and degradation products of polyester and AA graft.

DTA of MAA-g and MAA-g-P PET

Table VI also gives DTA data for MAA-g PET (96% graft) and the same after phosphorylation (2.31% P content). It seems that due to introduction of P in the MAA-g PET, two new exothermic peaks at 100°C and 155°C as well as one more additional endotherm at 120°C occur. They seem to represent the changes that are taking place in the crystallization of polymer chains and reorganization of the crystals so formed. A major change occurred in the exotherm at 380°C, which is reduced in size and shape and shifted to lower region at 350-365°C accompanied by the reappearance of the heat sink endotherm in the region of 390-395°C. It seems, therefore, that the decomposition process is shifted to the higher temperature zone of 390-395°C from 380°C due to the presence of phosphorus in the sample.

DTA of MAm-g and MAm-g-P PET

Figures 7, 8 and *Table VI* give DTA curves and data for the MAm-g and MAm-g-P PET samples at different levels of graft and P content in the polyester fibers. The 18.6%g-0.44%-P containing PET sample show notable changes as compared to the parent grafted fiber as well as the control polyester. The first important change that occurs is in the M. P. of the substrate.

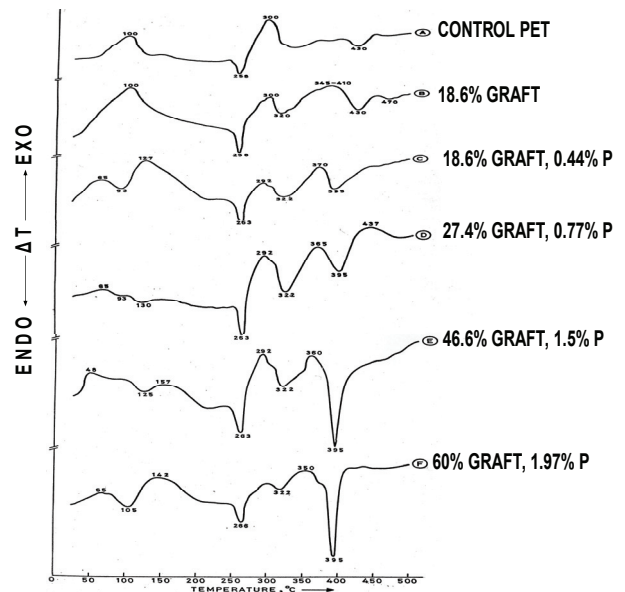


FIGURE 7. DTA curves of MAm-grafted-phosphorylated polyester fibers

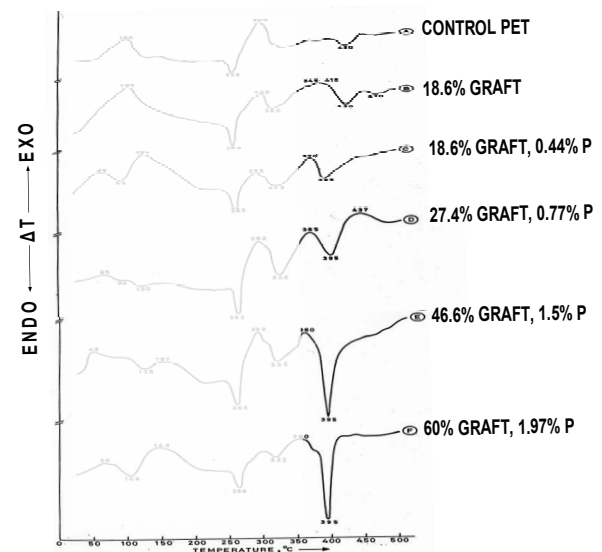


FIGURE 8. DTA evidence for P-N synergism in MAm-grafted-phosphorylated polyester fibers

It has increased from 258°C to 263°C, showing better heat stability of the phosphorylated grafted polyester fiber. Further, the crystallization peak at 100°C is split into two – at 65°C & 127°C - with an additional endotherm at 93°C, which seems to be due to the re-organization of crystals leading to the higher M. P. of the substrate. The crystallization peaks at 65°C and

127°C seem to be due to step-wise process of crystallization of the heterogeneous polymeric material containing polyester, polymethacrylamide (PMAm) graft and phosphorus. It seems that the chemical bonding between P & N (P – N) of PMAm graft influences the crystallization process giving the two exotherms at 65°C and 127°C as against a single one 100°C for the control.

