Properties of Filaments Spun from Poly(ethylene terephthalate) Chips Containing PET–Dust*

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Synopsis

It is observed that the thick portions in a poly(ethylene terephthalate) (PET) filament differ from the rest in their solution viscosity and birefringence, indicating that they are caused by the inhomogeneity of the polymer melt. To identify the cause of the latter, the PET chips are critically examined. It is found that the waferlike tails on the edge of the PET chips and PET–dust have slightly higher viscosity than the chips. The behavior of the chips and the dust during drying and melt spinning are examined to find whether the dust becomes postpolymerized during drying. Such dried PET–dust exhibits substantially different melting behavior than the chips. The filaments spun from the mixture of chips and PET–dust exhibit significantly higher nonuniformity in properties than the filaments spun from the chips only. It is concluded that the PET–dust entering the extruder with the chips can cause thick portions in the filaments.

INTRODUCTION

One of the recurring defects in melt-spun filaments is the presence of thick portions. According to Aver'yanov and Arkhipov, thick portions in polyamide filaments could be due to mechanically trapped foreign impurities. On the other hand, they may be due to nonuniform drawing of the filaments. At times, these defects are latent in the undrawn fibers which are irregular due to homophase variation in the polymer viscosity.[1] Manabe has correlated viscosity with diameter variation in undrawn filaments.[2] Datye and Garg,[3] while studying the defects in PET filaments, observed that the thick portions have lower birefringence and higher viscosity than the normal fiber. They did not observe any mechanically trapped foreign impurities. Thus, they concluded that the nonuniformity in the filaments could be due to melt inhomogeneity which remains in the melt-spun filaments as thick portions.

The inhomogeneity in the melt can be due to small variations in the molecular weight of the polymer. A preliminary analysis of the chips does not show any significant difference in intrinsic viscosity within a given lot. Further examination of the chips reveals that there is always some dust and wafer-shaped tails adhering to the surface of the chips. In the continuous chips-drying unit, a cyclone separator has been provided to remove the dust. However, some dust and wafer-shaped tails on the chips remain with the chips and enter the extruder. They may be the source of melt inhomogeneity.

The purpose of the present work is to confirm the melt inhomogeneity resulting from the PET–dust and to confirm how the concentration of these inhomogeneities effect the properties of the spun filaments.
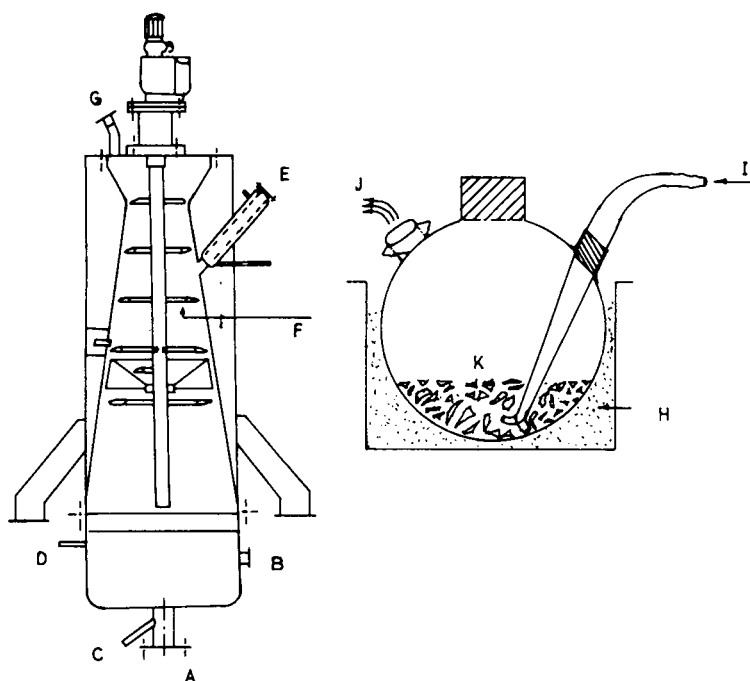
Fig. 1. Continuous dryer and laboratory setup for fluidized drying: (A) chips outlet; (B) gas inlet; (C) sampling connection; (D) pressure gauge; (E) chips inlet; (F) agitator blades; (G) gas outlet; (H) oil bath; (I) gas inlet; (J) gas outlet; (K) PET–dust.

