

# Thermal Characteristics of Poly(ethylene Terephthalate) Fiber Grafted with Poly(vinyl Acetate) and Poly(vinyl Alcohol)

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## Synopsis

Poly(ethylene terephthalate) (PET) fibers were grafted with poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (PVA). The effects of graft copolymers PVAc and PVA on morphological properties of PET were evaluated by differential thermal analysis, differential scanning calorimetry, and thermogravimetric analysis. Melting temperature, heat of fusion, and mass fractional crystallinity of PET was not affected by graft PVAc and PVA. No individual glass transition and melting points corresponding to the graft PVAc and PVA were observed, indicating thereby that graft copolymer mainly exists in the form of free chains inside the PET matrix. Poly(vinyl alcohol) graft copolymer degraded at much lower temperatures than poly(vinyl alcohol) in powder form. Thermal stability of PET fiber was not affected by graft PVAc, where as PET-g-PVA showed an additional degradation point at 360°C.

## INTRODUCTION

Polyester fibers were grafted with poly(vinyl acetate)<sup>1</sup> and poly(vinyl alcohol)<sup>2</sup> so as to have fibers with controlled hydrophobic/hydrophilic balance. Dyeing characteristics of grafted polyester fibers with disperse dyes were evaluated in relation to the graft.

It was observed that PET-g-PVAc had higher saturation dye uptake,<sup>3</sup> whereas in case of PET-g-PVA saturation dye uptake increased up to a certain value and then decreased with increase in PVA content.<sup>4</sup> These observations lead one to believe that disperse dye uptake increases with hydrophobicity of the fiber which is not in agreement with previous reports such as decrease in dye uptake with increase in acetylation of cellulose acetate fiber<sup>5</sup> and increase in dye uptake with increase in hydrophilicity of polyester-graft-acrylic acid/acrylonitrile fibers.<sup>6</sup>

Dyeing characteristics to a great extent are determined by morphological structure of the fiber, and, since in previous reports<sup>5,6</sup> these factors were not assessed, it was difficult to arrive at any specific common conclusion.

Morphological structural parameters of PET-g-PVAc and PET-g-PVA were evaluated by IR, X-ray diffraction and optical birefringence methods, and it was observed that the crystallinity index, crystallite size, crystalline orientation, and lattice parameters of polyester fiber were unaffected by grafting of poly(vinyl acetate)<sup>7</sup> and poly(vinyl alcohol).<sup>8</sup>

Infrared, X-ray, and optical methods at normal room temperature give structural characteristics at static conditions, whereas dyeing is carried out at higher temperatures, at which the relative influence of the graft on the morphology of the fiber with respect to temperature shall be a more appropriate indicator of the dyeing behavior and hence, in continuation of the above work, thermal characterization of grafted PET fiber was carried out.

## EXPERIMENTAL

### Materials

#### *Fiber (PET)*

Polyester fibers were poly(ethylene terephthalate) (PET) monofilaments. 3.16 denier, drawn and dull in luster, manufactured by J. K. Synthetics, Ltd. (India).

#### *Polyester Fibers Grafted with Vinyl Acetate (PET-g-PVAc)*

Poly(ethylene terephthalate) (PET) fibers were grafted with vinyl acetate in presence of methanol and 1,2-dichloroethane by one-step simultaneous swelling and irradiation technique using gamma radiation from cobalt 60.<sup>1</sup>

#### *Polyester Fibers Grafted with Poly(vinyl Alcohol) (PET-g-PVA)*

Polyester fibers were initially grafted with poly(vinyl acetate) using  $\gamma$ -radiation. Graft poly(vinyl acetate) was selectively hydrolyzed using 10% hydrochloric acid at 100°C for predetermined period.<sup>2</sup>

### Differential Thermal Analysis (DTA)

Differential thermal analysis was carried out using an AMINCO thermal analyzer.

Fibers were cut into fine pieces of about 200 mesh in size. About 25–40 mg of the cut fiber was placed sandwiched between two layers of calcined alumina in the sample holder. The reference cell was filled with an equivalent amount of calcined alumina. Nitrogen gas was passed to purge the apparatus and the rate of heating was adjusted to 6°C/min.

