Flame-Retardant Viscose–Polyester Fabrics

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Synopsis

For many purposes the natural-synthetic fiber-blend fabrics are more suitable than pure natural or synthetic products. It is often possible to obtain a maximum in clothing and textile technical properties by compensating the defects of one fiber by using an other totally different fiber. Many problems, however, have arisen in the production of flame-retardant fabrics because the use of synthetic fibers often makes the fire retardancy less effective. In our 2-year research project different fire-retardant (FR) viscose–polyester fabrics were prapared at first in the laboratory scale. The natural type raw materials were Modal Prima viscose and normal FR–viscose cotton type staple fibers. The synthetic raw materials were FR–polyesters of the same type with two different flame retardants. Test fabrics were knitted in the laboratory by using seven blended yarns in the ratios 100/0, 80/20, 65/35, and 50/50 and vice versa. Cotton type PVC–fiber was also used in some experiments. All these test fabrics were also finished chemically by using normal crease-resistant (DMU, DMEU, DMDHEU, and TMM) and flame-retardant (N,-methylolphosphonopropionamide and THPC) finishing chemicals. The textile and fire-retardant properties of the original and finished fabrics were estimated by using add-on, tensile strength, LOI-value, and vertical flame test determinations. The mechanism of flame retardancy was also studied with DSC technique, P- and N-analysis and char investigations. The test results of viscose/polyester studies were compared with the results of cotton/polyester studies. After laboratory studies the best methods for FR–viscose/polyester fabric production were chosen, and the fabrics were manufactured. The fabrics were home-washed 20–50 times, and the textile and FR-properties were determined after each 10 washings. These results were again compared with results of cotton/polyester fabrics.

INTRODUCTION

The Properties of Starting Materials

The versatility of cellulose–polyester blended fabrics increases the use of these fabrics also in areas where certain flame retardancy is needed. These include some types of working clothings, furnishing, and bedding textiles and outwear camping textiles. The blend ratios most used today are 50/50 and 65/35 polyester–cotton or polyester–viscose blends if the total usage of these types of fabrics is taken into account. Although the wash and wear properties and the dimensional stability of the fabrics is improved by adding polyester fiber into cellulose fibers, they still need light crease resist or other chemical finish.

Cellulose and poly(ethylene terephtalate) polymers and fibers show a totally different thermal behavior. The high content of hydrogen and oxygen in the form of hydroxyl and ether bonds in cellulose anhydroglucose unit gives rise to hydrophilicity and importance of hydrogen bonds for the fiber properties. The large number of free oxygen electron pairs make the cel-

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lulose molecule also sensitive to radical forming and attack of electrophilic electrolytes and chemical groups. The depolymerization of cellulose in the presence of oxygen begins at a very low temperature (120–250°C), where the main reactions are dehydration, oxidization, hydrolysis of ether bonds, and decarboxylation. The depolymerization mechanism of cellulose can be considered to proceed through two possible routes.[1] The first one is based on boat-chair equilibrium states of cellulose molecule and comprises the ring opening and formation of five-membered oxygen containing rings and levoglucosan every one of which is an easily burning (flash point 300–400°C) compound. The formation of tar and levoglucosane is more favorable in the case of viscose fiber because the more amorphous structure prefers the ring openings. The ionic mechanism begins with proton attack at the other oxygen and proceeds with carbonium ion formation producing small-molecular oxygen containing compounds as carbon oxides, glycolaldehyde, furan, glyoxal, and acrolein.

The oxygen index (LOI) and the ignition time of cellulose fabrics is very low, and the latter depends on mass weight and other physical factors. The self-ignition temperature can be as low as 266°C when measured with cotton fabric and a little bit lower with viscose fabrics. The temperature of the flame is very high (about 970°C), but the heat of combustion quite low compared with other fibers. The most popular polyester, poly(ethylene terephthalate) (PET), has its softening point at 230–250°C and its melting point at 256–260°C. Both depend on the polymerization degree and on the quality and amount of polymer additives and copolymers.[2] The glass transition temperature of PET is about 80°C and also depends on polymer nature and additives. PET begins to turn to brownish when heated above its melting point (280–325°C). The initiation step of pyrolysis in the presence of oxygen includes the hydroperoxy transition state and the activated macromolecule. After the primary decomposition stage the amount of carboxyl and carbonyl groups increases followed by the formation of carbon dioxide and hydrogen radicals. The initial pyrolysis produces oligomers, *p*-acetylbenzoic acid, vinyl benzoate, vinyl benzene, naphthalene, and acetophenone. The route and speed of pyrolysis are strongly dependent on temperature. When the temperature rises the amount of gaseous products increases. The maximum amount of tarry products is formed when the temperature is 500–600°C. The main products are terephthalic acid, benzoic acid, acetaldehyde, and carbon oxides. Aromatic compounds among the pyrolysis products cause the black smoke typical of burning polyester. The self-ignition temperature of PET is 508°C, the oxygen index (LOI) 22.0%, and the ignition time at 650°C much longer than that of cotton, 9.5 s. The dropping effect reduces the ignition time.

The thermal behavior of cellulose–polyester blends is the sum of components when considered below the decomposition stage of cellulose. There is, however, a tendency to little more exothermic reactions which indicates some interaction between the component polymers. The weight losses and rates of weight losses of pyrolyzing blended (50/50) fibers are slightly higher compared with the sum of components. This is connected with the larger amounts of flammable pyrolysis products and a high heat of combustion of PET which accelerates the pyrolysis. The cellulose part of blend burns rapidly and forms a char netting which keeps the polyester part together until the higher pyrolysis temperature is reached and the polyester part burns away. Other observations support the theory that cellulose fibers are surrounded by polyester, which burns first, forming a source of flame for the cellulose part. The ignition time of CELL/PETP fabrics is always shorter than the time of both components alone. The ignition time is always shorter than the average time of the component fibers, and it also decreases with rising ignition temperature.

Flame-Retardation Possibilities of Starting Materials

The very wide scale of cellulose flame retardants is well known. However, there are only a few methods fullfilling the most important easy care, dimensioal stability, durability, dye shade, and toxicological requirements. The negative affect of durable cellulose flame retardants on tensile strength and dimensional stability of fabrics demands the use of polyester blends. Usually there is a possibility of adding 15–20 % normal polyester into cellulose without drastical reduction of the flame-retardant properties. These "low-blend" fabrics are used to compemsate the defects caused by durable cellulose flame retardants.

The fire-retardation mechanism of the mostly used durable cotton fire retardants is based on phosphorylation, dehydration, and depolymerization reactions of electrophilic P–N compounds.[3] The amount of flammable gases is reduced, and the reactions produce small-molecular nonflammable gases and more char. These reactions also require more energy which affects the energy balance of burning material. There are also some possibilities for flame proofing of cellulose materials by using binder–pigment systems based on polymer latexes with halogen-containing nonsoluble flame retardants (PVC or chlorocarbons with Sb_2O_3 and decabromodiphenyloxide, DBDPO): the nature and properties of these methods are however, more suitable for technical purposes. The retardant systems mostly act in the gaseous phase.

Viscose fibers can be flame-retarded as well by using finishing chemicals such as adding the retardant into the spinning dope. Phosphorus-, nitrogen-, and sulfur-containing pigments as dope additives are widely used. Also some chemicals based on aliphatic or aromatic halogenated phosphates are commercially available.

PET fibers can also be flame-retarded by finishing and by using polymer additives or flame-retardant monomers in the polycondensation process. Phosphorus-containing chemicals usually increase the amount of pyrolyzed water and carbon oxides. Certain flame retardants can produce polyphosphoric acid, which reacts with PE terminal hydroxyl groups to form ether bonds and vinyl groups via dehydration of halogen-containing retardants, or they can additionally act via sublimation. With halogenated phosphates there exists the possibility that both mechanisms take place. Possible common flame retardants for viscose, cotton, and polyester fibers and most popular *N*-methylol durable press finishing compounds for cellulose fabrics are presented in Table I.