EXPERIMENTAL

Preparation of Polymer. Polyethylene terephthalate (PET) was prepared from dimethyl terephthalate and ethylene glycol by the conventional method[4] in a commercial plant using sodium acetate and manganese acetate as transesterification catalysts, antimony trioxide as polycondensation catalyst and triphenyl phosphite as a stabilizer. The polymer was extruded from the reactor as a sheet which was cut into chips of 4 × 2 × 2 mm size.

Drying of Polymer Chips. The chips were dried at 145°C for 5 h in a rotary vacuum drier under a pressure of 50 mm Hg in the first step and then in a continuous drier using a countercurrent flow of air at 180°C (Fig. 1). After drying, the chips and PET–dust were collected for the study. In another experiment, PET–dust collected from the cyclone separator and the chips were dried as follows. A two-necked round-bottom flask containing chips or dust was kept in a bath at 180°C for different intervals of time. Heated air or nitrogen at 190°C was passed into the flask through a nozzle fitted in the inlet neck. The outlet was covered by an air permeable cotton cloth through which the gas passed out of the flask (Fig. 1). In another experiment, the chips were dried in an experimental fluidized-bed drier by passing hot air at 140°C for different intervals of time.

Melt Spinning. Monofilaments were spun from the PET chips, dust, or their mixtures. The chips were coated with 0.5%, 1.0%, 1.5%, and 2.0% of dust by

TABLE I
Intrinsic Viscosity of PET Chips and PET–Dust after Drying at 180°C for 7 h in the Continuous Drier

| Sample | Intrinsic viscosity (dL/g) | |
	Chips	Dust
1	0.659	0.679
2	0.659	0.681
3	0.661	0.683
4	0.661	0.681
5	0.650	0.679
6	0.659	0.677
7	0.653	0.677
8	0.653	0.678
9	0.651	0.677

tumbling and were spun using a laboratory-scale melt-spinning system described by Copley and Chamberlin.[5] A spinneret assembly similar to the one used in the commercial spinning plant, containing a sand filter and a seven-pack wire-mesh filter, was used. Filaments produced using this spinning system will be hereafter denoted as fiber A. Monofilaments were also spun using melt-spinning unit containing an extruder. (Fuji Melt Spinning Tester, Type C). Filaments produced using this unit will be denoted as Fiber B. All the filaments were cold-drawn at a speed of 10 mm/min to a draw ratio of 1:4 using an Instron Tensile Tester, and they were allowed to relax for 20 h before testing.

Characterization of Polymer and Fiber. The intrinsic viscosity of chips and the dust was measured by the standard method.[6] The density values of the chips and dust were determined by using a density gradient column and were used for getting crystallinity values. The melt viscosity of the chips, dust, and their mixtures was determined at $275 \pm 1°C$ using Frank Melt Flow Index Tester according to the method described in ASTM D1238. The diameter and bire-fringence (Δn) values of the fibers were determined using a Leitz Polarising Microscope. The mechanical properties of the fibers were evaluated by an In-stron Tensile Tester under standard conditions ($65 \pm 2\%RH$ and $25 \pm 2°C$) with
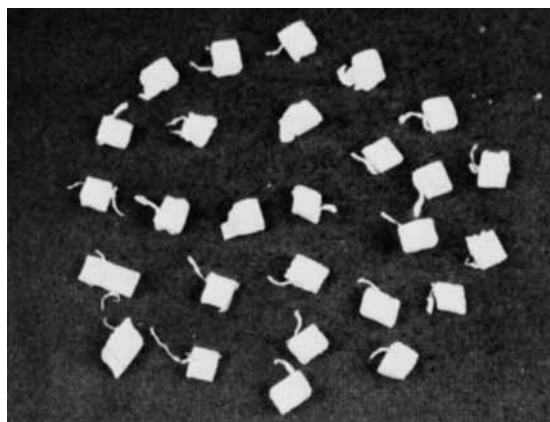

Fig. 2. Waferlike tails on the edges of PET chips.