Thermograms were recorded from 23°C to 400°C under nitrogen atmosphere.

### Heat of Fusion ( $\Delta H$ )

$\Delta H$  was estimated using ultrapure benzoic acid as the standard, with melting point 122.3°C and heat of fusion equivalent to 33.9 cal/g.

Heat of fusion was calculated as

$$\Delta H = 33.9 \frac{A_1 W_2}{A_2 W_1}$$

where  $A_1$  and  $A_2$  are the areas and  $W_1$  and  $W_2$  the weights corresponding to fiber and the benzoic acid, respectively.

### Percentage Crystallinity

Mass percentage crystallinity  $\beta$  is given by

$$\beta = \frac{\Delta H}{\Delta H_f} \times 100$$

$\Delta H$  is the measured heat of fusion of the fiber and  $\Delta H_f$  is the heat of fusion of completely crystalline PET. Heat of fusion ( $\Delta H_f$ ) was taken as 28.1 cal/g.<sup>9</sup>

Correction due to graft was applied in the case of grafted polyester fibers.

### Differential Scanning Calorimetry (DSC)

Differential scanning calorimetric studies were carried out using a Perkin-Elmer DSC-IB instrument.

About 10 mg of the finely cut fiber was accurately weighed in a pan, closed with a lid, and sealed under pressure. It was placed on the sample holder, and an empty pan of identical weight was used as the reference. The apparatus was purged with nitrogen gas and then cooled with liquid nitrogen.

Scanning was done from  $-32^\circ\text{C}$  to  $300^\circ\text{C}$  under nitrogen atmosphere at a rate of heating of  $16^\circ\text{C}/\text{min}$  and a range of 8 mcal/s.

### Heat of Fusion ( $\Delta H$ )

$$\text{Heat of fusion } \Delta H = \frac{A \times R \times 60}{A_0 \times W}$$

$A_0$  = area of rectangle defined by chart width  $\times$  chart speed (unit length/min)

$A$  = area under fusion peak

$W$  = weight of sample (mg)

$R$  = range (8 mcal/s)

### Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis was carried out using AMINCO thermal analyzer with attached TGA unit.

The TGA apparatus consists of a vertical double spring balance with an attached transducer unit and a sample holder at the bottom end. A movable thermostatically controlled electric furnace was used to heat the sample at desired rates.

About 100–200 mg of finely cut fiber was weighed accurately in a crucible and kept in the sample holder, which was placed in a pyrex glass furnace tube. The spring-balance chamber was maintained at a constant temperature of  $55^\circ\text{C}$  by water circulation through a double-walled glass chamber. The instrument was then calibrated and the sensitivity adjusted to 10 mg/in. of the chart deflection.

The sample was heated under vacuum ( $50 \mu\text{m Hg}$ ) at  $6^\circ\text{C}/\text{min}$ , and the loss in weight of the sample was recorded against temperature from  $23^\circ$  to  $400^\circ\text{C}$ .

In all the above cases, thermal analysis was carried out only up to  $400^\circ\text{C}$ , as further experimentation had no bearing on morphological characteristics due to predominant degradation of PET.

TABLE I  
Effect of Poly(vinyl Acetate) Graft on Heat of Fusion and Percentage Crystallinity of the Grafted Polyester Fibers

Fiber graft PVAc	$T_m$ ( $^{\circ}\text{C}$ )	Heat of fusion (cal/g)	Crystallinity (mass %)
PET (control)	248	12.20	43.4
5	248	11.48	41.0
10	251	11.48	41.0
15	249	11.48	41.0
20	249	11.52	41.0
25	250	12.55	44.6

## RESULTS AND DISCUSSION

The heats of fusion, crystallinity (mass fractional crystallinity) and melting temperatures of polyester fibers grafted with poly(vinyl acetate) are given in Table I.

It is apparent that neither heat of fusion nor percentage crystallinity of PET is changed due to grafting of poly(vinyl acetate), which is in agreement with infrared and X-ray investigations.<sup>7</sup> DTA thermograms are shown in Figure 1.

