

Inherent flame retardant polyester fibre using organophosphorous compounds as dope additives

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Abstract: Flame retardant polyester fibres have been produced using various organo-phosphorous compounds as melt additives. To ensure proper blending at the molecular level and stability at the spinning temperatures, four organo-phosphorous compounds with melting point lower than that of polyethylene terephthalate (PET) and boiling point higher than the processing temperature were selected. These compounds are triphenylphosphine oxide (TPPO), diphenylchloro phosphate (DPCP), phenyl phosphonic acid (PPA), and 2,4-diterbutylphenyl phosphite (DTBPP). The flame retardant polyester fibres are melt spun at 80 m/min on a laboratory melt-spinning unit and subsequently drawn-heatset. The limiting oxygen index (LOI) has been found to be in the range 25-27 at 2.5 -10.0% loading. The effect of additives on mechanical properties of fibres has been investigated and correlated with the structure of the fibres. The TPPO is found to be most appropriate additive among the selected compounds for providing adequate flame retardancy with very small loss in mechanical properties. The, flame retardant PET fibres containing 10% TPPO showed tenacity comparable to control sample. The study suggests the possibility of developing mechanically strong flame retardant polyester fibres using a more economical dope additive route.

Key Words: Flame retardant (FR), Melt additive, Limiting oxygen index (LOI), Draw ratio (DR)

I. Introduction

Flame retardant polyester fibres may be produced using variety of approaches, which includes application of flame retardant (FR) compounds on the fabric using as finishing agent, addition of FR agents as dope additives, or inclusion of FR moieties within polymer backbone. Durability and compatibility with other functional finishes are prime drawback of FR textiles developed through finishing route. The addition of FR additives in the melt is a simple and economically favourable process for obtaining inherently flame retardant fibres. However, this route has attracted less attention commercially. This is due to the fact that inclusion of necessary quantity of FR additives in melt dope may significantly affect the mechanical properties of the FR polyester fibres. Also, a wide particle size distribution of the FR additives may interfere with desirable uninterrupted and smooth melt spinning operation. Because of these reasons, FR fibres are normally produced using modified polymers containing FR moiety as a comonomer. The present work attempts to address the issue of developing high tenacity FR polyester using a simpler and less expensive FR additive route. Bajaj and Sengupta [1] discussed that, compounds of phosphorous appear to be effective flame retardant without undesirable toxic effects, and therefore, phosphorous-based compounds are appropriate applicants for producing flame retardant polyester fibres.

In a continuing effort to develop halogen free flame retardants for practical applications, in the present work, four organo-phosphorous compounds, namely, triphenylphosphine oxide (TPPO), diphenylchloro phosphite(DPCP), phenyl phosphonic acid (PPA), and 2,4-diterbutylphenyl phosphite (DTBPP) have been selected. Organo-phosphorous flame retardants primarily function in the condensed phase as carbonaceous char promoters [2,3]. The advantage of selecting compounds on spinnability and eventually on structure-mechanical properties of the fibres was investigated to ascertain their suitability for producing flame retardant fibres with good mechanical properties.

II. Experimental Details

2.1 Materials

Semi-dull chips were obtained from Modipon Fibres Company, Modinagar , UP (India). Intrinsic viscosity (η) in phenol/tetrachloroethane (60/40 wt/wt) solution at $25 \pm 1^\circ$ was found to be 0.575 dl g^{-1} . The organo-phosphorous compounds, TPPO, DPCP, DTBPP and PPA were procured from 'Aldrich Chemicals USA'. The details of the compounds are given in Table 1.

2.2 Molecular Weight

The molecular weight of PET chips is determined by intrinsic viscosity method. The chips are dissolved and prepared a polymer solution of 0.5 g/100 mol concentration in 1:1 (vol) phenol-tetrachloroethane mixture. The viscosity is measured at 25°C using Ubbelohde viscometer.

2.3 Drying of PET chips: Polyester chips are dried at 120°C/0.1 mm Hg for 10 hr in a vacuum oven. The moisture content in polyester chips after drying is measured to be about 0.011 wt%. The moisture content is measured using Metrohm 737KF coulometer and moisture extraction oven.

2.4 Moisture content of PET chips by Coulometric Karl Fischer (KF) Titration

The 737 KF coulometer is used for exact determination of small amounts of water. This method utilizes a methanolic solution of iodine, sulphur dioxide and a base as buffer. Moisture content in dried chips was measured to assure fault free melt spinning.

