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The effect of flame-retardants on the properties of acrylic and modacrylic fibres

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In this study, flame-retardant additives such as tributyl phosphate, tri(dibromopropyl) phosphate, aluminium hydroxide powder and aluminium hydroxide gel are used for acrylic fibre (acrylonitrile and vinyl acetate copolymer), and calcium phosphate and antimony oxide are introduced into modacrylic fibre (acrylonitrile and vinylidene chloride copolymer). Investigations are carried out on the effect of these flame-retardants on the thermal properties, mechanical properties, morphology and flammability of acrylic and modacrylic fibres. The results show that the effect of additives on the rate of a coagulation during spinning can be understood from the change of morphology of the fibres. Tri(dibromopropyl) phosphate and antimony oxide are a good flame-retardant and a good synergistic flame-retardant, respectively.

1. Introduction

Acrylic fibres are recognized by the rules of the US Federal Trade Commission as a manufactured fibre in which the fibre-forming substance is any long-chain synthetic polymer composed of at least 85% by weight of acrylonitrile chain. Modacrylic fibres are defined as those containing 35–85% acrylonitrile by weight, and the modacrylics commercially available contain 25–60% of monomers such as vinyl chloride or vinylidene chloride, and consequently possess a high degree of flame-resistance. Acrylic fibres shrink when heated, decreasing the opportunity for accidental ignition. However, once ignited they burn vigorously, especially those of high pile or loose weave construction, producing clouds of black smoke. Of all the synthetic fibres in the market-place today, acrylic fibres have received the greatest attention in trying to develop improved resistance. The approaches which have been used to gain flame-resistance can be classified as follows [1] :

(i) copolymer or blend of polymers,
(ii) finish,
(iii) additives,
(iv) chemical modification.

Since acrylonitrile and vinylidene chloride are suspension-polymerized by sodium hydrogen sulphite, ammonium persulphate and ferrous sulphate catalysts, the copolymerization exhibits a higher conversion [2]. Modacrylic fibres spun with N, N-dimethylacetamide (DMAC) solvent usually have much greater flame resistance than acrylic fibres and commercial modacrylic fibres, such as SNIA and Kanekalon modacrylic fibres [3]. A summary of the additives investigated is as follows:

(i) tris(dibromopropyl) phosphate [4],
(ii) trialkyl phosphates of 6-16C in alkyl [5],
(iii) telomers of bromo- and chloromethanes and unsaturated phosphates that are brominated [6],
(iv) 2-cyanoethyltetramethyl diamidophosphate [7],
(v) bromine-containing phosphonates + an insoluble calcium phosphate [8],
(vi) esters of polyhalo fatty acids [9],
(vii) brominated N,N-dialkylamides of unsaturated fatty acids [10],
(viii) polyepihalohydrin + an insoluble calcium phosphate or antimony oxide [11, 12],
(ix) polybromochlorocyclohexanes [13],
(x) halogen-containing polymeric phosphonates [14],
(xi) salts of metals (> bivalent) [15].

In this paper, we discuss the effect that additives such as tributyl phosphate, tri(dibromopropyl) phosphate, aluminium hydroxide powder and aluminium hydroxide gel have on the crystallization during spinning and flame-resistance of acrylic fibres. It is further found that a synergistic effect for the flame-resistance of modacrylic fibre can be obtained by using insoluble antimony oxide additive, and that calcium phosphate exhibits no synergistic effect for modacrylic fibre.

2. Experimental procedure

The acrylonitrile (AN) –vinylidene chloride (VCl_2) copolymers (modacrylics) and acrylonitrile–vinyl acetate (VAC) copolymers (acrylics) used in this study were copolymerized by the suspension method with a redox catalyst, such as sodium hydrogen sulphite, ammonium persulphate and ferrous sulphate, at 25 °C (modacrylic) or 60 °C (acrylic) under nitrogen gas. The feed ratios of monomers were 50:50 and 91:9 (by

TABLE I Amounts of flame-retardant for modacrylic and acrylic fibres

Sample	Copolymer composition	Flame-retardant	Amount of flame-retardant (%)
PA1	AN-VAC	Tributyl phosphate	25
PA2	AN-VAC	Aluminium hydroxide powder	25
PA3	AN-VAC	Tri(dibromopropyl) phosphate	25
PA4	AN-VAC	None	0
PA5	AN-VAC	Aluminium hydroxide gel	15
PA6	AN-VCl_2	Calcium phosphate	7
PA7	AN-VCl_2	Antimony oxide	7
PNDC	AN-VCl_2	None	0

weight) for acrylonitrile–vinylidene chloride copolymers and acrylonitrile–vinyl acetate copolymers, respectively. The slurry of polymer was filtered by centrifugation to form polymeric powder, and simultaneously the polymeric powder was washed several times with water, then dried in a vacuum oven at 100 °C. Flame-retardants were mixed in the spinning dope, and the amounts of flame-retardant used in this study are shown in Table I. The spinning dope contained 24% of the polymer in N,N-dimethylacetamide, and was spun through a coagulation bath to form modacrylic fibre and acrylic fibre which were stretched in boiling water and dried. The diameter of the spinneret hole was 0.06 mm ($L/d = 1$).