At the higher levels of MAm grafting (60%) corresponding to higher phosphorus content (1.97%), even much better results were obtained as compared to the above one. Here also the crystallization peak is split into two peaks that occur at 65°C and 142°C with an additional endotherm at 105°C. The M. P. of the substrate is further enhanced to 266°C from 258°C for the control polyester and the heat sink endotherm at 395°C became bigger and sharper as compared to the one obtained in the previously discussed sample. All these changes are attributed to the presence of P – N bond in the MAm-g-P FR polyester sample.

Correlation Between DTA and Flammability Characteristics of FR Polyester Fibers

From the DTA studies of the phosphorylated grafted polyester fiber, it is clear that in case of the AA- and MAA-g PET fibers, there is a broad exothermic peak in the region of 380°C, possibly due to rapid decomposition of fibers resulting in the formation of volatile combustible hydrocarbons that had evolved along with carbon dioxide (Figs. 7 & 8 and Table VI). These combustible products are responsible for the ease of burning process. After the introduction of P, the said peak seems to have been reduced in size, indicating that the presence of P has suppressed the evolution of combustible gases. Moreover, the additional endothermic peak in 390-395°C-region, works as heat sink for the flame that seems to be the main reason for slower burning.

In case of MAm-g PET, the exothermic peak at 380°C seems to have been reduced to a considerably smaller size post-phosphorylation, indicating restriction imposed by the system against the evolution of combustible gases. Also, the melting point (M. P.) of the FR sample increased from 258°C to 266°C, giving better heat stability to the phosphorylated grafted PET fibers. Similarly, the presence of a characteristic endotherm at 395°C also speaks for the heat sink phenomenon upsetting the heating and burning processes. This peak becomes bigger but sharper with the increase in the amount of g and P in the substrates.

The thermal evolution of phosphorus acid alters pyrolytic decomposition of the substrate in such a way, that the decomposition products undergo qualitative changes resulting in the formation of carbonaceous char [24]. It brings down the heat transfer from the flame to the condensed phase by interfering in heating and decomposing processes. All these factors contribute in rendering the MAm-g-P PET fibers fire retardant. These results are similar to those obtained for the AM-g-P polyester fibers discussed in the earlier section.

Change of Rate of Burning of g-P Polyester and Efficiency of Phosphorus in the FR System

An increase/(--)/decrease in the rate of burning with respect to the amount of graft add-on of the polyester fibers pre-phosphorylation and post-phosphorylation was calculated and the data presented in Table VII. It is interesting to note that AM-grafted-phosphorylated (AM-g-P) was the best among the five monomers studied giving 8.10% decrease in the rate of burning followed by MAm-g-P (2.45% decrease), while AN was the worst, which actually enhanced rate of burning even post-phosphorylation.

TABLE VI. DTA Analysis (°C) of AA-, MAA- and MAm-GRAFTED-Phosphorylated PET Fibers

PET	M.P.	Cryst. Peak	Oxd. Peak	Decom Peak	Endotherm	Exotherm
Control	258	100	300	430	258 & 430	300
MAm-Grafted (18.6%g)	258	100	300	430	320 & 430	345 – 410 (385)
MAm-g- P (18.6%g, 0.44% P)	263	65 & 127	-	-	93, 322 & 395	292 & 370
MAm-g-P (60% g, 1.97% P)	266	65 & 142	292 (Smaller)	-	395 (Larger, Sharper)	350
AA-Grafted (45.2% g)	258	100	300	400	315 & 445	350-425 & 380
AA-g-P (45.2%g., 1.53%P)	258	100	300	360 & 375	315, 365 & 390-395	418
MAA-Grafted (96% g)	256	100	300	-	232, 315 & 470 (Small)	380 (Broad)
MAA-g-P (96%g, 2.31% P)	258	100 & 155	300	-	120, 232, 315 & 390 -395 (Sharp).	250, 350-365 (Sharp) & 410

Efficiency of phosphorus was calculated in terms of the phosphorus content vis-à-vis its performance in imparting fire retardant property to polyester. These results are given in *Figure 9*, which is in the form of a Bar Diagram. The efficiency of as high as 263% was achieved in case of AM-g-P samples followed by 90% for MAm-g-P polyester, AN-g-P, on the contrary gave a figure of -12% (negative Efficiency).