2.5 Blending: To 100 gm of dried poly(ethylene terephthalate) PET chips, silicone oil (500 centi poise viscosity) 0.5 wt % is added and thoroughly mixed to obtain thin coating of the oil on all the chips. Thereafter, 2.5 – 10.0 wt % of FR additives are added to the above mixer and physically mixed. The mixture is again subjected to vacuum drying for 4-5 h prior to melt spinning.

2.6 Melt spinning, drawing and heat setting: The blended, control and virgin (pure PET) samples is melt spun on a laboratory melt-spinning machine having a spinneret of length to diameter (L/D) ratio of 3.33. The as-spun polyester monofilaments are drawn on a laboratory model double step drawing machine. In two-step drawing, the first zone drawing ($\lambda_1 = 2.33$) was carried out at 90°C (filament contact time of 8 seconds) followed by second zone drawing ($\lambda_2 = 2.5$) at 120°C with filament contact time of about 6 seconds. The total Draw Ratio (TDR) was approximately 6 because initially filaments denier is very heavy. The two stage drawn samples are annealed in silicone oil bath at 160°C for 10 min under taught condition. A total stress, equivalent to 0.6 gpd was applied on the filaments during the annealing treatment.

Table 1 - Sample nomenclature and details

Sample Code	Sample details
PET ₀	Polyethylene terephthalate (PET) fibre without any additive
PET ₁	PET fibre having 0.5% silicone oil as dope additive
PET ₂	PET fibre having 2.5% TPPO as melt additive
PET ₃	PET fibre having 2.5% PPA as melt additive
PET ₄	PET fibre having 2.5 % DPCP as melt additive
PET ₅	PET fibre having 2.5% DTBPP as melt additive
PET ₆	PET fibre having 10.0 % TPPO as melt additive
PET ₇	PET fibre having 10.0% PPA as melt additive

2.7 Knitting

The FR polyester monofilaments are knitted on a Kenzler knitting machine with 18 gauge cylinder and four supply packages.

2.8 Mechanical Properties: Tensile properties of as-spun and drawn fibres were measured on Instron 4202 model by using 1 kg load cell. Samples were mounted on a paper window and tested using 25 mm gauge length and cross-head speeds are kept to maintain the breaking time 20 ± 2 s as per ASTM D3822-07

2.9 Sonic modulus: The sonic modulus of drawn and heat-set filaments are measured on PPM 5R Sonic Modulus Tester at constant tension with chart speed 25 in/min, scanner speed 2.5 in/min, and for a maximum time of 100 μ s. The sonic modulus test is performed under the guidelines of ASTM D5300. The sonic modulus (E) is calculated using the following relation.

$$E = 11.3 \times C^2$$

where C= (distance along the fibre in km)/ (transit time in μ s). An average of 10 readings was taken for calculating sonic modulus of each sample.

$$C = \frac{\text{Distance along fibre (in km)}}{\text{Transit time in (micro seconds)}}$$

2.10 Density by density gradient column:

The density values of virgin and FR polyester fibres are measured by Density Gradient Column (Devonport, London) comprising a mixture of n-heptane ($\rho = 1.28 \text{ gcm}^{-3}$) and carbon tetrachloride ($\rho = 1.48 \text{ gcm}^{-3}$) as per ASTM D-1505 as used by Bajaj and Khanna [4].

2.11 X-ray diffraction measurements

2.11.1 Crystallinity: X-ray diffraction patterns are obtained on a Philips X-ray diffractometer equipped with a scintillation counter and recorder. The x-ray diffractograms are divided into crystalline and amorphous regions according to the methods suggested by Bell and Dumbleton [5]. The samples are scanned for 2θ ranging from 10° to 30° at the rate of $1^\circ/\text{min}$ using symmetrical reflection geometry. The degree of crystallinity is evaluated using the following expression as proposed by Farrow and Preston [6].

$$X = \frac{C}{C + A} \times 100$$

where C is the area under the crystalline curve and A is the area under the amorphous curve

X: X-ray crystallinity, A: Area of amorphous region, and C: Area of crystalline region

2.12 Bi-refringence

The bi-refringence (Δn) is measured by Vickers Polarizing Microscope. The phase difference occurs due to the difference in velocities of the light waves along the parallel and perpendicular direction of the fibre axis and is calculated from the following expression.

$$\Delta n = \frac{L \times R}{t} = \frac{f}{t} = \frac{6.18 \times \text{Phase difference (nm)}}{100 \times \text{Fibre diameter } (\mu)}$$

Where, L Wavelength of polarised light, R: Retardation (phase difference), f : Retardation in specific thickness (nm) and 6.18 is the compensator constant and t is fibre diameter in micron.