TABLE II
Intrinsic Viscosity of PET–Dust after Drying at 180°C for 7 h in the Laboratory Setup Using Air and Nitrogen

Time (h)	Intrinsic viscosity (dL/g)	
	Air[a]	Nitrogen
0	0.673	0.673
1	x	0.690
2	x	0.705
3	x	0.709
4	x	0.712
5	x	0.723
6	0.702	0.727

[a] x = data not available.

a crosshead speed of 20 mm/min, chart speed of 100 mm/min, and a gauge length of 50 mm. The critical dissolution time (CDT) of the drawn fibers was determined in a mixture of phenol:tetrachloroethane (1:3) at 25°C, according to the method described by Galil.[7] Differential scanning calorimetric (DSC) studies of PET chips and PET–dust were made by using a DuPont thermal analyser.

RESULTS AND DISCUSSION

Effect of Drying

The intrinsic viscosity of dried chips and PET–dust are given in Table I. It is seen that the viscosity values of the dust are always higher than those of the chips. When PET is subjected to temperatures above 180°C under vacuum or in a current of hot nitrogen, it becomes postpolymerized.[8,9] The rate of postpolymerization depends on the following factors: (i) temperature and time; (ii) diffusion of molecules out of the polymer phase which is a function of surface area which, in turn, depends on the particle size; (iii) removal of the diffused product away from the surface of the polymer. The PET–dust, because of its
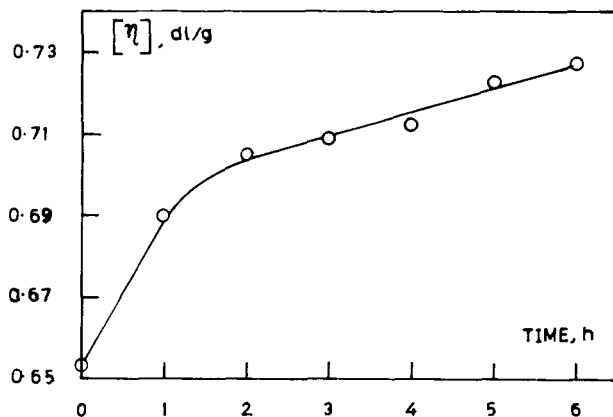

Fig. 3. Intrinsic viscosity {[η](dL/g)} of PET–dust on drying with N_2 at 180°C in laboratory setup for different lengths of time.

TABLE III
Properties of PET Chips and Dust after Drying in Continuous Air Drier

Sample	Dust in chips (g/kg)		% Crystallinity after drying	
	Before drying	After drying	Chips	Dust
1	1.43	2.67	42	54
2	2.53	5.53	42	—
3	0.49	1.34	43	56
4	0.73	1.77	44	—
5	1.50	3.23	46	58

small, thin, waferlike shape (Fig. 2) has a higher surface area per unit weight than the chips. This facilitates the postpolymerization allowing ethylene glycol (EG) molecules formed during the reaction to diffuse out of the polymer phase rapidly. Thus, under the drying conditions, the dust and waferlike tails become postpolymerized and their viscosity increases with time. However, under the mild drying conditions, chips do not become postpolymerized to a significant extent. When the hot air or nitrogen flow is high enough to keep the dust in a fluidized state, the removal of EG from the surface of the dust is very rapid, which, in turn, increases the diffusion of EG to the polymer surface facilitating rapid postpolymerization (Table II). The relationship between the time of drying in the laboratory setup, and the intrinsic viscosity of the dust is shown in Figure 3. The intrinsic viscosity of the dust increases rapidly in the initial period of 90 min of drying and thereafter very slowly in an asymptotic manner. The dust coming with the chips into the continuous drier is flushed out and removed by the cyclone separator. One would, therefore, expect that the dust content measured after drying will be less than that before drying. The actual data on five occasions is given in Table III. The results clearly indicate that the dust content after drying has in fact increased. This may be explained by assuming that the waferlike tails sticking at the surface of the chips may be abraded by the movement of the agitator in the drier and may become loose dust. The dust formation by the abrasion process may be facilitated by the crystallization of the dust. The crystallinity of the dust and chips, after drying is also shown in Table III, which is in agreement with the above contention.
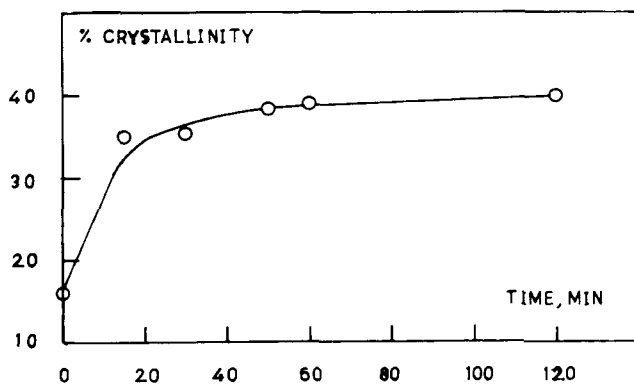