Synergistic Influence of Amido Nitrogen in P-N Bond in FR Polyester Fibers

To determine how nitrogen contributes to the flame resistance of phosphorus-containing material, it is necessary to know if the source of nitrogen makes any difference in this regard. Perhaps the simplest way of getting at this question is to compare the flame resistance imparted by the nitrogen, say, in two different forms, viz. N attached to polyester through grafting of acrylamide and acrylonitrile as well as their derivatives. In the case of acrylamide, nitrogen is in the amido form, while it is nitrile nitrogen in acrylonitrile. From the results of the present investigation, it may be concluded that the amide nitrogen increases fire retardancy, whereas the nitrile nitrogen on the contrary helps burning. The effectiveness of high order of the FR system containing acrylamide-phosphorus and methacrylamide-phosphorus system over the acrylonitrile-phosphorus combination as well as the control, suggests the possibility of P – N synergism that contributes to the high efficiency of the FR. The results of the preliminary investigation described initially have been confirmed. The present work reveals that polyester could be made fire-retardant very effectively through grafting with acrylamide (AM) and methacrylamide (MAm) followed by treatment with phosphorus oxychloride. It may also be noted that due to synergistic effect, much lesser amount of phosphorus is sufficient to impart the desired level of fire-retardancy to the PET fibers as compared to AN-grafted-phosphorylated polyester.

Secondary Properties of FR Polyester: Moisture Absorption and Cationic Dyeability

With a view to study the changes in absorption characteristics in polyester fibers due to g –P reactions, moisture regain (m.r.) and dyeability studies were conducted (*Figure 10* and *Tables VIII & IX*)

TABLE VII. Change of Rate of Burning of AA-, MAA-, MAm-, AN- and AM-Grafted Polyester Before and After Phosphorylation in Terms of Graft- and Phosphorus-Content

Monomer	Content	Increase/(-Decrease) in Rate of Burning with-respect-to Graft Content (%)	Acceleration/(-Deceleration) in Rate of Burning with-respect-to Phosphorus Content (%)
AA	g	0.26	15.71
	g-P	-0.96	-61.53
MAA	g	-0.14	-18.84
	g-P	-0.52	-71.64
MAm	g	0.05	4.28
	g-P	-2.45	-100
AN	g	0.63	41.31
	g-P	0.22	15.90
AM	g	0.78	6.71
	g-P	-8.10	-100

g, grafted; g-P, grafted-phosphorylated polyester

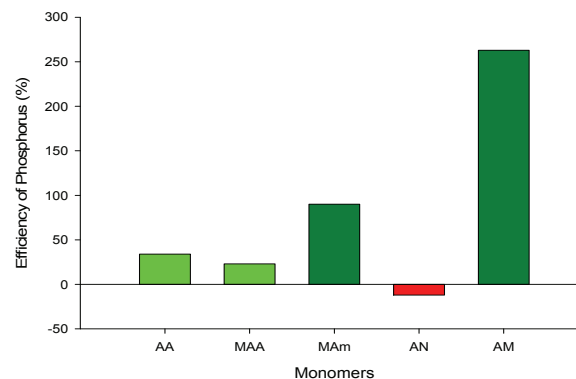


FIGURE 9. Efficiency of phosphorus during FR of AA-, MAA-, MAm-, AN- and AM-Grafted- phosphorylated polyester fibers

Moisture Absorption of Grafted-Phosphorylated Polyester Fibers

Figure 10 illustrates typical results of moisture absorption by AA-, MAA-, MAm, AN- and AM-g-P polyester samples. Results indicate that the hydrophobic polyester fibers (with just 0.4% m.r.) were made hydrophilic (with e. g. 8.0% m.r. for MAA-g-P PET) as a result of the introduction of different types and amounts of grafts in the substrate. The phosphorylation treatment on the grafted polymers had negligible adverse effect on the moisture absorption characteristics of the grafted substrates. It seems that the anticipated decrease in m.r. in the phosphorylated PET fibers is perhaps compensated by the additional openings created in the grafted fiber structure during the phosphorylation treatment. The tiny molecular size of moisture (H₂O) could have possibly helped easy penetration in the

grafted fiber structure. It may also be noted that the polyester substrate was rendered anti-static in nature, which is another desired property for these substrates.