TABLE I
Possible Common Flame Retardants for Viscose, Cotton, and Polyester Fibers and Durable Press Finishing Compounds for Cellulose Fabrics

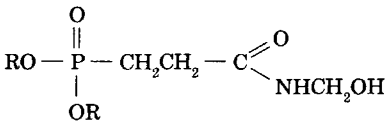
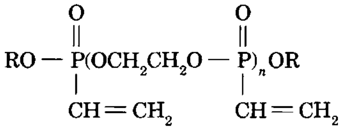
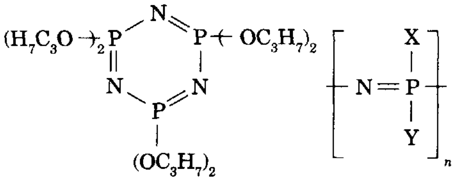
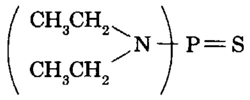
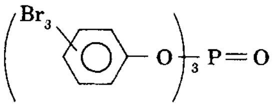
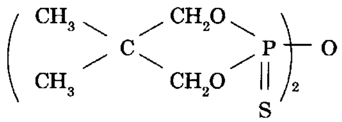
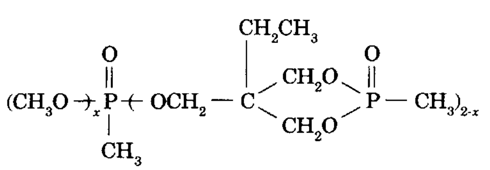
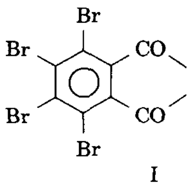
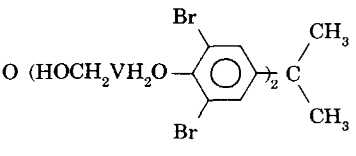
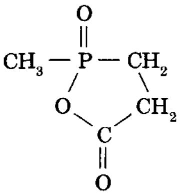
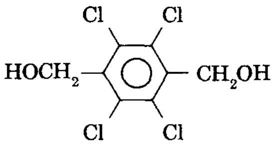
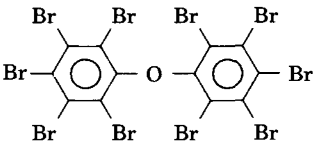
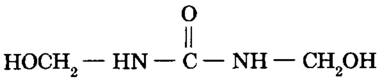
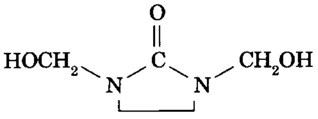
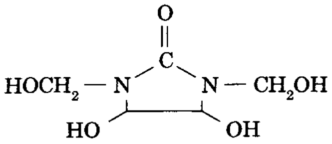
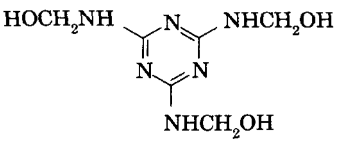
Compound	Formula
Cotton	
Urea Phosphate (Firextra)	$H_3PO_4\cdot(NH_2)_2CO$
Tetrakis (hydroxymethyl) Phosphonium chloride (Proban)	$(HOCH_2)_4P^{\oplus}Cl^{\ominus}$
N-Methylol-3-(dimethoxy)-phosphonopropionamide (Pyrovatex CP, Protenyl P/N S)	
Alkylvinylphosphonate oligomer (Fyrol 76)	
Viscose	
Hexapropoxyphosphazene	 X, Y = OR $n = 1, \ldots, 10$
Tris-(*N,N*)-Diethylfosfoniumtriamide	
Tris-(2,3)-dibromopropyl phosphate	$(CH_2BrCHBrCH_2O)_3P=O$
Tribromophenyl Phosphates	
2,2′-Oxybis(5,5-dimethyl-1,3,2-dioxaphosphor-2,2-disulfide) (Sandoflam 5060)	
Polyethyleneterephtalate	
Cyclic Phosphonate oligomer (antiblaze)	
Tetrabromo phtalic anhydride (I)	
Tetrabromo bisphenol-A (II)	
2-Methyl-2,5-dioxo-1,2-oxaphospholane (glycol adduct with trevira CS) (IV)	 I  II

TABLE I

Possible Common Flame Retardants for Viscose, Cotton, and Polyester Fibers and Durable Press Finishing Compounds for Cellulose Fabrics (*Continued*)

1,4-Dimethyloltetrachlorobenzene (III)	 IV  III
Decabromo diphenyl oxide (Caliban, DBDPO)	
Durable press finishing compounds	
N,N'-dimethylol urea (UF)	 $HOCH_2-HN-\overset{O}{\overset{\|}{C}}-NH-CH_2OH$
N,N'-dimethylol ethylene urea (DMEU)	
N,N'-dimethylol-3,4-dihodroxy ethylene urea (DMDHEU)	
Trimethylol melamine (TMM)	

Flame-Retardation Possibilities of CELL/PETP Blends

The main problems arise in the chemical finishing and manufacturing of flame-retardant Cell/Pet fabrics because of the opposite nature of the fibers. The most effective fire retardants for both fibers work with quite different mechanisms: cellulose retardants in the solid and the retardants for PET mostly in the gaseous phase. Thus it is difficult to reach satisfactory fire retardancy by using only one fire retardant. Most effective chemicals must act in both phases.

Blends having the PET content smaller than 25–30 % can be treated with cellulose fire retardants. In the case of 65/35–35/65 blends, the amount of cellulose flame retardant necessary for satisfactory results must be very high, 30–40 %, and the textile and physical properties of the fabrics are disturbed too much.

The framework of flame retardation of cellulose–polyester blends is limited to four types of starting materials. Theoretically there are three different possibilities for combining the different fibers in the production of one flame retardant blend. The results have been estimated as measured by LOI value when using phosphonate finished cotton,[5] as seen in Figure 1.

When flame-retardant PET (aromatic bromine retardant) is used instead of the normal PET in 50/50 cotton blend, there is no remarkable change among the pyrolysis products. The additional cellulose-reactive finishing causes an increase in the amount of pyrolyzed water and LOI value to the level of 26%. It is evident that both phosphorus and bromine are necessary for extinguishing the flame. This example demonstrates the conclusive importance of the chemical nature of fire retardant chemicals and the synergism in the flame retarding process. For manufacturing Cell/PET blends four different pathways can be used as follows:

1. Spinning of two different flame retardant fibers together.
2. Spinning of one normal and one FR fiber together and finishing the fabric with FR chemicals suitable for the normal fiber.
3. Chemical finishing of normal Cell/PETP blended fabric in one or two stages.
4. Spinning of other types of FR fibers together with Cell/PET blends.

As important as the nature of the fire retardants in the Figure 1 is the nature of FR additives in the pathways 1–2 and 4.

In practice, some finishing methods for the Cell/PET blends have been studied. Different modifications of THPC-finishing methods have provided to be as most useful. The PET content can be 50% and both phosphorus (3–4 %) and bromine (3–6 %) are necessary for effective flame retardancy.[6-11] Phosphorus and bromine can also be elements in one flame retardant, where

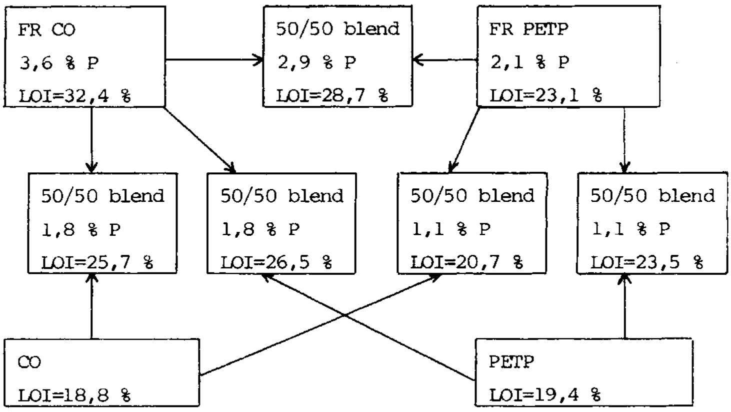


Fig. 1. Different possibilities for the flame retarding of cotton/polyester blends with phosphonate retardant.

haloalkylphosphonates are most suitable chemicals.[8] Self-extinguishing products can be manufactured also by using THPC or THPOH method combined with PVBr or PVC polymer emulsios.[12,13] Chlorine-containing vinylphosphonate and THPC were used together with acrylamide and melamine polymers to produce self-extinguishing durable Cell/PET blends.[14] The add-ons were very high (44–51 %), but the flame retardancy was quite satisfactory. Prescouring or impregnation of Cell/PET blended fabric with 7.5–3.9% sodium hydroxide solution followed with 15–30 s steaming opens the structure of PET and improves the affinity of THPC and phosphine oxide to PET.[15] The flame retardancy of blend fabric (50/50) is durable during 50 home launderings.