2.13 FTIR studies

The micro FTIR system used in the studies comprises a Jasco Micro FTIR-200 which integrated an interferometer and infrared (IR) microscope. The spectra are recorded over a range of $700\text{--}2000\text{ cm}^{-1}$ with parallel (0°) and perpendicular (90°) polarization with respect to fibre direction.

2.14 Scanning electron microscopy (SEM)

The SEM studies are carried out on Cambridge Stereoscan Model S360 instrument. The fractured in liquid nitrogen, in which the break was closed to the middle of the fibre, were mounted on the sample disc and subjected to scanning by SEM to understand the fracture behaviour.

2.15 Limiting oxygen index (LOI)

The LOI measurements are performed on Stanton Redcroft FTA flammability unit as per the ASTM D-2863, by measuring the minimum amount of oxygen required to sustain the combustion. All tests are conducted in vertical sample position under O_2/N_2 mixture and flame from top as described by Dutkiewicz *et. al*⁸.

III. Results and discussion

3.1 Physico-mechanical Properties

The density of drawn virgin polyester fibres is 1.379 g.cm^{-3} . In case of FR polyester fibres, the density decreases with increase in FR filler. However, the drop is maximum in PET_4 ($\rho=1.359\text{ gcm}^{-3}$) having DPCP liquid FR. Yield stress of PET_0 and PET_6 is found to be around 0.4 gpd when the winding speed was kept 80 m/min. Natural draw ratio (NDR) and Maximum Draw ratio (MDR) has also been calculated from the stress-strain curves of PET_0 and PET_6 as-spun fibres. The NDRs of PET_0 and PET_6 are found to be 3.0 and 4.5, respectively. This indicates that strain hardening and stress induced crystallization occurs at a later stage, at higher draw ratio in PET_6 fibre. This is also verified by FTIR data in Table 4 showing higher gauche content in PET_6 fibre at draw ratio 5.0 which is attributed due to more coiling of the molecular chains.

Discernible trends in tenacity values are obtained for two FR additives, PPA and TPPO. The tenacity decreased with increasing concentration of TPPO in the range of 2.5 to 10% as shown in Table 2. Furthermore, the sample containing PPA were found to be brittle in nature at higher loading than 2.5%. In comparison, extensibility in TPPO containing FR-PET samples remained high for all samples. These trends may be explained on the basis of chemical nature of additives. The PPA is reactive additive and may react with PET chains presumably to form cross-linked structure. On the other hand TPPO is a non reactive additive and would only reduce the inter-molecular chain interactions.

Table 2 Mechanical properties of flame retardant polyester fibres

Specimen	Tenacity (gpd)	Elongation (%)	Initial Modulus (gpd)	Limiting Oxygen Index LOI
PET ₀	3.98	28.9	139.8	21.0
PET ₁	3.97	29.1	138.5	21.0
PET ₂	3.3	28.7	135.8	24.5
PET ₃	2.7	26.8	80.9	25.5
PET ₄	3.4	21.4	125.7	24.2
PET ₅	2.9	27.5	119.3	24.5
PET ₆	2.9	40.4	104.0	27.5
PET ₇	Brittle in nature			27.4

Values of initial modulus for PPA containing FR-PET showed an interesting trend. Compared to virgin PET, initial modulus of FR polyester fibres with 2.5% PPA decreased by about 45%. However, with increasing concentration of PPA from 2.5 % to 10.0 % in FR polyester, the fibre becomes brittle. On the contrary, FR polyester fibres with TPPO in general, showed lower initial modulus values compared to FR polyester with PPA as shown in Fig.1. From the above results, PPA was found to be unacceptable FR additive since its reactive nature resulted in mechanically brittle fibres. Whereas, TPPO did not show any undesirable effect except its mechanical properties were lower than that of virgin PET.