The chlorine content in the copolymer was obtained from titrating absorbent liquid, in which copolymer was burned in an oxygen flask and then absorbed, by using mercury ion. Thermograms of modacrylic and acrylic fibre were obtained by using the Perkin-Elmer system 7/4 thermogravimeter. Samples with 3 mg weight were heated under an air purge at a rate of 20°C min^{-1}. A scanning electron microscope (SEM), Cambridge S-360, was used to examine the cross-section and surface of the fibres. The limiting oxygen index (LOI) was determined by the method of a Japanese patent [16]. X-ray data were determined by a Scintage DMS 2000 X-ray diffractometer using Ni-filtered CuK_α radiation. The crystallite size (L_c) was calculated from the equation

$$L_c = \frac{K\lambda}{B\cos\theta}$$

where λ is the wavelength of CuK_α X-rays, B is the width at half-maximum intensity of the peak at $2\theta = 17°$, and K is 0.89 (a constant). The crystal orientation of the fibres was determined by an X-ray diffractometer (Rigaku) combined with a fibre specimen attachment. The fibres were located at around 17° (2θ) and the 360° azimuthal circle used to permit the fibre axis to be rotated 360° about the vertical; crystal orientation O was calculated from

$$O\% = \frac{360 - H}{360} \times 100\%$$

where H is the half-width (deg) of the curve of intensity versus azimuthal angle. The mechanical properties of the fibres were determined using the Microcomputer Universal Material Tester type 8104 (Hung Ta Co. Ltd) with a crosshead speed of 10 mm min^{-1}, load cell 30 g, and 2 cm testing gauge. The contents of carbon, nitrogen, and hydrogen in acrylic and modacrylic fibres were determined by the well-known method of elemental analysis (Table II) using a Carlo Erba elemental analyser.

TABLE II Elemental analysis of acrylic and modacrylic fibres

Sample	C (%)	H (%)	N (%)
PA1-1	65.160	5.695	23.075
PA1-2	65.100	5.860	22.730
PA1-3	65.070	5.905	22.645
PA2-1	65.075	5.770	23.305
PA2-2	64.975	5.695	23.240
PA3-1	59.995	5.395	21.275
PA3-2	59.605	5.225	21.060
PA3-3	58.780	5.260	20.435
PA5	58.830	5.285	21.265
PA6-1	50.240	4.565	16.100
PA6-2	48.420	4.280	15.110

3. Results and discussion

3.1. Thermal properties

Fig. 1 shows that tributyl phosphate exhibits a small exothermic reaction at about 230 °C and an endothermic peak at approximately 310 °C, and the acrylic fibre modified with 25% tributyl phosphate shows a decrease in exothermic heat compared with virgin acrylic fibre. In modified acrylic fibres the higher the drawing ratio, the sharper the exothermic peak, and the lower the temperature of the exothermic peak which is similar to the behaviour of the virgin acrylic fibre at the peak temperature. Tributyl phosphate flame-retardant has a larger weight-loss at 130 °C in the thermogravimetric analysis (TGA) curve (Fig. 2), and the TGA behaviour for the modified acrylic fibres is similar to that of the virgin acrylic fibre, but the modified acrylic fibres have a larger weight-loss at 470 °C than the acrylic fibre without a flame-retardant.

Tri(dibromopropyl) phosphate flame-retardant exhibits a sharp exotherm at approximately 330 °C, (Fig. 3). The acrylic fibres modified with tri(dibromopropyl) phosphate have a broad exothermic phenomenon containing two peaks. Tri(dibromopropyl) phosphate has a two-step weight-loss which is different from that of tributyl phosphate. The acrylic fibre modified with