Fig. 4. The % crystallinity of PET chips on drying in an experimental fluidized bed drier for different lengths of time.
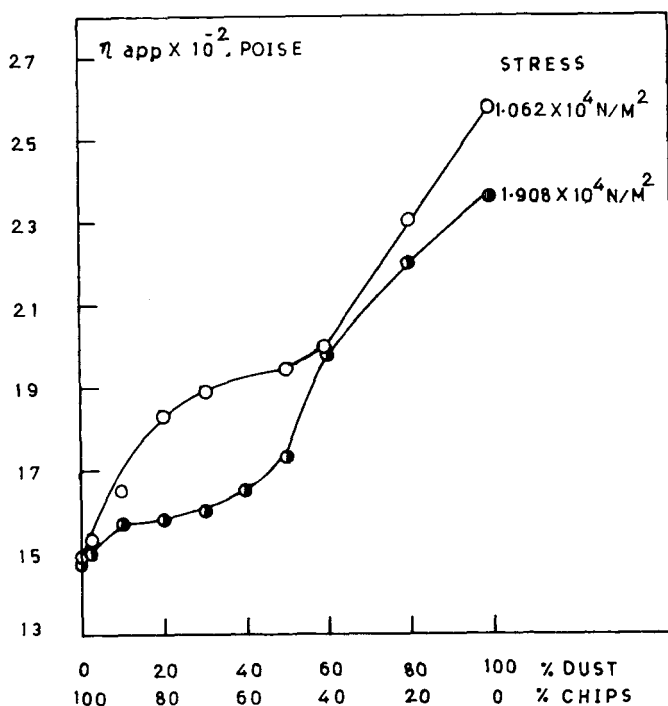
Fig. 5. Relationship between apparent melt viscosity [η_{app} (P)] and composition of mixture of dried PET–dust and chips.

The heat of fusion (ΔH_f obtained from DSC) of dust is 4.92 cal/g while that of chips is 4.14 cal/g only. This is consistent with the crystallinity data in Table III. The relationship between the crystallinity of chips, dried in fluidized-bed drier and the time of drying is shown in Figure 4. It appears that, after its rapid rise in the initial period of 30 min, the crystallinity remains almost constant.

Thus, the ΔH_f and percentage crystallinity of the dust are distinctly higher than those of the chips. It is, therefore, expected that the melting behavior and the melt rheology of the dust will differ from those of the chips.

Melt Viscosity

The influence of concentration of the dust on melt viscosity is studied by tumbling the dust and chips in different ratios for about an hour and by transferring the entire mixture to the Frank Melt Flow Index Tester. Several readings are taken, and the average of 10 consistent readings is recorded as the apparent melt viscosity for the given shear stress. A typical relationship between the composition of the mixture and the apparent melt viscosity (η_{app}) is shown in Figure 5. It is seen from the figure that the η_{app} increases with the proportion of the PET–dust in the mixture. The relationship in Figure 5 deviates from linearity when the dust is between 20% and 60%. The trend is the same for both the shear stresses. It has been reported[10] that η_{app} of a blend of PET and nylon 6 shows a similar deviation until the concentration of nylon in the blend reaches 60%. When the nylon concentration is low, it acts as a disperse phase. When

TABLE IV
Mechanical Properties of PET Fibers Produced from Chips Containing Different Percentages of PET–Dust

% Dust	Load[a] (g)	% CV[b]	% Elongation[a]	% CV[b]
		Fiber A		
0	48.27	5.23	104.4	3.46
0.2	52.46	8.24	120.0	7.95
0.4	84.36	6.55	119.0	5.05
1.0	59.85	6.90	101.8	7.83
2.0	63.66	4.36	129.5	5.60
3.0	88.50	7.30	122.8	7.23
4.0	69.60	6.06	112.3	5.74
6.0	88.10	6.40	102.0	5.70
		Fiber B		
0.0	51.50	12.8	88.8	17.2
1.0	64.15	6.9	103.2	11.6
2.0	58.10	24.7	90.5	23.2
3.0	63.04	8.3	106.5	16.5
4.0	67.10	14.1	11.6	12.5
5.0	64.90	16.4	65.4	19.6

[a] Average value of 20 readings.
[b] Calculated from readings taken for 20 samples.

the concentration of nylon is around 60%, the phase inversion takes place, and, thereafter, the PET acts as a disperse phase. The mixture of PET chips and the dust in the present case also appears to behave like a blend of two noncompatible polymers, even though they are from the same parent polymer.