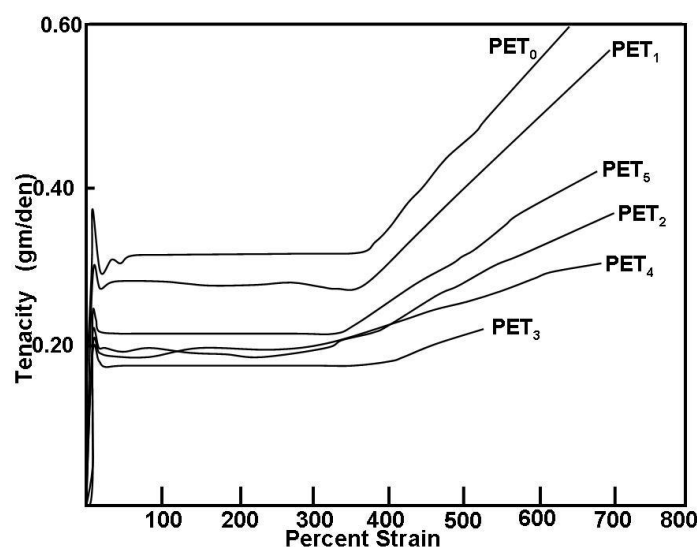


Fig. 1 Stress-Strain behaviour of as-spun FR PET fibres

Table 3 Mechanical Properties of Drawn and As-spun fibres

Samples	Den/filament	Tenacity (gpd)	Elongation at break	Initial Modulus (gpd)
As spun Fibres				
PET ₀	150.0	0.61	692.7	12.1
PET ₆	146.0	0.39	643.1	12.7
Drawn Fibres				
PET ₀ (DR 5.0)	35.0	3.98	28.9	135.8
PET ₀ (DR 9.0)	25.0	5.45	10.2	156.7
PET ₆ (DR5.0)	33.0	3.3	30.6	134.6
PET ₆ (DR9.0)	26.7	4.56	14.5	163.1

Tensile tests have been conducted on as-spun state and compared in Fig: 1. Now, it is easy to conclude that the presence of FR additives decreasing the yield stress than virgin PET (PET₀). The elongation at break in presence of FR additives is significantly decreasing only in presence of PPA which may be attributed to its reactive nature with PET polymer. The maximum tensile strength at break is also decreasing in presence of FR additives which indicates that PET is a specific polymer which does not accept any impurities easily in its morphology.

Natural draw ratios (NDR) of the FR-PET fibres are around 3.0 to 4.0 respectively at 2.5 % loading, and maximum draw ratios (MDR) are 5.4 to 6.8. This suggested that the strain hardening and stress-induced crystallization in FR PET fibres would occur at similar draw ratio to PET₁ fibres except PPA containing PET₃. This was also verified by polarized micro-FTIR analysis of the samples, which showed high gauche content in PET₆ fibres drawn at draw ratio 4.0. The gauche content is attributed due to coiling of the molecular chains.

Also, a higher value of MDR in TPPO filled sample indicated that higher drawing of the as-spun fibres might lead to better tensile properties.

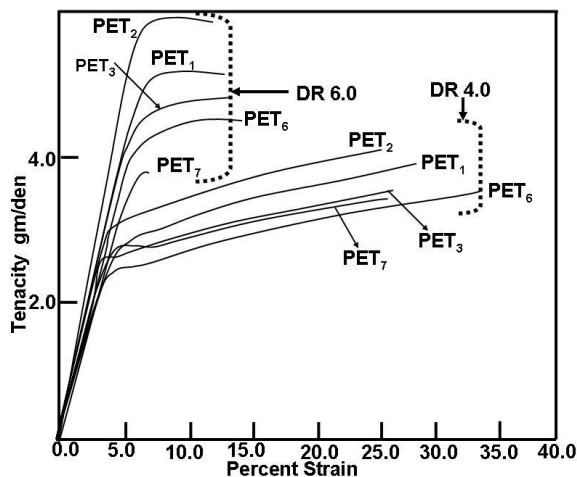


Fig. 2. Effect of drawing on mechanical behaviour FR-PET fibres with TPPO and PPA