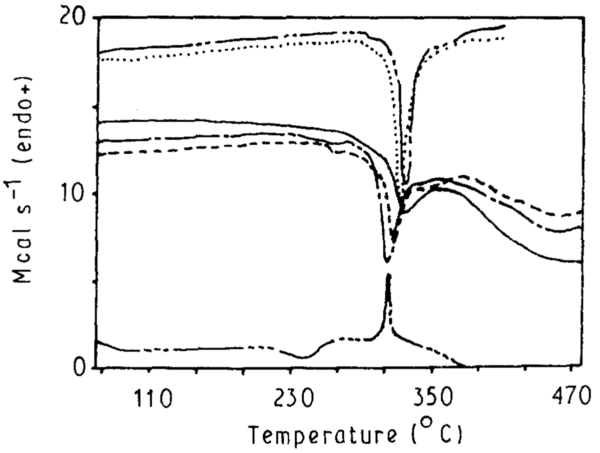

Figure 1 DSC curves of acrylic fibres with tributyl phosphate flame-retardant: (——) PA1-1, (- - -) PA1-2, (— - —) PA1-3, (— - - - —) tributyl phosphate, (— - - -) PA4-1, (. . .) PA4-2.

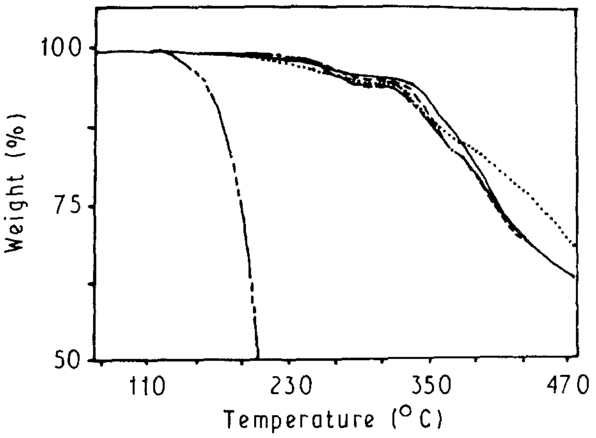

Figure 2 TGA curves of acrylic fibres with tributyl phosphate flame-retardant: (—) PA1-1, (- - -) PA1-2, (— - —) PA1-3, (— - - - - —) tributyl phosphate, (. . .) PA4-2.

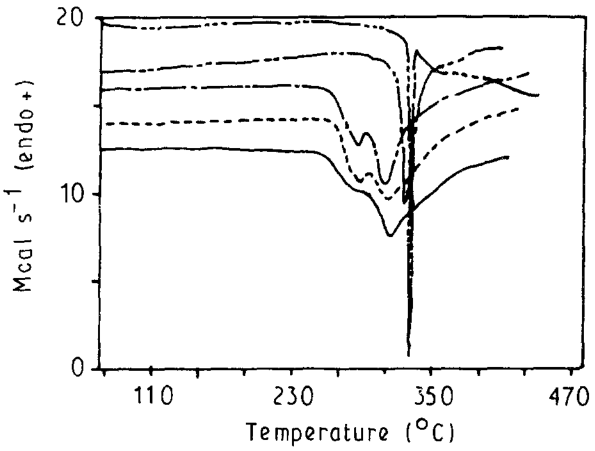

Figure 3 DSC curves of acrylic fibres with tri(dibromopropyl) phosphate flame-retardant: (— - —) PA3-1, (- - -) PA3-2, (—) PA3-3, (— - - —) PA4-1, (— - - - -) tri(dibromopropyl) phosphate.

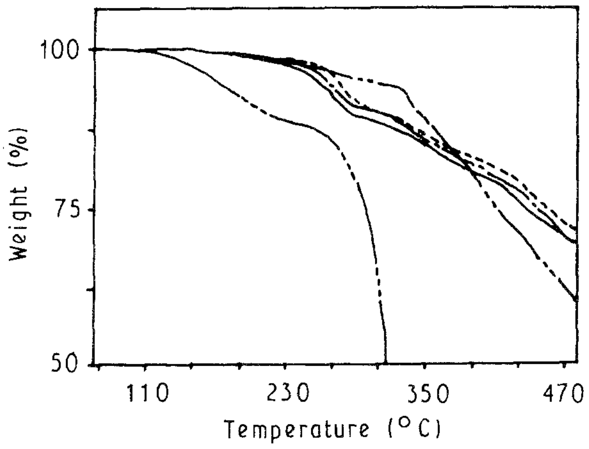

Figure 4 TGA curves of acrylic fibres with tri(dibromopropyl) phosphate flame-retardant: (— - —) PA3-1, (- - -) PA3-2, (—) PA3-3, (— - - —) PA4-1, (— - - - -) tri(dibromopropyl) phosphate.