Thermal characteristics of polyester fibers grafted with poly(vinyl alcohol) were investigated by differential scanning calorimetry. Heats of fusion and percentage crystallinity of polyester fibers grafted with poly(vinyl alcohol) at different percentage levels are shown in Table II. The average value of heat of fusion was found to be 12.6 cal/g, and percentage crystallinity, 45%. In this case also it is evident that graft poly(vinyl alcohol) did not appreciably alter the heat of fusion and the crystallinity of the polyester fiber. Similar inference was drawn from X-ray and IR analysis.<sup>8</sup> Thermograms are shown in Figure 2.

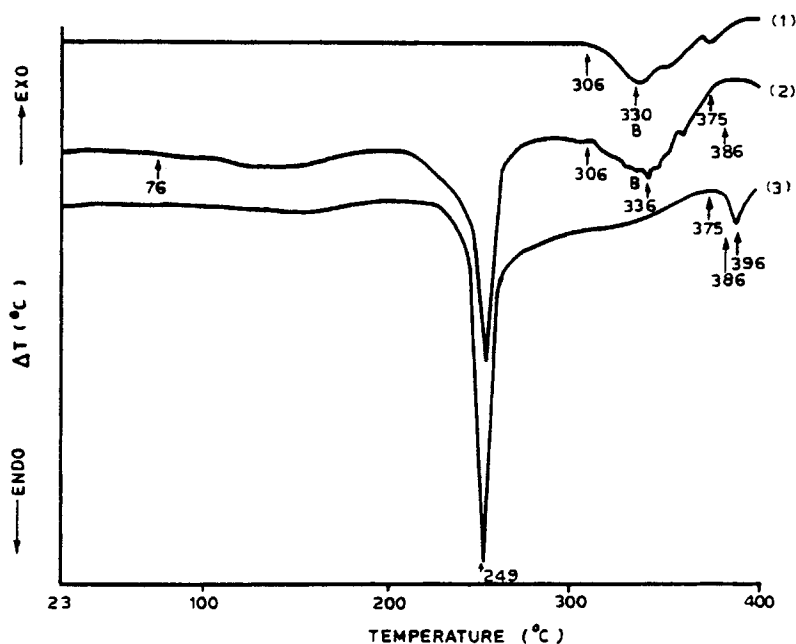


Fig. 1. DTA Thermograms: (1) PVAc, (2) PET-PVAc, (3) PET.

TABLE II  
Effect of Poly(vinyl Alcohol) Graft on Heat of Fusion and Percentage Crystallinity of the Grafted Polyester Fiber

Fiber graft (PVA)	$T_m$ (°C)	Heat of fusion (cal/g)	Crystallinity (mass %)
PET (control)	252	11.62	41.3
PET (acid-treated)	254	13.20	47.0
3.0	257	12.46	44.5
5.8	257	13.40	47.7
7.5	255	12.44	44.3
9.7	255	12.35	44.0
13.0	254	12.40	44.0
15.6	254	12.89	45.9

Thermogravimetric data for poly(vinyl alcohol) powder, poly(vinyl acetate) bulk form, and poly(ethylene terephthalate) fiber is represented in Figure 3.

Loss in weight due to bound moisture in the case of PVA was of an order of 2.6%. Thermal degradation was apparent at about 234°C and no loss in weight was evident after 290°C up to 410°C. Total loss in weight at 290°C equaled 63.5%.

Poly(vinyl acetate) started degrading at about 300°C and loss of weight at 386°C was 67.5%. No further loss in weight was noticed up to 420°C.

Thermogravimetric plots for PET-*g*-PVAc and PET-*g*-PVA are shown in Figures 4 and 5.