Both bromine- and nirogen-containing tetramethylol-substituted 1,3,5-triazine (TM-DABT) can be used with colloiding Sb_2O_3 to finish cotton/polyester blends (50/50) durable flame proof.[16] Vinyl compounds are also possible flame retardants for Cell/PET blends because they can be graft polymerized onto fibers with electron beam radiation. The most effective results have been achieved by using *N*-(dimethyl phosphonomethyl) acrylamide with 2,3-dibromopropyl acrylate and vinyl phosphonate with *N*-methylol acrylamide.[17–19] Other finishing chemicals studied for Cell/PET blends include methyl phosphonic diamide, methylol ureidoalkyl phosphonates, and bromine-containing cyclic phosphoric amidates; however, the washing durability in most cases is insufficient.[20–23]

MATERIAL AND METHODS

Materials

The starting cellulosic fibrous materials were (1.7 dtex/38 mm) HWM-viscose Modal Prima and FR viscose (Sandoflam 5060) by Kermira Oy Säteri, Finland. Thickness of 1.7 dtex corresponds to the weight of 1.7 g of 10^4 m of fiber and about 6 μm. Poly(ethylene terephthalate) fibers used were (1.7 dtex/38 mm) Trevira normal, FR polyester Trevira CS (Hoechst AG, FRG), and Toyobo GH (Toyobo Co, Japan). The PVC fiber used was (2.8 dtex/50 mm) Clevyl by Rhone Poulenc, France. The fibers were spun into 20 dtex 100% and blended yarns with twist Z 720 without spinning oil by using SKF-Spinntester 82.

The blend ratios (%) were 0/100, 20/80, 35/65, and 50/50 Cell/PET and vice versa. PVC fibers were spun into blends 35/65, 50/50, and 65/35, 5% of the fiber in each case. The yarns were knitted with a Degoisey laboratory machine to 80–112 g/m^2 knittings and the filling coefficient (the volume share of solid material inside the porous textile plane structure, 0–1) was 0.09–0.14. Knitted fabrics were finished with different *N*-methylol durable press chemicals as follows: active chemical content of solutions 6.7 % catalyst NH_4Cl 4.8 g/L, pick-up 60–65 %, drying 110°C, curing 140°C/4min, and wash afterwards with water at 40°C. Chemicals used were DMDHEU (A), DMEU (B), UF (C), and trimethylol melamine (D). Flame-retardant finishes were applied to the knitted fabrics also by using foam finishing method. The concentration of chemicals were as follows:

Chemical(g/L) / Recipe	E	F	G
Pyrovatex CP	500		
Protenyl		500	
Proban LUSX			320
Lyofix DML	100	100	
Tinovetin JU	10	10	1
Turpex NPF	25		
Knittex Kat. AD	18	30	
Diphasol EP	5	5	5
Prox FU		36	

The foam ratio was 12.5–15.0 L/gk, pick-up 35%, drying at 120°C, curing 160°C/4 min (E) and 180°C/1,5 min (F), and wash afterwards with 1% soda ash with hot and cold rinsing. In case G, the moisture of dried fabrics was 7–12% when they were treated with NH_3 gas for 10 min. After ammonia curing, the samples were washed oxidatively with 7% H_2O_2 solution, and rinsed with soda, water, bisulfite, and water. Cotton/PET and viscose/PET fabrics (50/50) were also finished with recipe E.

Test Methods

Fabrics were weighed in standard circumstances (20°C, 65% RH) before and after finishing. The tensile strength was measured with an Alwetron TCT 10 apparatus according to the Finnish Standard 2983. DSC-curves of the 5-mg samples were run with a Perkin-Elmer calorimeter within the temperature range of 50–450°C with a heating rate of 10°/min. All measurements were done in nitrogen atmosphere. Indium was used as the external melting point standard.

The limiting oxygen index (LOI) was measured according to ASTM-D 2863-76 standard with a Stanton Redcroff apparatus. Vertical flame tests were carried out at 90° and 45° according to standards DIN 54335 and 53906. The burning rate was also calculated.

The nitrogen of finished and unfinished samples was determined by the Kjehldahl method and phosphorus spectrophotometrically as a molybdenum complex.

RESULTS AND DISCUSSION

Viscose Fiber Blends with FR Polyesters

The fixation of finishes A–D to VI/PET in the case of Trevira CS was 3–4 % from the initial fabric weight also when 100% PETP fabrics were finished. Flame retardant finished E and F increased the mass of fabrics by 12–18 % depending more on the VI/PET ratio. The flame-retardant finish (THPC) using a reactive cure with gaseous ammonia caused the add-on ony about 5% probably because of the incomplete curing phase.

The fixation of finishes was nearly the same when using Toyobo GH fiber instead of Trevira CS. The dependence of the fabric mass add-on on the blend ratio with different finishing methods is presented in Figure 2.

When considering the tensile strength of durable-press-finished fabrics, it can be noted that both viscose and Trevira CS lose strength in the finishing process. The loss of viscose strength is 33–55 % and of Trevira CS 5–30 %. The strength increases with the increasing polyester content and reaches an optimum when the blend ratio is about 40/60–30/70. The weight loss of viscose is compensated when the polyester content is about 30% with DMDHEU, DMEU and UF finishes. The melamine finish affects more the tensile strength of the fabrics: The weight loss in 100% viscose fabric is 55%, but it is compensated with 10–20% polyester. The situation is about the same regarding the Toyobo fiber; however, there is no weight loss when treating 100% fiber, and the optimum area is more dependent on the finishing chemical.

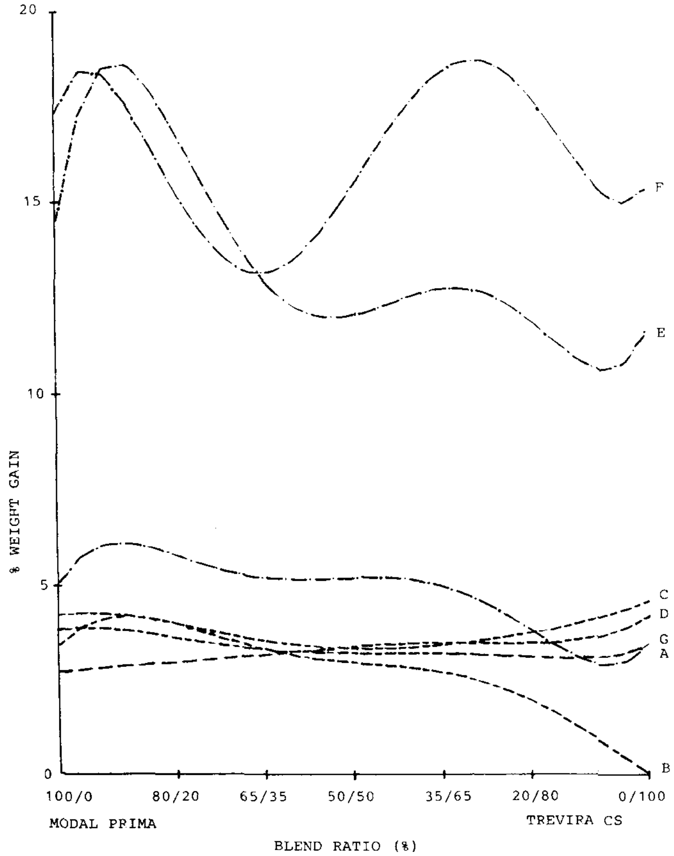


Fig. 2(a). The dependence of fabric mass add-on on the blend ratio (VI/FR PET) with different finishes (A–F) (Trevira CS).