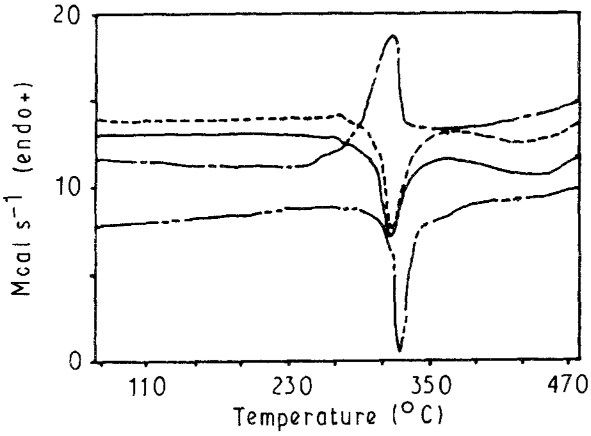

Figure 5 DSC curves of acrylic fibres with aluminium hydroxide powder flame-retardant: (—) PA2-1, (- - -) PA2-2, (— - —) aluminium hydroxide powder, (— - - —) PA4-1.

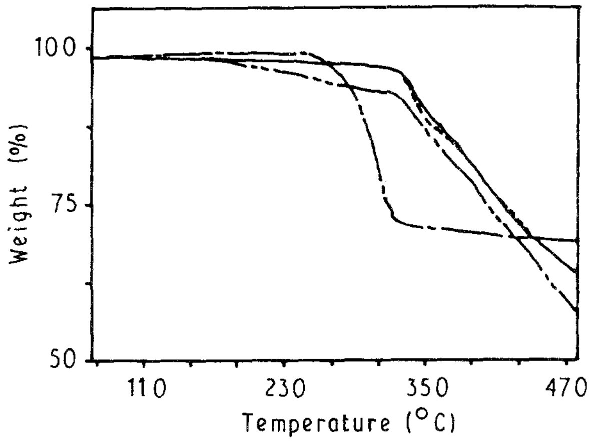

Figure 6 TGA curves of acrylic fibres with aluminium hydroxide powder flame-retardant: (—) PA2-1, (- - -) PA2-2, (— - —) aluminium hydroxide powder, (— - - —) PA4-1.

tri(dibromopropyl) phosphate has an earlier weight-loss in the TGA curve and a lower weight-loss at 470 °C than its original acrylic fibre (Fig. 4).

Aluminium hydroxide powder shows an endothermic behaviour in the differential scanning calorimetry (DSC) curve (Fig. 5). The DSC curve for the modified acrylic fibre is similar to that for the original acrylic fibre, only the peak temperature for the modified fibre is lower than for its original fibre. Aluminium hydroxide powder displays a larger weight-loss at about 250 °C and no weight-loss above 330°C (Fig. 6). The TGA curve of the modified fibre is similar to that

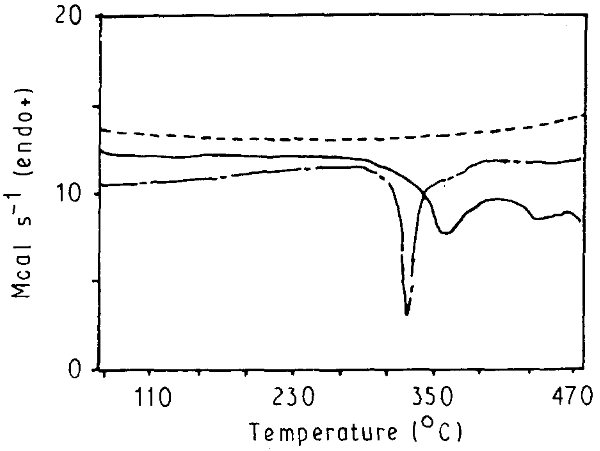

Figure 7 DSC curves of acrylic fibres with aluminium hydroxide gel flame-retardant: ( ) PA5, (- - -) aluminium hydroxide gel, (-) PA4-1.

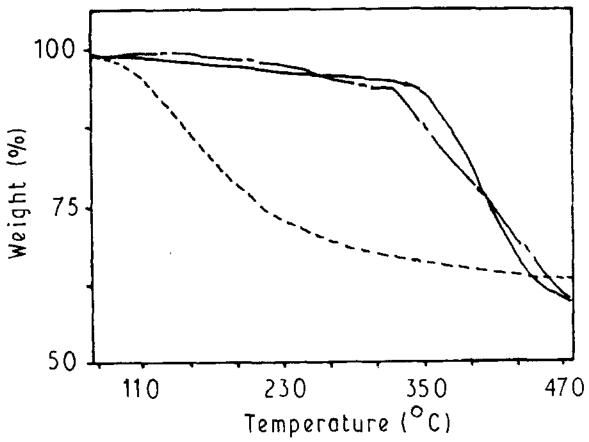

Figure 8 TGA curves of acrylic fibres with aluminium hydroxide gel flame-retardant: (—) PA5, (- - -) aluminium hydroxide gel, (-) PA4-1.