In the case of PET-*g*-PVAc the degradation point at 300°C indicates loss in weight due to poly(vinyl acetate) degradation. The plateau at 372–386°C indicates complete degradation of poly(vinyl acetate) due to the loss of acetic

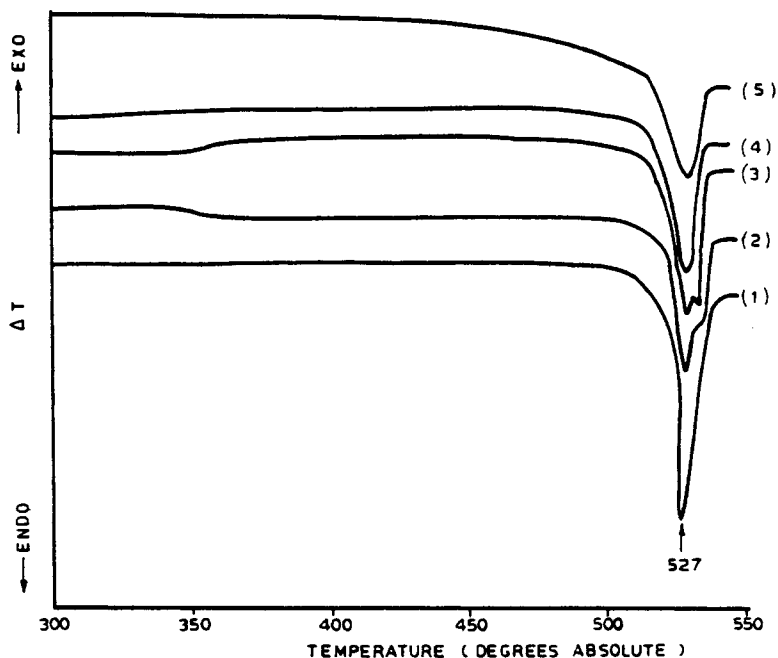


Fig. 2. DSC thermograms for PET fiber grafted with PVA: (1) PET (control), (2) PET (hydrolyzed), (3) PVA graft—3%, (4) PVA graft—9.7%, (5) PVA graft—15.6%.

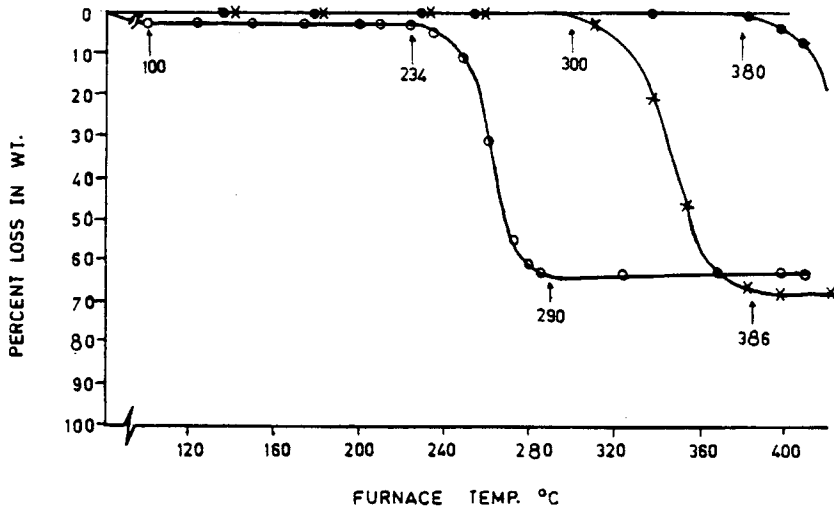


Fig. 3. Dynamic thermogravimetric plots: (●) PET, (X) PVAc, (O) PVA. Rate of heating, 6°/min.; Vacuum, 50  $\mu$  of Hg.

acid.<sup>9-11</sup> Loss in weight after 386°C is due to degradation of PET fiber (Fig. 4). The differential thermogravimetric plot showed maxima at 350°C and minima at 380°C (Fig. 5), which corresponds to PVAc degradation peaks.

From the above results it is obvious that graft poly(vinyl acetate) and polyester (PET) behaves like an intimate mixture at elevated temperatures.