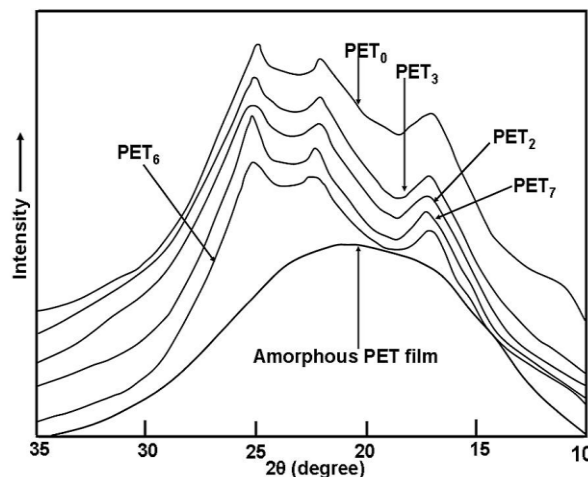


Fig.3 X-ray diffraction of FR PET Fibres

Tenacity decreases with increasing concentration of TPPO in the range of 2.5 % to 10%. These trends may be explained on the basis of chemical nature of additives. TPPO is non reactive additive, which would only reduce the inter-polymer chain interactions. However, these trends should be read with caution, as experiments are not optimized and some more exercise is necessary to optimize the trend.

Drawn fibres

It is evident from Table 3 that FR dope additives have significant effect on the mechanical properties of FR fibres. The tenacity of most of the FR fibres is in the range of 2.7 to 3.4 gpd at DR 5.0 which is 15-32% lower than that of regular PET. Fibre samples PET₀ and PET₆ are drawn using two-stage drawing. Interestingly, there is a remarkable improvement in mechanical properties (Table 3). Tenacity increases from 3.3 to 4.56 gpd in PET₆ fibre. Initial modulus also increases from 134.6 to 163.1 gpd. This may be attributed to strain hardening and stress induced crystallization at a high draw ratio as suggested by Sengupta [8]. By comparing the stress-strain behaviour of PET₀ and PET₆ at DR 9.0 it is observed that tenacity of PET₆ is 4.56 which is lower than PET₀ (5.45 gpd) but elongation at break in PET₆ is higher than PET₀ and as an indication of plasticization effect of TPPO.

Higher value of initial modulus in PET₆ may be attributed to its higher orientation as observed from birefringence (Δn) from Table 5. It is concluded here that TPPO has encountered better compatibility with PET as clearly visible by tensile behaviour even at 10 % loading.

FTIR

Two fibres, PET₀ and PET₆ are considered for FTIR spectra as shown in Fig. 4-7. Gupta et al., [9] has reported that transient changes in crystalline and amorphous orientation can be derived from dichroic function of 972 cm⁻¹ and 1578 cm⁻¹ absorption bands respectively. Gupta et al. [9] and Siesler et al. [10] suggested that the absorption bands at 1342, 972 and 846 cm⁻¹ have been assigned to the trans-conformation of the PET molecule, whereas the absorption band at 1370 cm⁻¹ and 896 cm⁻¹ belong to gauche conformation. Dichroic functions of the absorption bands at 1410 cm⁻¹ and 875 cm⁻¹ have been reported to represent overall molecular orientation. The gauche content is calculated from the total absorbance of the gauche band at 1370 cm⁻¹ as reported by Jain and Gupta [17] where absorbance parallel to fibre axis ($A_{||}$) and absorbance perpendicular to fibre axis A_{\perp} are absorbance bands measured with radiations polarized parallel and perpendicular to the fibre axis respectively taking absorbance band 1506 cm⁻¹ as reference (Table 4).