Freeman and Coplan[11] have observed that the presence of gel-type high viscosity material in a normal polymer gives a nonuniform filament material. The gel-type, high-viscosity material causes fluctuations in the melt pressure and, consequently, produces thick and thin portions in the filament. In the present case, the variation in melt viscosity and, hence, the fluctuations in melt pressure caused by the presence of melt from the dust is not as large as in the case of gels formed by crosslinking. It is, therefore, expected that the mechanism operating in the case of crosslinked gels causing thick and thin portions may not be fully applicable in the present case.

When a polymer melt leaves the spinneret, the die swell, which is indicative of elasticity of the melt, occurs. It is not large for polyamides and polyesters[12] and becomes predominant when the temperature at the spinneret is low. Under normal conditions of spinning, the die swell gets evened out during the process of solidification and takeup. However, when a nonhomogeneous melt is extruded, the die swell may not be completely evened out during spinning, and may remain as a thick portion in the filament. This is clearly seen in the case of polypropylene (PP).[11] If the lower viscosity PP enters the spinning line, the higher stress in the line may cause the deformation to occur proportionately in the region occupied by the lower viscosity material, even though its cross section may be larger. According to this hypothesis, lower viscosity material would be disposed in the thinner portions and the high viscosity material would be disposed in the thicker portions. This, in fact, was observed by Datye and Garg[3]
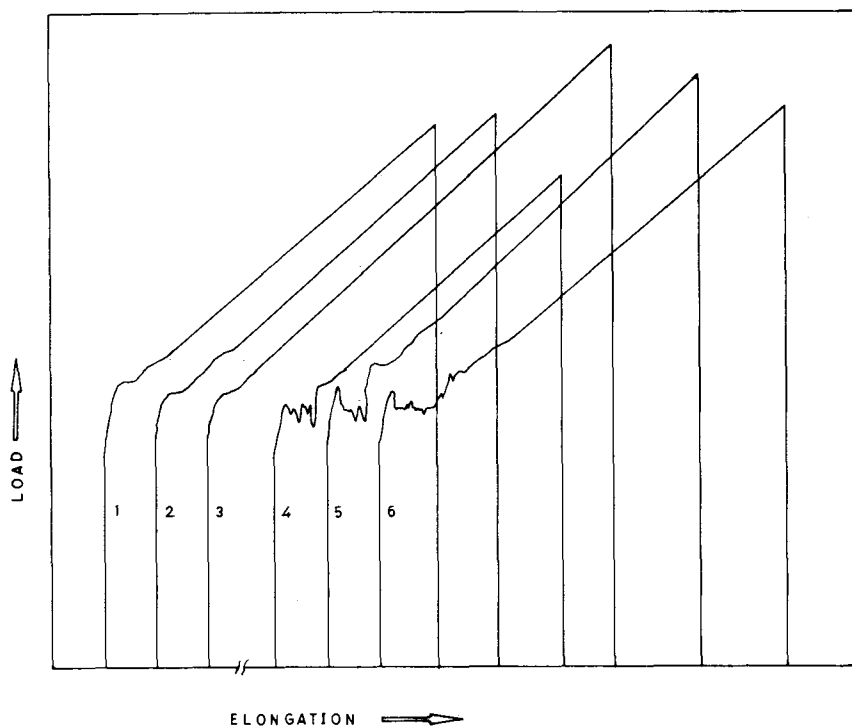
Fig. 6. A typical load–elongation curve of normal fibers (1,2,3) and fibers produced from chips containing dust (4,5,6).

by collecting hundreds of thick portions from PET filaments and analyzing them for intrinsic viscosity. They found that the viscosity of thick portions was always higher than that of normal fibers. Thus the above mechanism may be operative in the present case.