Poly(vinyl alcohol) is known to degrade in two stages: The first stage occurs around 240°C and is due to dehydration accompanied with some volatile products. During the second stage, aldehydes and low molecular weight compounds are formed between 260°C and 390°C; however, yellow oil is liberated after 400°C.<sup>12,13</sup>

The reported temperatures corresponding to different degradation stages of

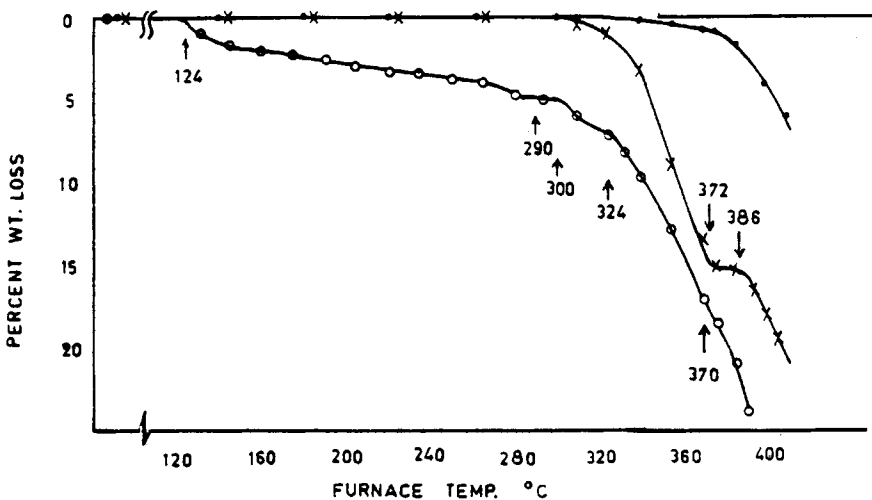


Fig. 4. Dynamic thermogravimetric plots of grafted PET fiber: (●) PET, (X) PET-grafted PVAc, (O) PET-g-PVA. Rate of heating, 6°C/min.; vacuum, 50  $\mu$  of Hg.

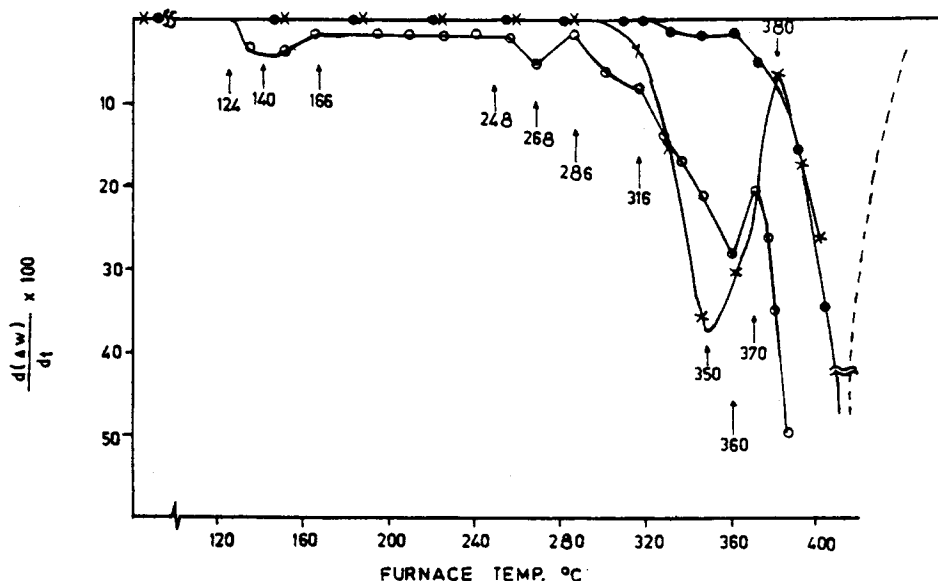


Fig. 5. Differential thermogravimetric plots for grafted PET fibers: (●) polyester, (X) PET-grafted PVAc (O) PET-*g*-PVA. Rate of heating, 6°C/min; vacuum, 50  $\mu$  of Hg.

PVA are not consistent.<sup>12-17</sup> This may be due to different experimental parameters or to a different molecular configuration of poly(vinyl alcohol).

In the case of PET-*g*-poly(vinyl alcohol), loss in weight due to degradation was evident at 124°C and attained a plateau at 290°C; further loss in weight was observed between 300–324°C. After 324°C there was a steep fall in the curve up to 370°C; further, this loss in weight was still faster, as indicated by a sharp change in the slope of the curve (Fig. 4).