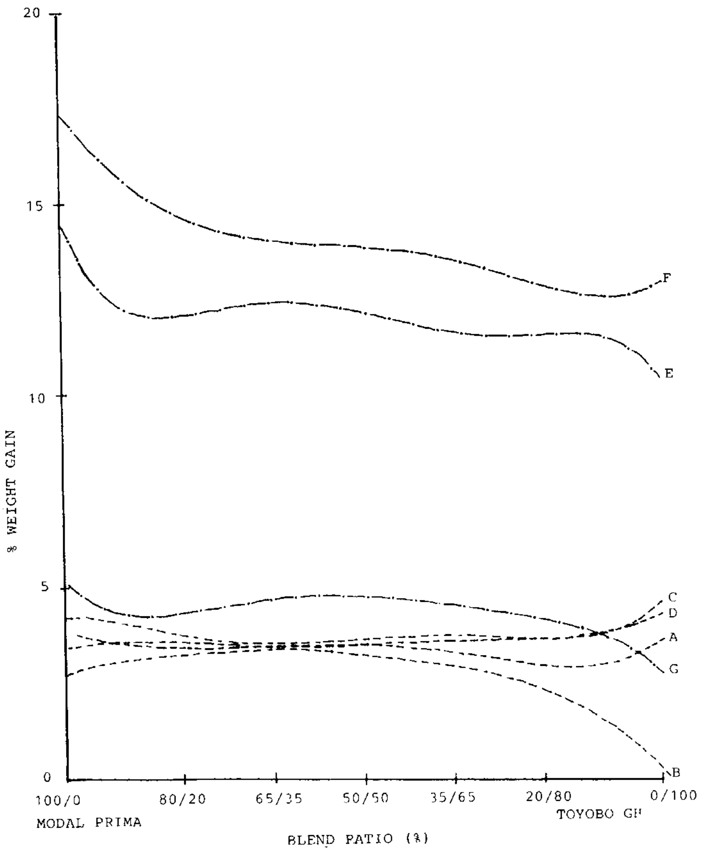


Fig. 2(b). The dependence of fabric mass add-on on the blend ratio (VI/FR PET) with different finishes (A–F) (Toyobo GH).

It was very surprising that the tensile strength of viscose/FR polyester blends was generally much higher when compared with unfinished blends. When the different treatments are considered, it can be noted that durable press finishing affects the loss both on the tensile strength and elongation in the case of Trevira CS, but flame-retardant finishings cause increase in both quantities. It is evident that this phenomenom is caused by melamine homopolymerization on the fiber surface. The dependence of the tensile strength of the fabrics compared with unfinished fabrics with different finishing chemicals is presented in Figure 3. The LOI value of unfinished blends remains below 20% until more than 70% FR polyesters are blended with viscose. After that, there is a slight increase with increasing polyester content. The durable press finishing caused a 1.5–3.0% increase of the LOI value when considering Trevira CS blends and a 2.5–3.5% increase with regard to Toyobo GH fiber. Flame-retardant finishings caused an increase of the LOI value to the level of 23–25.5%, depending on the blended fiber and the finishing chemical. The highest values were obtained when finishing 65/35 VI/Trevira CS fabrics with Pyrovatex CP. This was also higher when the viscose content was 80%. The values were lower in the case of Toyobo

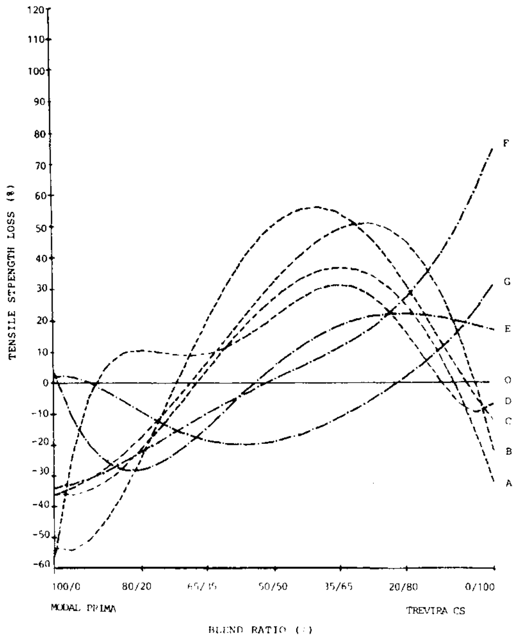


Fig. 3(a). The dependence of tensile strength on the blend ratio (VI/FR PET) with different finishes (A-F, O = unfinished) (Trevira CS).

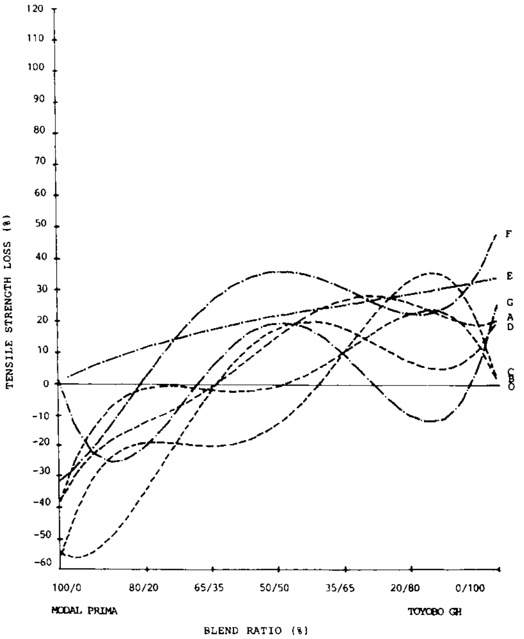


Fig. 3(b). The dependence of tensile strength on the blend ratio (VI/FR PET) with different finishes (A-F, O = unfinished) (Toyobo GH).

fiber, about 23–24%. In both cases the effect of THPC finish to the LOI value was remarkable with regard to the low add-on. It seems evident that it is possible to achieve higher LOI values when using the THPC method than with methylol phosphono propionamide method. The LOI values of finished and unfinished fabrics are presented in Figure 4.

FR Viscose Fiber Blends with FR Polyesters

The weight add-ons of FR VI/FR PET blends were generally about 2–4.5% in the case of durable press finishes and 11–15 % with flame retardants except with recipe 6 (about 4%). It appeared that the affinity of FR chemicals to FR viscose fibers is smaller than with normal viscose. The tensile strength loss of the durable press finished fabrics was 20–45 %. Flame-retardant finishes caused a smaller loss of 5–20 % in 100% FR viscose samples. The losses were nearly compensated with 20% polyester and were higher than originally with finishes B, C, E, and F. The zero level was often near the ratio 50/50. The tensile strength loss of finished FR VI/