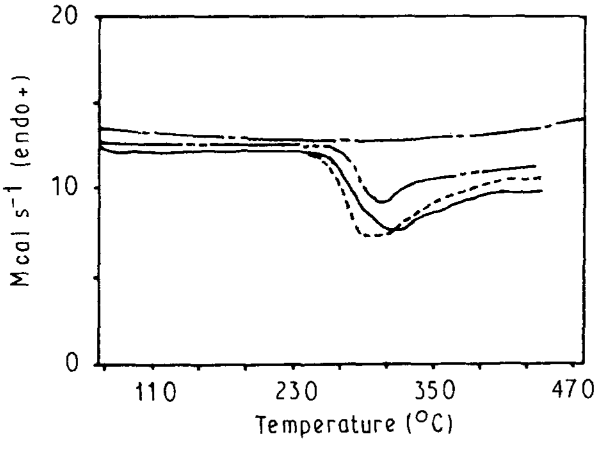

Figure 9 DSC curves of modacrylic fibres with calcium phosphate flame-retardant: (—) PA6-1, (- - -) PA6-2, (— - —) calcium phosphate, (— - - - —) modacrylic fibre with no flame-retardant.

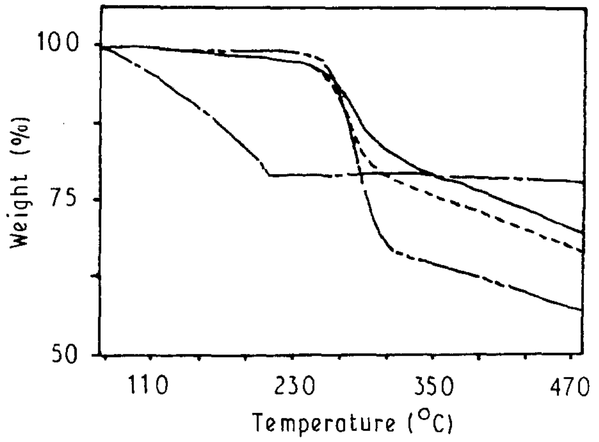

Figure 10 TGA curves of modacrylic fibres with calcium phosphate flame-retardant: (—) PA6-1, (- - -) PA6-2, (— - - -) calcium phosphate, (- -) modacrylic fibre with no flame-retardant.

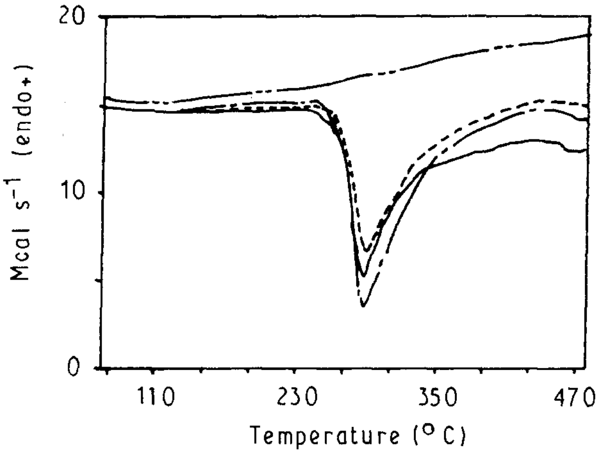

Figure 11 DSC curves of modacrylic fibres with antimony oxide flame-retardant: (—) PA7-1, (- - -) PA7-2, (- - —) PA7-3, (— - - - —) antimony oxide.

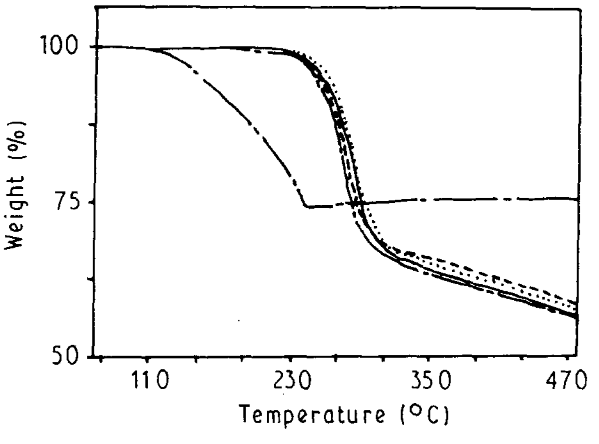

Figure 12 TGA curves of modacrylic fibres with antimony oxide flame-retardant: (—) PA7-1, (- - -) PA7-2, (- - —) PA7-3, (— - - —) antimony oxide, (···) modacrylic fibre with no flame-retardant.

of its original fibre, but the weight-loss for the modified fibre is lower.