$$A_0 = \frac{(A_{||} + A_{\perp})}{3}$$

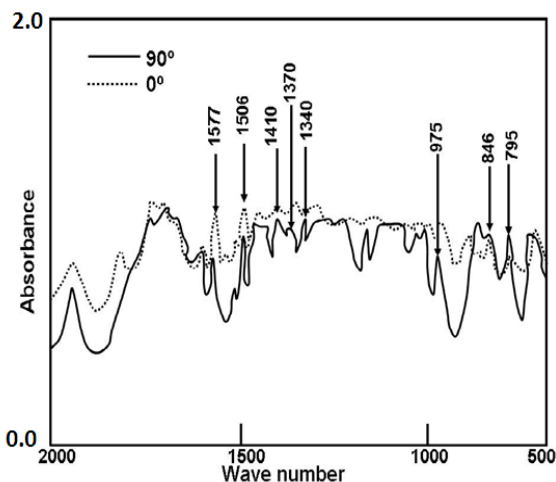


Fig. 4 FTIR Spectra of PET₀ DR 5.0

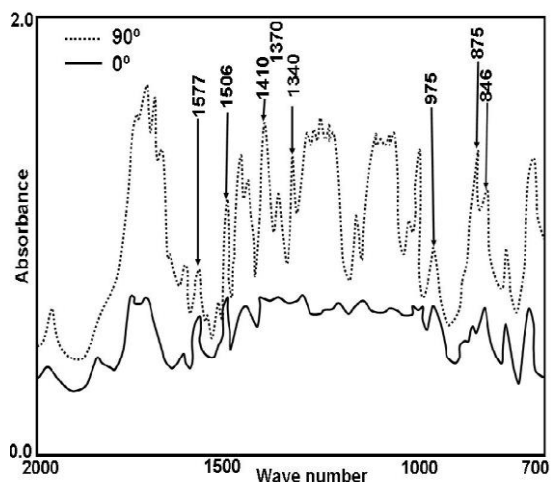


Fig. 5 FTIR Spectra of PET₀ DR 9.0

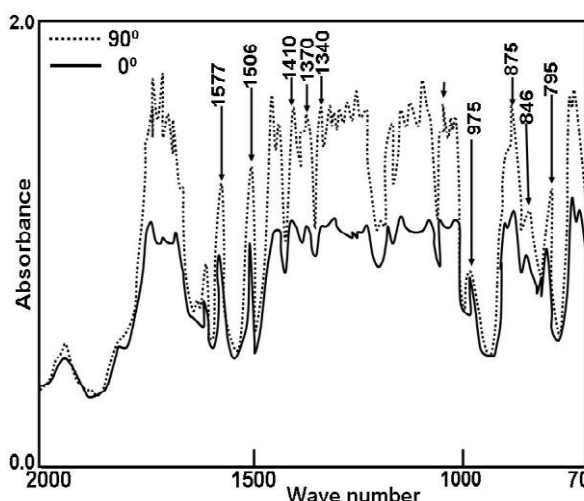


Fig. 6 FTIR Spectra of PET₆ DR 5.0

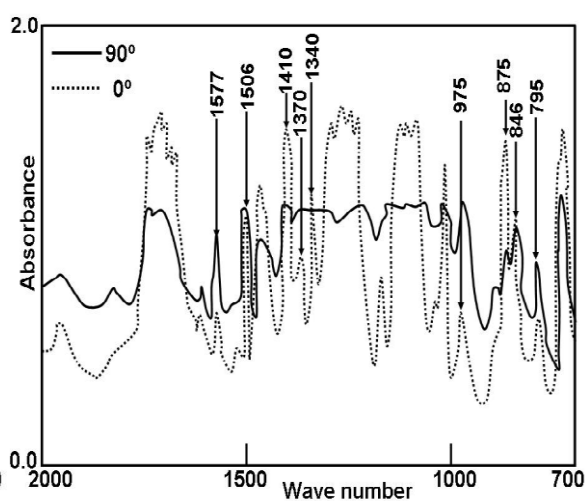


Fig. 7 FTIR Spectra of PET₆ DR 9.0

The dichroic function (DF) has been calculated from the absorbance ratios in parallel and perpendicular direction. Dichroic function (DF) which is a measure of orientation has been defined by Garlton et al., [11].

$$DF = \frac{D-1}{D+2} = P_2(\theta_m) - \langle P_2(\theta) \rangle_{ir}$$

where, $P_2(\theta_m) = \frac{1}{2}(3\cos^2\theta_m - 1)$ is a constant quantity determined by the angle θ_m between the transition moment of the absorbing group and the chain axis of the polymer depending only on the molecular structure of the polymer. The quantity $\langle P_2(\theta) \rangle_{ir}$ is defined as the mean value

$P_2(\theta_m) = \frac{1}{2}(3\cos^2\theta_m - 1)$ as determined by the infrared method and is the absolute measurement of the

chain axis orientation. If the volume θ_m is known from other experiments or structural data, we can determine the absolute orientation factor, $\langle P_2(\theta) \rangle$ from the measured infrared dichroic functions.