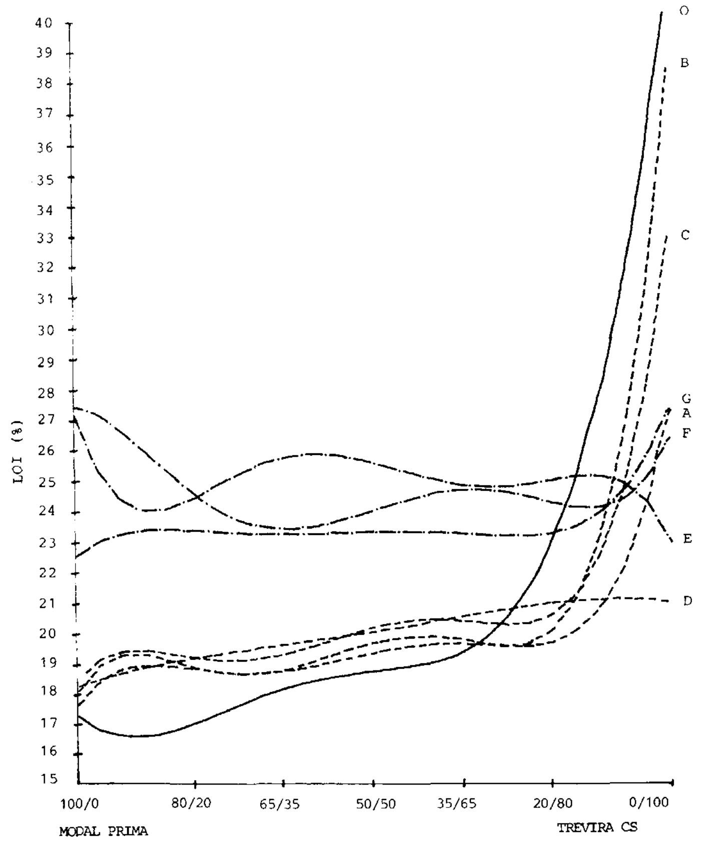


Fig. 4(a). The dependence of oxygen index (LOI) on the blend ratio (VI/FR PET) with different finishes (A–F, O = unfinished) (Trevira CS).

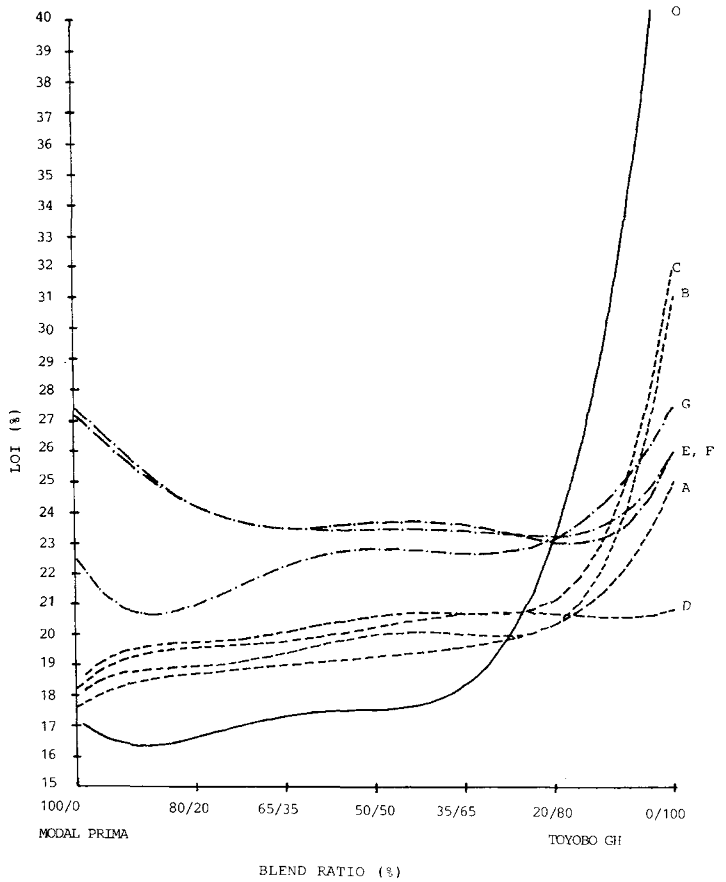


Fig. 4(b). The dependence of oxygen index (LOI) on the blend ratio (VI/FR PET) with different finishes (A–F, O = unfinished) (Toyobo GH).

FR PET blends cannot be so easily compensated with the polyester part in the mixture compared with VI/FR PET blends. The main reason is the effect of the flame-retardant particles inside the viscose fiber. The add-ons and losses of tensile strength concerning different FR VI/FR PET blends are presented in Figures 5 and 6. The LOI curve of unfinished FR VI/FR PET blends has the slowly sinking shape between LOI values of 21 and 26 until the share of FR PET is about 80%. The effect of durable press finishing is about 0.9–1.4 units increase in the LOI value with every blend. The level of LOI value 25–25.5 can be achieved with blends 65/35–70/30 of FR VI/FR PET. If the blends are finished with flame retardants, the LOI value can be improved by 2.5–3.4 units having in the case of the 65/35 FRVI/FRPETP a blend magnity of 27%. It must be pointed out that these experiments were made with very light knitted fabrics having a low-filling coefficient. Thus the flame retardancy can be improved by increasing the mass per unit area. The LOI vaues of FR VI/FR PET knitted fabrics are presented in Figure 7.

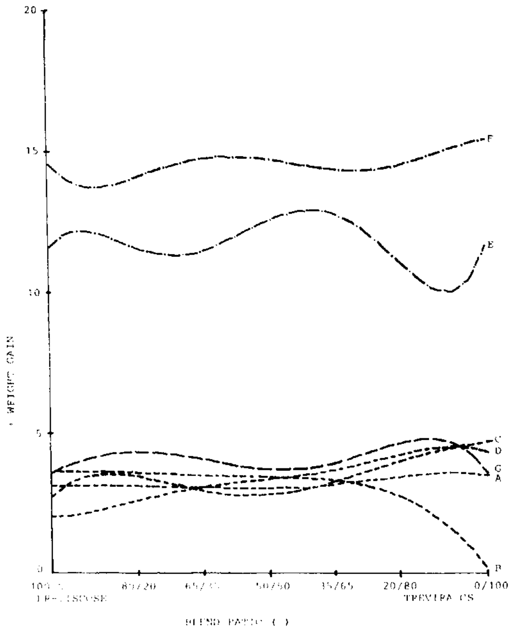


Fig. 5. The dependence of fabric mass add-on on the blend ratio (FR VI/FR PET) with different finishes (A–F, Trevira CS).

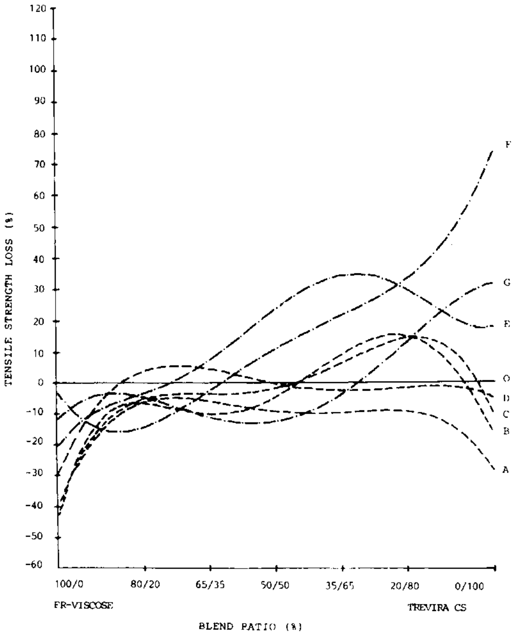


Fig. 6. The dependence of tensile strength on the blend ratio (FR VI/FR PET) with different finishes (A–F, O = unfinished, Trevira CS).