Aluminium hydroxide gel does not disclose any exothermic or endothermic behaviour (Fig. 7). The acrylic fibre modified with aluminium hydroxide gel exhibits multi-peaks in the exotherm, and the peak temperature shifts to a higher temperature. Aluminium hydroxide gel has a gradual weight-loss from 70 °C (Fig. 8). The acrylic fibre modified with aluminium hydroxide gel does not show a larger change in the TGA curve compared with its original fibre.

Calcium phosphate has no exothermic or endothermic reaction (Fig. 9). The modacrylic fibre modified by calcium phosphate has a similar curve to its virgin

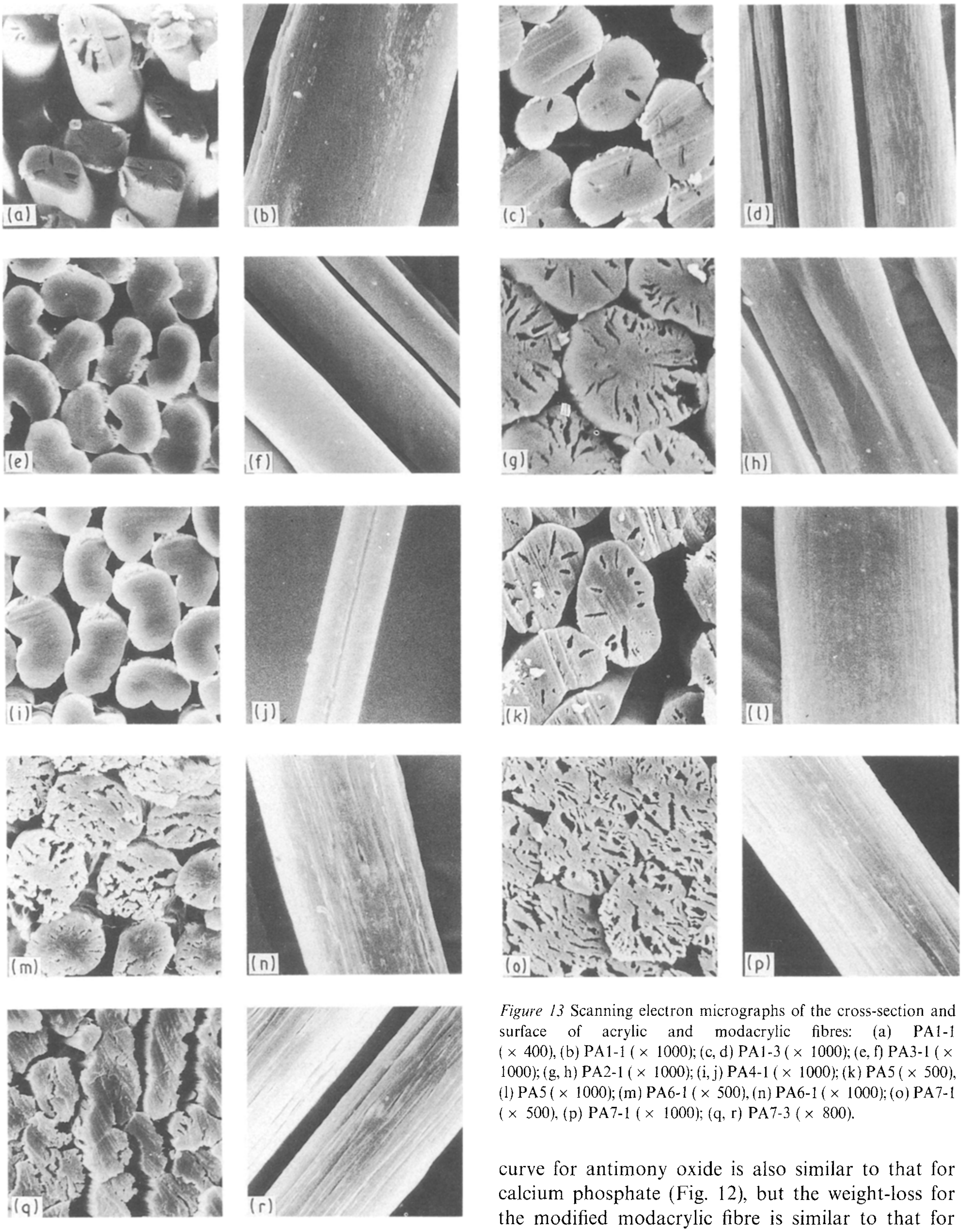

Figure 13 Scanning electron micrographs of the cross-section and surface of acrylic and modacrylic fibres: (a) PA1-1 (× 400), (b) PA1-1 (× 1000); (c, d) PA1-3 (× 1000); (e, f) PA3-1 (× 1000); (g, h) PA2-1 (× 1000); (i, j) PA4-1 (× 1000); (k) PA5 (× 500), (l) PA5 (× 1000); (m) PA6-1 (× 500), (n) PA6-1 (× 1000); (o) PA7-1 (× 500), (p) PA7-1 (× 1000); (q, r) PA7-3 (× 800).