Table 4 FTIR study of FR-PET fibres

Wave number cm ⁻¹	Absorbance				Assignment	
	Polarization	PET ₀ DR 5.0	DR 6.0	PET ₆ DR 5.0		DR 6.0
972/1506	parallel	0.961	0.994	0.802	1.033	CH ₂ -O Stretching
	perpendicular	1.078	0.837	0.623	0.653	Trans-conformation
1342/1506	parallel	1.008	1.023	1.036	0.971	Trans-conformation
	perpendicular	1.063	1.181	1.153	0.905	Trans-conformation
1370/1506	parallel	1.008	1.019	1.019	1.004	Gauche conformation
	perpendicular	1.045	1.020	1.153	0.883	
1578/1506	parallel	0.977	0.914	0.932	0.875	Amorphous orientation
	perpendicular	0.885	0.751	0.910	0.651	

Dichroic functions (DF) at wave number 972 cm⁻¹ and 1578 cm⁻¹ have been calculated for comparative study of trans- and amorphous orientation respectively. The DF at wave number 972 cm⁻¹, for PET₀ fibre at draw ratio 5.0 is 0.037 which increases to 0.06, when the fibre is drawn to DR 6.0. Similarly in PET₆ fibre, the DF increases from 0.087 to 0.164 by increasing the draw ratio in same manner. This is attributed to the increase in trans-orientation with draw ratio, which is higher in FR fibre PET₆. The amorphous orientation, which is represented by DF at wave number 1578 cm⁻¹ increase with draw ratio in both set of samples and is also higher in FR fibre PET₆ at DR 6.0. Thus, it is evident that starting with the randomly oriented sample DR 5.0, a significant increase in orientation of amorphous and crystalline region is observed after drawing. This may be attributed to the alignment of molecular chains parallel to the fibre axis. It is clearly evident that most mechanically successful FR fibres among the ones studied here in this study PET₆ is not lacking at fine structure level from virgin PET fibre (PET₀).

Siesler¹¹ has utilized absorbance of 972cm⁻¹ to analyse changes in crystallinity during drawing. In PET₀, the difference in absorbance at draw ratio 6.0 and 5.0 is 0.301, whereas as in PET₆ fibre it is 0.295. Hence, the crystallinity appears to increase in both fibres with draw ratio due to stress-induced crystallization. The gauche content as calculated from wave number 1370 cm⁻¹ is high in PET₀ and PET₆ at DR 5.0. It exhibited lower value in both fibres at DR 6.0 due to increasing crystalline content due to the implementation of crystallization process during drawing in which some of the gauche- conformations in amorphous region might have been converted to trans-conformations because of reorganization of molecular chains as reported by Koul et al¹³. Thus, the dichroic functions and gauche content revealed that high degree of orientation persists in PET₆ fibre at draw ratio 9.0. Birefringence values of these samples also support the high overall orientation of PET₆ fibre as observed from FTIR spectra.

Birefringence

The birefringence is the measurement of overall orientation of amorphous and crystalline segments and birefringence data are presented in Table 5. Birefringence measurement of virgin and FR fibres drawn to DR 5.0 did not display any prominent fringe. Therefore, the fibres were subsequently drawn to total draw ratio 6.0 by two-step drawing. The birefringence of drawn PET₀ is 0.192 which is decreased in case of PET₃ to 0.137 and indicates that the presence of PPA is decreasing the possibility of molecular chain straightening. This may be attributed to the reactive nature of the PPA. In TPPO filled FR-PET fibres, the birefringence value increases from 0.163 at 2.5% loading to 0.258 at 10% loading. As stated earlier the higher orientation in these samples reflected in terms of birefringence may be attributed to plasticization effect.

X-ray diffraction studies

X-ray diffraction is the most effective way to infer the crystal structure of polymers. The PET has a triclinic crystal structure. X-ray crystallinity data are given in Table 5. In the diffraction pattern of PET, sharp peaks come into sight where the 2θ angles values are 17.34, 22.48 and 26.20 corresponding to the [0, 1, 0], [1, 1, 0], and [1, 0, 0] crystal faces, respectively. WAXD patterns of FR-PET filaments drawn by two-step drawing at 90°C and 120°C temperature of first and second heater plate respectively are scanned and some representative WAXD patterns are compiled in Fig 13. At 2.5% loading of organo-phosphorous compounds, the position and shape of diffraction peaks of FR fibres in WAXD patterns are similar to those of virgin PET fibre PET₀ except PET₃, indicating that these melt additives have not destroyed the crystal structure of PET. As the loading of TPPO has increased to 10%, TPPO has still maintained compatibility by exhibiting sharp reflections as PET.