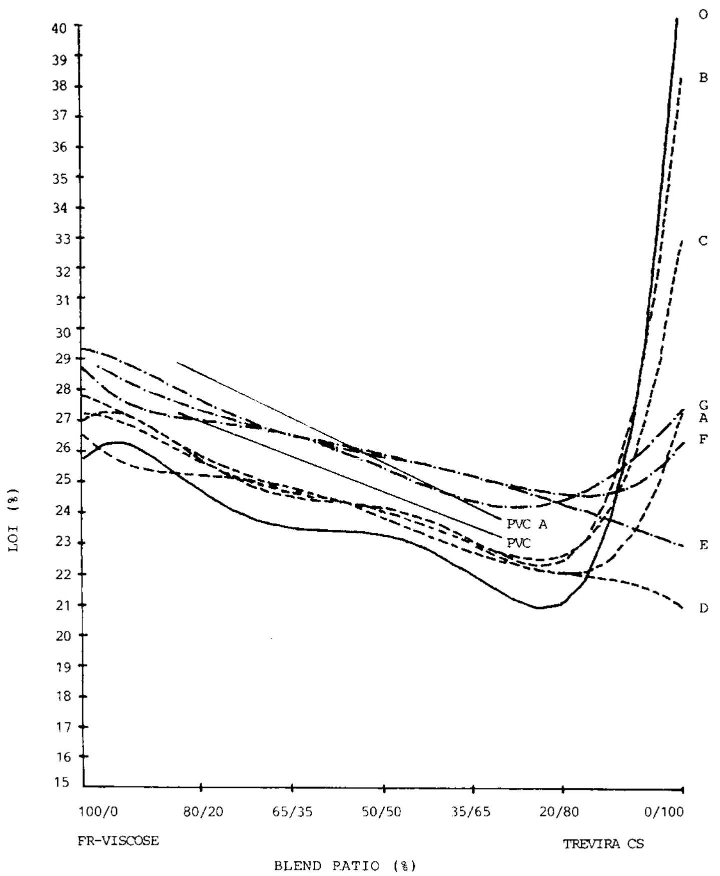


Fig. 7. The dependence of oxygen index (LOI) on the blend ratio (FR VI/FR PET) with different finishes (A–F, O = unfinished, Trevira CS).

When FR VI/FR PET/PVC fabrics containing 5% PVC were used (47.5/47.5/5 and 62.5/32.5/5 ratios), the initial LOI values of unfinished fabrics were about 1.5–2.5 units higher than in the case of FR VI/FR PET fabrics. When these fabrics were finished with durable press chemicals, the effect was as high as with flame retardants as seen in Figure 7. PVC can be considered as a flame retardant, the add-ons of which are smaller than with finished flame retardants. The higher coefficients of the PVC slopes are connected with phosphorous–halogen synergism because the phosphorous content increases with increasing FR VI content.

The nitrogen content of finished fabrics varied between 0.5 and 1.5% with chemicals A–D having the highest values with C and D. Flame retardants raised the concentration up to 2–3 % while the chemical F (Protenyl) caused the highest value. The nitrogen concentration after THPC finish was only about 0.7%. Phosphorous concentrations were more dependent on the blend ratio because the FR VI fiber contained 2.5 % phosphorous and FR PET fibers 0.3–0.5 %. From the curves presented in Figure 8 it can be concluded that a phosphorous content of 2–2.5 % and a nitrogen content of 2.1–2.7%

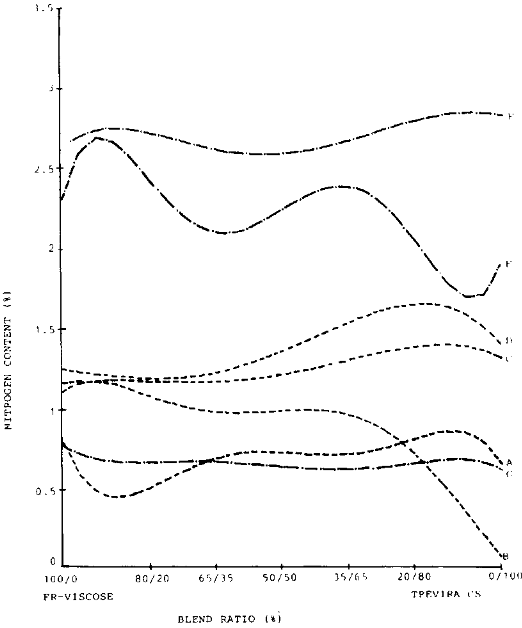


Fig. 8(a). The dependence of nitrogen content on the blend ratio (FR VI/FR PET) with different finishes (A–F, O = unfinished, Trevira CS).

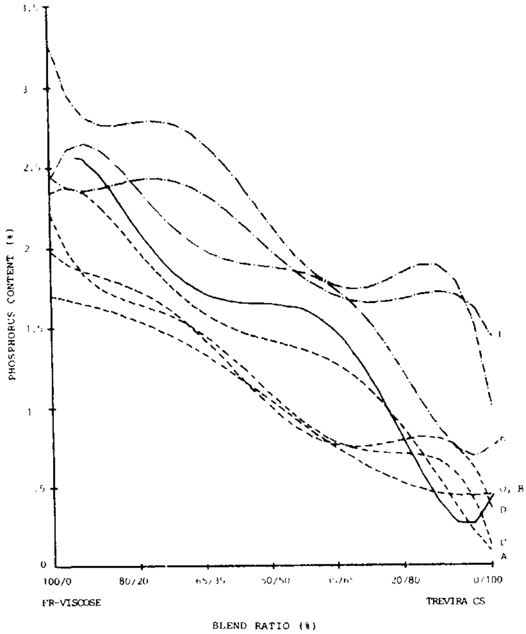


Fig. 8(b). The dependence of phosphorus content on the blend ratio (FR VI/FR PET) with different finishes (A–F, O = unfinished, Trevira CS).

is necessary for flame-retarding VI/PET blends 50/50–65/35. However, the nitrogen content can be smaller in the case of THPC finish, which proved to be the most effective for VI/PET blends.

Textile Properties and Washing Durability

Laboratory scale studies were followed with full scale production experiments, and some investigations of fabric textile and burning behaviour properties compared with blends of cotton and polyamide. The results are presented in Table II. The results in Table II demonstrate some trends about the properties of different FR cotton and viscose polyester-blended fabrics. Finishing of CO/PETP, VI/PETP, and CO/polyamide 6.6 fabrics with the mixture flame retardants containing P/N and bromine retardants with *N*-methylol acryl amide binder can only be effective via very high add-on. It is self-evident that the hand of this type of fabrics is not satisfactory for clothing purposes. The LOI values of the fabrics are on the same level in the case of FR VI/FR PET; however, the flame-retardant properties are most durable. The effect of mass per unit area increase compared with the results in Figure 7 is about 0.8 units (23.6–24.2) without finishing and 1.1 units with DMDHEU finishing. Thus the more suitable blend ratio for medium weight twill fabrics is 65/35 FR VI/FR PET finished with DMDHEU. The expected LOI value is then about 26.3%. If the blend contains also 5% PVC or other synergistically active polymer or chemical, the flame retardancy is furthermore improved up to the LOI value ≥ 27.4 %. Thus the most effective flame retardancy and satisfactory textile properties can be obtained, when the composition of the fabric is as presented in Table III. The weight percentages of chemicals and elements are based on the known sturcture of flame retardants.

The results in Table III are in good accordance with the earlier studies of the phosphorous–halogen synergism in cotton/PET blends.[24] The role of nitrogen is to decrease the necessary phosphorus and chlorine contents. The amounts of cellulose viscose and PET polymers is about 79% calculated from the FR mixture and weight ratio of 2:1 (67/33 blend).