modacrylic fibre. The onset of weight-loss for calcium phosphate occurs at about 70 °C, but weight-loss does not occur above 210 °C (Fig. 10). As calcium phosphate is introduced into modacrylic fibre, the weight-loss at the first step in the TGA curve for modified modacrylic fibre is very much lower than that for its virgin modacrylic fibre.

The DSC behaviour for antimony oxide is similar to that for calcium phosphate (Fig. 11). The modified modacrylic fibre exhibits a larger exotherm. The TGA curve for antimony oxide is also similar to that for calcium phosphate (Fig. 12), but the weight-loss for the modified modacrylic fibre is similar to that for unmodified modacrylic fibre.

3.2. Morphology of fibres

Fig. 13 shows that a variety of flame-retardants have an effect on the morphology of acrylic and modacrylic fibres. The change of the morphology is attributed to the rate of coagulation during spinning. It is suggested that the best spinning condition can be adjusted based on the phenomenon of the morphology. All samples in this study were spun with 55% of N,N-dimethylacetamide in a coagulation bath and at 40 °C. The

TABLE III Effect of tributyl phosphate on the properties of acrylic fibres

Sample	Drawing ratio	Tensile strength (gd^{-1})	Elongation (%)	X-ray 2θ (deg)	L_c (nm)	Orientation (%)	LOI
PA1-1	4	1.54	21.9	16.91	5.71	51.56	38.46
PA1-2	6	1.66	15.1	16.89	5.46	53.55	37.98
PA1-3	8	3.23	15.0	16.88	5.10	62.10	39.66
PA4-1	4	2.50	20.7	17.07	7.878	54.20	33.31
PA4-2	6	3.40	17.4	17.15	6.06	62.22	33.31

TABLE IV Effect of aluminium hydroxide on the properties of acrylic fibres

Sample	Drawing ratio	Tensile strength (gd^{-1})	Elongation (%)	X-ray 2θ (deg)	L_c (nm)	Orientation (%)	LOI
PA2-1	4	1.94	22.86	16.91	5.29	50.2	43.26
PA2-2	6	2.64	18.55	16.89	4.87	53.3	43.26
PA5	4	1.72	18.20	17.01	5.37	48.6	43.26

TABLE V Effect of tri(dibromopropyl) phosphate on the properties of acrylic fibres

Sample	Drawing ratio	Tensile strength (gd^{-1})	Elongation (%)	X-ray 2θ (deg)	L_c (nm)	Orientation (%)	LOI
PA3-1	4	2.56	32.5	16.90	9.18	53.8	43.3
PA3-2	6	2.75	22.6	16.90	6.32	58.7	47.0
PA3-3	8	3.52	21.3	16.86	4.58	60.0	50.0

virgin acrylic fibre exhibits a bean-shaped cross-section due to a low rate of the coagulation, as shown by sample PA4-1 (Fig. 13i). As tributyl phosphate is introduced into the spinning dope, the rate of the coagulation for the modified acrylic fibre (PA1-1) becomes fast, which results in a cross-section containing some pores (Fig. 13a). When the drawing ratio for acrylic fibre (PA1-3) modified with tributyl phosphate is increased, the rate of coagulation becomes low due to decreasing jet stretch ratio in the coagulation bath; therefore, its cross-section exhibits a bean shape containing a few pores (Fig. 13c), and its surface (Fig. 13d) exhibits many grooves which is a typical morphology of the surface for acrylic fibre spun with N, N-dimethylacetamide or N,N-dimethylsulphoxide [17]. Tri(dibromopropyl) phosphate does not affect the rate of the coagulation, and the cross-section of acrylic fibre modified with it (PA3-1 Fig. 13e) is similar to that of its virgin acrylic fibre (PA4-1 Fig. 13i). Aluminium hydroxide powder and aluminium hydroxide gel can increase the coagulation rate of acrylic fibres such as samples PA2-1 (Fig. 13g and h) and PA5 (Fig. 13k and l). The acrylic fibre modified with aluminium hydroxide powder has a more circular shape of cross-section containing many pores due to its having a higher coagulation rate, and a large size of grooves on the surface. Calcium phosphate and antimony oxide also affect the rate of coagulation for modacrylic fibre, and these flame-retardants result in more pores in the cross-section of modified modacrylic fibre than for unmodified modacrylic fibre. Sample PA7-3 has a flat cross-section (Fig. 13q) which may be produced by the drawing roller at higher drawing ratios with a high tension.