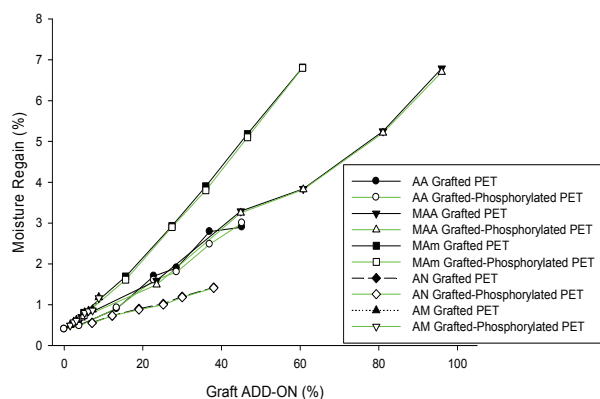


FIGURE 10. Relation between AA-, MAA-, MAM-, AN- and AM-graft add-on and moisture regain of grafted-phosphorylated polyester fibers

Dyeability of Grafted-phosphorylated Polyester Fibers with Cationic and Acid Dyes

Dyeability studies on grafted-phosphorylated polyester fibers were carried out with a cationic dye on AA-, MAA- & AN-g-P and with an acid dye on MAM- & AM-g-P polyester fibers.

It is possible that the residual homopolymer, if any, could also be absorbing the ionized dyes during dyeing process. Nevertheless, in the present investigation, the shade obtained increases in proportion to the graft add-on. Therefore, it is unlikely that the homopolymer absorption could be the

main reason for getting such deep shades, especially when retarders and scavengers are added to the grafting baths to suppress and/or eliminate the possible formation of homopolymer itself. Shalaby et al. [25] grafted acrylonitrile on nylon 6, without formation of homopolymer using a surface-active substance as a scavenger. Bond and Lee [26] used transition metal salts to reduce the extent of homopolymer formation in graft copolymerization reactions of several vinyl monomers on synthetic fibers.

The dyeability studies on the grafted-phosphorylated polyester fibers indicate that deep shades could be dyed on the substrates using the ionic dyestuffs (both cationic and acid dyes). Representative results for cationic dyeing on AA- & MAA-g-P and dyeing with an acid dye on MAM-g-P have been given in *Tables VIII & IX*, respectively. However, there was some decrease in the dye uptake as a result of phosphorylation as compared to the unphosphorylated grafted PET fibers (*Tables VIII & IX*).

Thus, the dye cationic content (C. I. Basic Blue 3) of 6.1-gm/kg fibers for AA-g PET (37% graft) decreased to 4.78-gm/kg fiber after phosphorylation. In case of MAA-g fibers containing 96% graft, it decreased from 12-gm/kg fibers to 10-gm/kg fiber post-phosphorylation (*Table VIII*).

The acid dye content (C. I. Acid Blue 40) decreased from 8.1-gm/kg fibers to 6.9-gm/kg fibers in case of 60% MAM-g containing polyester as a result of phosphorylation. This trend, perhaps, is anticipated as some of the functional groups of the graft copolymer might have been chemically blocked as a result of

TABLE VIII. Effect of Change In AA- and MAA-Graft Add-On on Cationic Dye Content of Grafted-Phosphorylated Polyester Fibers (Dye: Sandocryl Blue B3g - C.I. Basic Blue 3)

Monomer	GRAFT ADD-ON (%)	CATIONIC DYE CONTENT (g /Kg Fiber)	
		Before Phosphorylation	After Phosphorylation
AA	3.82	0.75	0.50
	13.34	1.50	1.20
	22.8	2.55	2.10
	28.6	4.95	2.85
	37.0	6.10	4.78
	46.2	7.90	8.10
MAA	4.4	0.50	0.35
	23.5	2.00	1.65
	44.9	4.75	3.75
	60.8	6.50	5.50
	85.0	10.00	8.00
	96.0	12.00	10.00

TABLE IX. Effect of Change in MAm-Graft Add-On on Acid Dye Content of Grafted- Phosphorylated Polyester Fibers (Dye: Nylosan Blue E2gl – C. I. Acid Blue 40)

	GRAFT Add-on (%)	ACID DYE CONTENT (g/Kg Fibers)	
		Before Phosphorylation	After Phosphorylation
MAm	5.0	1.5	1.3
	18.6	2.2	2.1
	27.4	3.3	3.0
	36.0	4.1	3.6
	46.6	5.2	4.3
	60.0	8.1	6.9

phosphorylation reaction resulting in some what lower dye content.