Burning Behaviour

The burning behavior of test fabrics having highest LOI values was determined according to standards DIN 54335 (45°) and DIN 53906 (90°). The burning rate was also calculated and divided into two categories: ≤450 mm/min and ≥450 mm/min. Results are presented in Table IV. Two fabrics in the category I did not ignite and had LOI values of about 26%. The other one (65/35, n. 16) had a very complex structure with double-viscose fire-retarding system. Very close to the category I are, in category II, FR-finished VI/FR PET fabrics[4,10] and 65/35 FR VI/FR PET fabric [16] finished with TMM. Thus it might be valuable to notice factors explained before (PVC, mass per unit area) when constructing self-extinguishing fabrics. A surprising phenomenom is the very low burning rate of 50/50 VI/ FR PET (Toyobo GH) fabrics[10] compared with their LOI values. Generally the dependence of burning rate on the LOI value seems obvious corresponding to

TABLE II

Some Textile and Burning Properties of Blended Viscose and Cotton Twill Fabrics Treated with Durable Press and Cellulose Reactive DBDPO and Binder Containing Flame Retardant Formulations(2,4)

Fabric			Add-on		Tensile	strength	Shrinkage		LOI	Char	Length
washings		Finishing	(%)	g/m²	WRP (N)	WT	WRP	(%) WT	(%)	vert	mm 45°
FRVI	0	No	—	314	1135	584	> 15	> 15	28.4	98	—
FRVI	0	DMDHEU	13.1	355	1132	630			29.4	95	—
	50		14.9	361	740	516	14.2	4.0	29.0	90	—
FRVI/FRPES		No	—	316	1318	738			24.2	BEL	4.5
50/50	0	DMDHEU	8.2	342	1311	706			25.4	BEL	38
	50		2.2	323	1246	717	2.4	±0	24.6	BEL	40
CO/PES		No	—	125	662	578			17.4	BEL	—
50/50	0	Pyrovatex	38.4	173	503	551			26.3	150	—
	50	Caliban P53	40.0	175	490	541	4.0	3.0	24.0	BEL	—
VI/PES		No	—	301	1750	933			19.2	BEL	BT
50/50	0	Pyrovatex	26.6	381	1370	737			25.7	BEL	40
	50	Caliban P71	36.2	410	1280	784	6.0	0.5	24.3	BEL	40
CO/PA		No	—	243	1920	854			19.3	BEL	—
50/50	0	Pyrovatex	39.9	340	1960	801			26.8	216	—
	50	Caliban P53	36.2	331	1940	577	0.2	±0	23.9	225	—
CO/PES		No	—	248	1420	717			18.2	BEL	
33/67	0	Pyrovatex	34.3	333	1440	733			25.8	200	
	50	Caliban P53	37.5	341	1405	714	6.4	1.5	24.2	BEL	

[a] g/m² = weight per unit area; WRP = warp direction; WT = weft direction; N = Newtons; LO = limiting oxygen index (%O_2); vert = test according to SIS 650082; 45° = test according to SIS 650083; BEL = burned entire length.

TABLE III
Synergistic P/N/Cl Formulation of Polymers and Additives for Flame-Retardant VI/PETP Fabrics

Component of FR formulation (wt %)	Polymers	Chemicals	Elements
Viscose cellulose	52.4		
Viscose FR additive (Sandoflan 5060)		7.3	
Phosphorus from viscose additive			2.4
Durable press chemical (DMDHEU)		7.6	
Nitrogen from durable press polymer			0.7
PETP fiber	26.1		
PETP fiber flame retardant (Trevira CS)	1.6		
Phosphorus from PETP fiber			0.4
PVC fiber	5.0		
Chlorine from PVC fiber			2.7
	85.1	14.9	6.2

some earlier studies.[24] The effect of fabric LOI value on the burning rate is presented in Figure 9. When the burning rate in Figure 9 is extrapolated to zero value, the corresponding self-extinguishing LOI value is about 27%.

Thermal Analysis

Modal viscose type cellulose decomposes within the temperature range of about 340–345°C, which is shifted to the area of 260–270°C, while the use of the inherent flame retardant causes an energy absorption in the temperature 229°C.

Durable press finishes did not have any effect on the DSC curves of 100% modal or FR modal fibers. On the contrary, the flame retardant finishing had a broadening effect on the DSC curve. The DSC data of different modal viscose fibers are presented in Figure 10.

The DSC curves of both FR/PET fibers showed the same type of shape having their melting point at 245°C Trevira CS fiber had an additional energy absorption peak at 234°C. The durable press finishing did not influence the curve, whereas the flame-retardant treatment lowered the decomposition temperature to about 45°C. The decomposition of Trevira CS takes place normally at 350°C and of Toyobo GH at 375°C which is about 75–100°C lower than with normal PETP. The difference between two FR polyesters seems to be in the solid–gaseous mechanism behavior. The DSC data of different polyester fibers is presented in Figure 11.

The earlier studies of cotton/PET blended fabrics showed a slight increase in decomposition rate, and in the rate of heat transfer compared with the sum of nonblended fibers.[2,20,21] This relates to larger amounts of flammable pyrolyze gases which are acting as fuels. In this study the DSC data indicate a lower (3–9°C) decomposition temperature of modal viscose when blended with FR polyesters. On the other hand, PET did not have the same influence on the low decomposition temperature of FR viscose. Thus the polyester

TABLE IV
The Dependence of the Burning Behavior on the Construction and Finishes of Viscose/PETP Knitted Fabrics[a]

No.	Fabric composition	Filling coefficient	Finish type symbol	Add-on (%)	g/m^2	Burning rate (mm/min)	LOI (%)	CL am DIN 53906	Category
15	80/20 FRVI/FRPETP CS	0.87	DMOHEU (A)	3.2	100.1	DNI	25.8	20	I
16	65/35 FRVI/FRPETP CS	0.86	MPPA CP (E)	11.6	108.3	DNI	26.6	11	I
4	50/50 VI/FRPETP CS	0.87	MPPA CP (E)	12.2	114.5	147	26.0	BEL	II
10	50/50 VI/FRPETP GH	0.88	MPPA CP (E)	12.2	114.5	211	23.4	BEL	II
10	50/50 VI/FRPETP GH	0.88	MPPA P/N (F)	13.9	116.2	430	23.6	BEL	II
16	65/35 FRVI/FRPETP CS	0.86	TMM CHN (D)	3.1	97.9	450	25.1	20	II
4	50/50 VI/FRPETP CS	0.87	MPPA P/N (F)	15.6	119.1	639	24.5	15	III
16	65/35 FRVI/FRPETP CS	0.86	DMOHEU (A)	3.1	101.0	762	24.9	21	III
4	50/50 VI/FRPETP CS	0.87	THPC (G)	5.3	108.5	825	23.1	BEL	III
10	50/50 VI/FRPETP GH	0.88	THPC (G)	4.8	106.9	943	22.6	BEL	III

[a] CS = Trevira CS/ GH = Toyobo GH; MPPA CP = Pyrovatex CP; MPPA P/N = Protenyl P/N S; BEL = burned entire length; CL = char length.

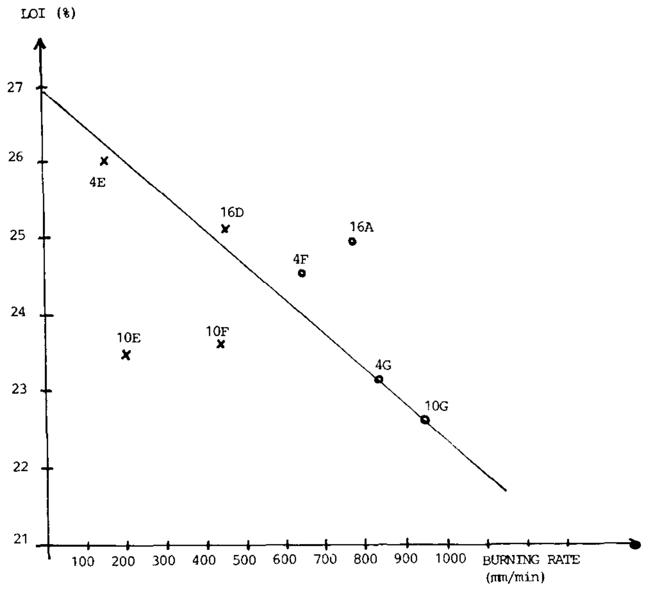


Fig. 9. The effect of oxygen index on the burning rate of light flame retarded viscose–polyester knitted fabrics.

flame retardants have an influence also on the cellulose fiber when blended fabrics are burned. The melting point of FR polyesters are independent of the nature of the blending component.