It has been reported that intrinsic viscosity and melt viscosity of a polymer influence its mechanical properties.[13] Therefore, the load–elongation properties of the filaments produced from the PET chips and the dust are evaluated.

Mechanical Properties

The average values of breaking load and percentage elongation of fiber A (fibers produced with minimum mixing of the melt) and fiber B (fibers spun with better mixing) are presented in Table IV. The samples used for testing are randomly selected in all the cases which ensures the representative analysis of the fibers. The breaking load and percentage elongation values are higher for the filaments spun from the chips containing dust than those for the filaments spun from the chips only. One may expect that the mixture of PET–dust and chips will have a higher average η_{app}, which, in turn, will give filaments of higher tensile strength. However, when the mixing is not uniform, the improvement in tensile properties also will not be uniform. It is important to note that the variation in properties of fiber B persists, even though they were spun using an extruder.
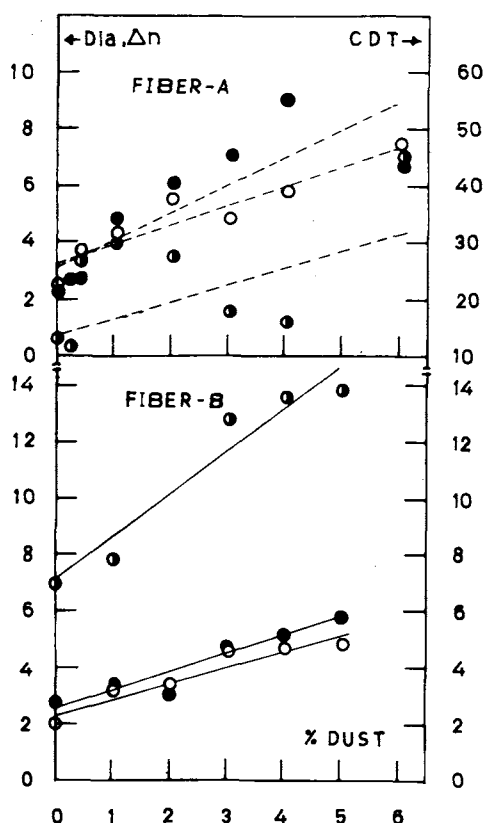
Fig. 7. % Coefficient of variation in the properties of fibers produced from chips containing different percentages of dust. (O) Dia; (●) Δn; (◐) CDT.

The thick portion which is of high molecular weight may not get stretched completely while drawing since it needs a higher force than the force required for the normal filament. Hence these thick portions may remain in the fiber even after stretching. A typical load-elongation behavior of the filaments containing thick portions is presented in Figure 6. It is seen from the figure that the thick portions which have remained as undrawn during the normal stretching get drawn and evened out while testing.

Diameter, Birefringence, and Critical Dissolution Time

The diameter, birefringence (Δn), and critical dissolution time (CDT) are determined for at least 20 samples of fiber A and fiber B. The relationship between the percentage coefficient of variation (% CV) in these properties and percentage dust in the chips is shown in Figure 7. It appears that the percentage CV increases with the dust content except for CDT in the case of fiber A. Since the spinning system used for fiber B enables improved mixing, the properties of fiber B show better relationships.

Galil[7] has observed that CDT is extremely sensitive to fiber crystallinity and is used for detecting small morphological differences in fibers. The structure

of the fibers spun from chips is likely to be different from that of the fibers spun from mixture of chips and dust. These structural differences would be small and random depending upon the distribution of high viscosity material in the fibers. Thus, one may expect less nonuniformity in fiber B, which is produced under better mixing conditions. However, one may conclude from the data that the high viscosity material from dust still appears to remain as a separate entity in thick portions, and it is not homogenized with the rest of the melt by the otherwise efficient mixing operation.

It may be noted that any mechanically embedded impurity which could produce short irregular portions is not observed in any of the filament samples. Furthermore, one may rule out thermal variations as a cause of observed irregularities in filaments since they are spun from chips and dust under identical conditions.

CONCLUSION

The fine dust and waferlike tails on PET chips exhibit, on drying, slightly higher intrinsic and melt viscosities than the chips. The melting behavior of the dust is also different from that of the chips. The dust and waferlike tails cause defects in the as-spun filaments, which are not removed by the drawing process. Thus it appears that the fine PET–dust and, particularly, waferlike tails on the chips can create problems of thick portions in polyester filaments.

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