Table 5 Physico-mechanical Properties of FR Polyester Fibres (DR 9.0)

Specimen	Density g cm ⁻³	X-ray Crystallinity %	Birefringence Δn	Sonic modulus gpd
PET ₀	1.379	25.9	0.192	172.0
PET ₂	1.375	23.7	0.164	153.0
PET ₃	1.365	28.0	0.137	148.5
PET ₄	1.359	23.8	0.127	097.1
PET ₅	1.364	25.8	0.173	145.4
PET ₆	1.362	20.9	0.258	125.0
PET ₇	1.370	33.0	Did not possible to measure	169.0

WAXD patterns of drawn virgin and FR fibres clearly indicate that the crystalline lattice is not affected by the incorporation of FR additives.

WAXD patterns show sharp peaks at $2\theta = 17, 23, \text{ and } 25^\circ$ for both virgin and FR fibres (Fig.3). The PPA filled fibres are showed sharper peaks which may be attributed to the formation of perfect crystals with uniform size distribution. In 2.5% TPPO loaded FR fibre; the crystallinity is only 23.7%, which further decreases to 21% at 10% loading. The broader peaks in TPPO filled PET fibres indicate broad crystal size dispersion. Koul et al., [13] have reported similar behaviour of BaSO₄ filled PET.

SEM Studies

The SEM investigation is concentrated on Virgin PET, mechanically most successful FR-PET fibre (PET₆) and mechanically most un-successful FR-PET fibre (PET₇) and compiled in Fig. 8. In PET₀, tensile rupture results in the formation of a V-notch. The fibre appears to have a skin and core structure. A V-notch is observed which appears to be confined to the skin. On reaching the core, the crack propagates transversely without any further appreciable extension of the remaining part of the fibre. In the core, along the fibre axis, there are layered plates like structural entities. The V-notch faces the platelet sideways. Mechanism of V-notch formation, as explained by Gupta et al., [12], a crack is initiated in the fibre surface, and while the crack propagates, the rest of the fibre is still stretched. This results in the formation of V-notch. In PET₆, fibre rupture seems to have occurred from the core indicating improved adhesion between TPPO filler and the PET matrix. Failure appears to be more ductile in nature, clearly suggesting the role of TPPO in integrating with the polymer substrate. Koul¹³ has reported similar type of fracture in case of fillers like BaSO₄ and coupling agents. In PET₇ fibre, failure seems to be like a stake and socket type as reported by Hearle[14]. This type of failure is reported to occur in PET fibres after prolonged hot wet treatment or by the presence of reactive chemicals.



Fig. 8 SEM Scans of fractured FR PET fibres

As discussed earlier, in mechanical properties that FR fibres containing PPA are brittle in nature, perhaps due to some reaction with PET which needs further investigation.

Limiting Oxygen Index (LOI)

Limiting oxygen Index is the measurement of required amount to oxygen to sustain the fire on any subjective substrate. The LOI of virgin PET is 21 as given in Table 2. The substrate which require more than 24% oxygen to sustain flame are called as flame retardants. It is evident from Table 2 that most of the FR fibres exhibited the LOI value higher than 24. The sample PET₆ and PET₇ containing 10 % TPPO and 10% PPA showed LOI values more than 27.

Conclusion

Modification of PET fibre by dope additive route is easier than other available methods to develop inherent flame retardancy. The addition of organophosphorus compounds can give PET better flame retardancy and almost similar tensile properties in PET. TPPO has proved the best dope additive in order to incorporate

inherent flame retardancy in PET fibres. Moreover, TPPO act as a plasticizing agent, and facilitates the movement of molecular chains during drawing s crystallinity. Tensile behaviour of TPPO containing FR PET proved that TPPO has better compatibility with PET at molecular level even at 10 % loading. Diphenylchloro phosphate (DPCP) and 2,4-diterbutylphenyl phosphite (DTBPP) have also exhibited potential to be used as FR dope additives to create inherent flame retardancy in PET fibres. The nature of phenyl phosphonic acid (PPA) is reactive with PET hence it cannot be suggested as dope additive to manufacture inherent FR PET fibres. Organo-phosphorus compounds such as triphenyl phosphine oxide (TPPO) can be used as effective FR melt additive up to 10% loading in regular PET to provide FR fibres with LOI value of 27.5.

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