The differential TGA plot for PET-*g*-PVA show a peak within the temperature range of 124°C to 140°C, which also corresponds to the glass transition temperature range of highly oriented polyester fiber. This leads one to the conclusion that graft PVA starts degrading at temperatures corresponding to  $t_g$  of polyester fiber. It is obvious that graft chains being held in the PET matrix are not free to relate below the glass transition temperature of the fiber and thermal degradation is possible only at temperatures higher than  $t_g$ , where free molecular vibrations are possible.

At lower temperatures, poly(vinyl alcohol) degrades by elimination of water due to the interaction between two adjacent hydroxyl OH; thus, in the case of individual PVA chain, the degradation temperature is expected to be much lower than that of bulk PVA, where the movement of OH groups is restricted, due to excessive hydrogen bondings. Similarly, in the case of PVA fiber, thermal vibrations of OH groups are further restricted, due to the high degree of orientation crystallization and cohesive forces, and, consequently, is found to have higher transition and degradation temperatures.<sup>16</sup>

Under identical experimental conditions, poly(vinyl alcohol)-graft-polymer degrades at lower temperatures compared to PVA in powder form (Figs. 3 and 4), indicating thereby that graft PVA is more in the form of free macromolecular chains.

## CONCLUSIONS

The melting point, heat of fusion, and mass fractional crystallinity of polyester fiber is not affected by graft poly(vinyl acetate) or poly(vinyl alcohol), indicating thereby that grafting takes place predominantly in amorphous region without influencing the crystalline nature of the fiber.

Graft copolymers PVAc and PVA do not show any separate glass transition or melting points and mainly exist as free macromolecular chains embaded in polyester matrix.

The overall behavior of PET-*g*-PVAc is like PET-blend-PVAc, whereas the thermal stability of PET is lowered by graft poly(vinyl alcohol).

## References

1. S. A. Faterpeker and S. P. Potnis, *Angew. Makromol. Chem.*, **90**, 69 (1980).
2. S. A. Faterpeker and S. P. Potnis, *Angew. Makromol. Chem.*, **93**, 111 (1981).
3. S. A. Faterpeker and S. P. Potnis, *Text. Res. J.*, **51**(7), 250 (1981).
4. S. A. Faterpeker and S. P. Potnis, *Text. Res. J.*, **51**(8), 502 (1981).
5. C. L. Bird and G. Tabbron, *J. Soc. Dyers Colour.*, **76**, 217 (1960).
6. P. D. Kale and H. T. Lokhande, *J. Appl. Polym. Sci.*, **19**, 461 (1975).
7. S. A. Faterpeker and S. P. Potnis, *Angew. Makromol. Chem.*, to appear.
8. S. A. Faterpeker and S. P. Potnis, *Angew. Makromol. Chem.* to appear.
9. B. B. Troitskii, G. A. Razuvaev, L. V. Khokhlova, and G. N. Bortnikov, *J. Polym. Sci. Symp.*, **42**, 1363 (1973).
10. E. Mihai, A. C. Biro, Ana Om, and L. A. Schneider, *Makromol. Chem.*, **175**, 3437 (1974).
11. A. Servotte and V. Desreux, *J. Polym. Sci. C*, **22**, 367 (1968).
12. Yoshio Tsuchiya and Kikuo Sumi, *J. Polym. Sci., A-1*, **7**, 3151 (1969).
13. B. Kaesche-Krischer, *Chem. Eng. Technol.*, **37**, 944 (1965); cf. Lio Reich, *Macromol. Rev.*, **3**, 73 (1968).
14. J. K. Gillham and R. F. Schwenker, Jr., *Appl. Polym. Symp.*, **2**, 59 (1966).
15. J. B. Gilbert, J. J. Kilpling, B. McEnaney, and J. N. Sherwood, *Polymer*, **3**, 1 (1962).
16. V. V. Polueklova, G. G. Tsurinov, and Z. S. Smutkina, *Strukt. Khim. Ugleroda Uglei*, 207 (1969); see *Chem. Abstr.*, **73**, 99306w (1969).
17. Fujiwara Yasuharu and Yasuda Takeshi, *Kobunshi Kagaku*, **28**(11) 906 (1971); see *Chem. Abstr.*, **76**, 100507h (1969).

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