3.3. Flammability and mechanical properties

The higher the drawing ratio for unmodified acrylic fibre, the larger the 2θ angle of X-ray diffraction and the smaller the crystal size, and the higher the orientation which leads to an increase in tensile strength for acrylic fibre and a decrease in elongation, as shown by samples PA4-1 and PA4-2 in Table III. The drawing ratio does not affect the LOI value of acrylic fibre. After tributyl phosphate is added to acrylic fibre, the crystal size, orientation and tensile strength for acrylic fibre are decreased, but the LOI value can increase to 38.46 from 33.31. As the drawing ratio is increased to 8, the LOI value of modified acrylic fibre (PA1-3) increases to 39.66 due to a higher tributyl phosphate content (N% decrease in Table II) which is because the jet stretch ratio decreases.

As aluminium hydroxide powder is added to acrylic fibre, the LOI value of acrylic fibre is evidently increased as shown in Table IV. Aluminium hydroxide gel also exhibits a good flame-resistance for acrylic fibre, but the spinnability of acrylic fibre is decreased by added aluminium hydroxide gel, e.g. the maximum drawing ratio is only 4.

The crystal size for acrylic fibre modified by tri(dibromopropyl) phosphate reaches 9.18 nm (Table V) due to the good compatibility between

TABLE VI Effect of calcium phosphate and antimony oxide on the properties of modacrylic fibres

Sample	Drawing ratio	Tensile strength (gd^{-1})	Elongation (%)	X-ray 2θ (deg)	L_c (nm)	Orientation (%)	LOI
PA6-1	4	2.16	13.53	17.20	5.38	55.2	40.74
PA6-2	6	3.13	15.79	16.68	4.40	56.8	39.39
PA7-1	4	1.96	19.66	16.75	5.23	55.4	44.66
PA7-2	6	3.01	13.55	16.71	4.48	56.6	45.58
PA7-3	8	3.37	13.61	16.47	5.01	63.2	50.00
PNDC-1	4	1.51	13.80	16.49	3.95	56.9	43.80
PNDC-2	6	2.13	14.22	16.43	4.34	57.3	43.80
PNDC-3	8	3.68	13.67	16.38	4.94	66.4	43.80

acrylic polymer and tri(dibromopropyl) phosphate [4]. Therefore, the cross section for acrylic fibre modified with tri(dibromopropyl) phosphate (PA3-1) is similar to that of its original acrylic fibre (PA4-1). When the drawing ratio is increased, the LOI value of modified acrylic fibre is evidently increased due to an increase in the tri(dibromopropyl) phosphate content (N% decrease in Table II).

Unmodified modacrylic fibre (PNDC) containing 27% chlorine content with a higher drawing ratio has a decrease in 2θ angle of X-ray diffraction and an increase in the crystal size, but has no change in the LOI value (Table VI). Calcium phosphate results in a decrease in the LOI value of modacrylic fibre. When modacrylic fibre modified with calcium phosphate is stretched to a higher drawing ratio, its LOI value decreases due to an increase in calcium phosphate content (see Table II). This indicates that calcium phosphate is not a synergistic flame-retardant for acrylonitrile–vinylidene chloride copolymer. From Fig. 10, the weight-loss at the first step in the TGA curve decreases for modacrylic fibre modified with calcium phosphate, and the weight-loss at the first step is related to the content of HCl during pyrolysis and to the LOI value [3]. Antimony oxide is an excellent synergistic flame-retardant for modacrylic fibre (Table VI), and the synergistic effect is increased with the drawing ratio.

4. Conclusions

1. Tri(dibromopropyl) phosphate is an excellent flame-retardant for acrylic fibre, has a good compatibility with acrylic fibre, does not affect the cross-section of the fibre, and exhibits a good spinnability.

2. Although aluminium hydroxide powder or gel can increase the flammability of acrylic fibre, it increases the coagulation rate during spinning which results in a more circular cross-section containing many pores, and decreases the spinnability without any surfactants.

3. A synergistic effect for modacrylic fibre can be obtained by the introduction of antimony oxide; calcium phosphate is not a synergistic flame-retardant for modacrylic fibre, and results in a decrease in the flammability of modacrylic fibre.

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