To summarize, results on the above secondary properties of the FR polyester highlight the importance of the eco-friendly process of making polyester fibers with additional desirable properties. The hydrophobic polyester is made hydrophilic, it is rendered anti-static and the method described here has opened the door to cationic dyes. The self-extinguishing behavior is achieved by incorporating as little as 7-8% graft corresponding to just 0.189% phosphorus in the polyester - a truly eco-friendly fire resistant poly (ethylene terephthalate) fiber with desirable secondary properties that open up commercial prospects to a great extent, apart from presenting a more eco-friendly footprint to the environment.

SUMMARY AND CONCLUSIONS

Phosphorus is known for imparting self extinguishing ability to polymeric materials when subjected to burning process. It has been acknowledged that phosphorus in combination with nitrogen gives synergistic results in case of cotton textiles. Low additions of FR chemicals on to the substrate are needed from the ecological point of view. This is best achieved by reactive phosphorus as one of the FR chemicals that bring about chemical modification of the fibers that has to be kept to the minimum in order to retain original physical characteristics of the modified substrate, and if possible, to impart additional desired properties to such a material. This is important not only from the environmental point of view but also it is desired from the commercial consideration. Such a system would be the ideal one if it achieves all these goals in one go. The present investigation of eco-friendly FR process on polyester fibers could be considered one such system. Polyester fibers were graft co-polymerized with five vinyl monomers – acrylic acid (AA), methacrylic acid (MAA), methacrylamide (MAm), acrylonitrile (AN) and acrylamide (AM) to introduce suitable reactive groups in the fiber structure, which on reaction with

phosphorus oxychloride undergo phosphorylation reaction rendering the modified polyester as self-extinguishing and fire-resistant. The carboxylic group (of AA and MAA), which is devoid of N, could impart only marginal FR property in spite of high phosphorus content. Out of the remaining three reactive groups viz, CONH, CN and NH₂ (of MAM, AN and AM), only CONH and NH₂ in combination with phosphorus imparted very high degree of self-extinguishing FR property to the modified polyester and that too at a relatively very low level of phosphorus content. On one hand, AN in combination with phosphorus not only did not impart any FR characteristic to polyester, but, on the other hand, enhanced the rate of burning to some extent Phosphorus is chemically bonded with nitrogen (P-N) in all the three systems. The contrasting behavior of P-N bond in case of MAM and AM on one hand and that of the AN on the other could be explained on the basis of N that is present in a particular type of group– amido/amino in the first instant and nitrile in the second. Like in case of cotton, P-N synergism is witnessed in case of polyester fibers as well. It is also noted that not all types of P-N bonds will give synergic effect for polyester, but that nitrogen that comes from amido or amino groups exhibit synergism of very high order.

The efficiency of phosphorus in imparting FR properties to polyester increases rapidly at the level of 263% for AM & 90% for MAM, as compared to 34% for AA (nitrogen-deficient monomer). It was, on the contrary, in the negative zone (-12%) for the AN system (N-containing monomer).

The modified polyester was rendered anti-static and hydrophilic like cotton; moisture regain increased to almost 7-8% as compared to 0.4% for the control (polyester). It was also dyed with cationic dyes in deep shades. These are the additional desired properties imparted to the polyester fibers, which has both eco-friendly foot-print as well as potentially commercial over tones. It may be speculated that if the grafting conditions are so chosen that there is no

wastage of monomer due to homopolymer formation, as is the case in the present work, then the cost of monomer used would be reasonably low. The conclusion is that the added cost of production per kg of fibers or per meter of fabric could be quite low when compared to the improvements effected. This may be further offset by the saving in dyestuff consumption as well as by the utilizing comparatively inexpensive dyes other than disperse dyes.

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