The treatments of VI/FR PET and FR VI/FR PET (50/50) with durable press and flame retardant chemicals did not effect the melting point of the polyester component. The effect of finishes on the decomposition temper-

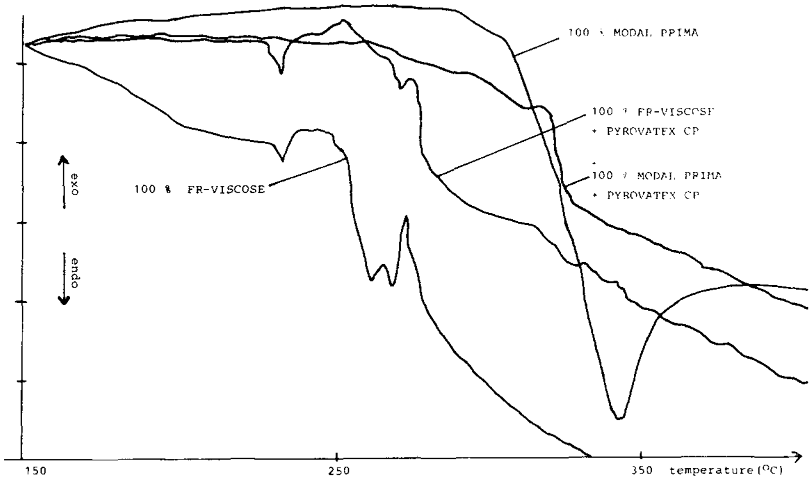


Fig. 10. The influence of flame-retardant finishing on thermal (DSC) properties of 100% viscose and FR viscose.

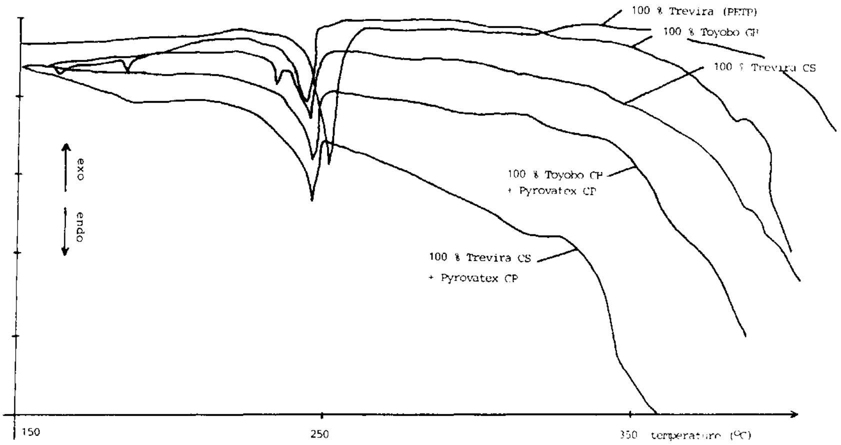


Fig. 11. The influence of flame-retardant finishing on thermal (DSC) properties of 100% polyesters.

ature of viscose component depends on the nature (FR or not) of the viscose fiber as follows:

—VI/FR PET: DP finishing increases and FR finishing decreases the decomposition temperature of viscose fiber, while the THPC finishing is most effective (80°C).

—FRVI/FRPETP: DP finishing reduces and FR finishing incrases the decomposition temperature of viscose fiber.

DSC curves of different VI/PET samples and a cotton sample are presented in Figures 12 and 13.

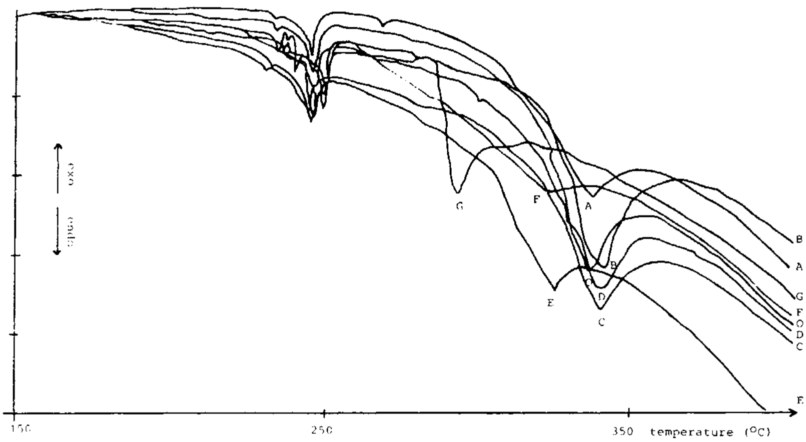


Fig. 12. The influence of DP (A–D) and flame-retardant (E–G) finishing on thermal (DSC) properties of viscose/Trevira CS (50/50) fabrics compared with untreated sample (O).

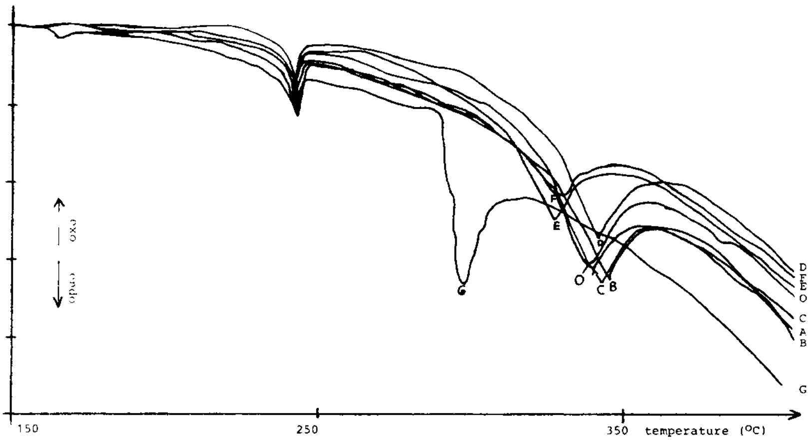


Fig. 13. The incluence of DP (A–D) and flame-retardant (E–G) finishing on thermal (DSC) properties of viscose/Toyobo GH (50/50) fabrics compared with an untreated sample (O).

CONCLUSIONS

Systematic investigations were carried out for producing flame-retardant viscose–polyester fabrics. The different nature of pyrolysis mechanism of cellulose and PETP fibers demands the flame-retardant chemicals to act both in solid and gaseous phase.

There are two main procedures for producing durable flame-retardant VI/PET fabrics. The first one if to use FR polyester fibers with normal or modal viscose fiber and to treat the 50/50–65/35 (VI/PET) blends with (THPC-based) flame retardants. The second higher level of flame retardancy can be achieved by using FR VI/FR PET blend together with durable press finishing treatments and a little amount of synergistic active halogen-containing fiber (PVC). The dropping effect of melted PET fiber can be eliminated by char-forming viscose fiber.

The protective efficiency of fabrics against radiative heat can be regulated with the mass per unit area and other constructive parameters or fabrics. Practically, the flame retardancy of VI/PET fabrics can reach the self-extinguishing level and behave in a way comparable with the FR cotton. Of course, the hand, strength, and some other textile properties are typically better than in the case of FR cotton.

Tensile strength, fixation degree, and oxygen index data of unfinished and finished VI/FR PET fabrics prefer blends of 65/35 VI/FR PET as most suitable for FR fabric production. When using FR VI/FR PET blends, the same oxygen index maximum of 25.5–26 can be achieved with DP finishing. The higher level of flame retardancy can be achieved by adding fibrous PVC during the spinning process. This is a further evidence of phosphorous–halogen synergism concerning the flame-retardant mechanism of PET. The overall concentration of phosphorous, nitrogen, and chlorine should be in the range of 2–2.8 %, 0.7 % (without chlorine 2.1–2.7%), and 2.7%, respectively. The role of sulfur in the flame-retardant chemical (Sandoflam 5060) is probably to produce sulfur dioxide, which is acting in gaseous phase.

Thermal DSC analysis of fabrics showed a slight influence of PET flame retardants on the decomposition temperature of FR viscose. Treatments afterwards of VI/FR PET and FR VI/FR PET with DP and FR chemicals did not affect on the melting point of the polyester component. The decomposition temperature of viscose fiber was increased with VI/FR PET fabrics when using DP finishing and decreased with FR finishing. When finishing FR VI/FR PET fabrics, the result was reversed, which was in good accordance with better FR properties of DP-finished FR VI/FR PET fabrics. In both cases the decomposition temperature of viscose fiber was lowest with THPC finish.

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