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DSC Analysis of Partially Oriented (Poy) and Textured Poly (Ethylene Terephthalate) Yarns

Yıldırım K[1]., Altun S[2]. and Ulcay Y[2].
[1]TÜBİTAK-BUTAL Bursa Test and Analysis Laboratory, Bursa 16190-TURKIYE
[2]Dept. of Textile Engi. College of Engineering and Architecture University of Uludag Gorukle, Bursa TURKIYE

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Abstract

Thermal behavior of poly(ethylene trephthalate) PET partially oriented and texturing yarn has been investigated. Yarns were produced in three different levels of each of selected parameters during melt spinning and false twist texturing. Yarns were analyzed by differential scanning calorimeter (DSC). DSC is the most widely used equipment of thermal techniques. DSC analysis could easily detect the change of winding speed since winding speed alters the molecular orientation of the fiber. Quenching air temperature and quenching air speed effects could not be detected clearly by DSC analysis. Texturing yarns and flat yarns could be differentiating via DSC thermograms.

Keywords: PET yarn, spinning factors, texturing factors, DSC analysis, thermal properties.

Introduction

Differential scanning calorimetry (DSC) is perhaps the best known example of the growing number of techniques which come under the broad heading of thermal analysis[1]. DSC measures the flow of energy into or out of the sample as a function of temperature or time. Heat flow changes the heat capacity (C_p) of polymer as a result of either endothermic or exothermic events or glass transition (T_g) as a step change in the heat capacity of polymer. Melting of a crystalline structure and stress relaxation are endothermic events. Formation of crystalline structure, cross-linking and decomposition are exothermic events[2].

The DSC analysis provides information about composition and physiochemical properties of polymers. Thermal transitions can be used to analyze molecular arrangements[3]. DSC is a sensitive device for characterizing the crystallinity of semi-crystalline polymers. During the heating of the sample in the DSC, molecular mobility in amorphous region, cold crystallization, partial melting, annealing, re-crystallization and complete melting are occurred[4].

Poly (ethylene terapthalate) (PET) yarn is produced by melt spinning where PET polymer is heated over melting temperatures, pushed through spin packs then cooled and simultaneously drawn. Main spinning parameters, winding speed, the quenching air speed and the quenching air temperature are affected fiber properties such as dyeing behavior, tensile strength, strain and some others[5-8].

Simultaneous draw texturing process is one of the very complicated textile processes where fibers are drawn, heated and twisted simultaneously. Draw ratio, D/Y ratio, heater temperatures and residence time change the yarn properties[9,10]. Some molecular rearrangements and cross sectional deformations also happen. Because DSC is a useful tool to examine some material properties, although researchers studied already in 1970 to investigate polymers, the studies are still continuing[11].

The thermogram, which is produced from the first heating (as-received) stage, involves information both about material features and thermal history such as production factors effect[2]. In the present study, some effects of melt spinning and false twist texturing process parameters on the poly (ethylene terepthalate) (PET) fibers produced in commercial conditions were investigated via DSC measurements.

Material and Methods

Melt Spinning: The melt spinning equipment consisted of a Barmag extruder with diameter D=45 mm and ratio of the length L to diameter D equal to 24. 167 dTex 96 filament semi-dull POY PET yarn were produced. The applied winding speeds were 2600 m/min, 3200 m/min and 3800 m/min, POY PET was used for the experiments. Cross-flow type cooling system with 3 different quenching air speeds, namely 0.3 m/s, 0.5 m/s, 0.7 m/s and 3 different quenching temperatures, namely 17^0C, 22^0C and 27^0C were used[5].

Draw Texturing: Lab-type Barmag AFK-M texturing machine with two heaters was used with 650 m/min process speed 9.5. First heater temperature values were 150^0C, 190^0C, 230^0C, D/Y values were 1.5, 2.0, and 2.5 and the draw ratios were 1.55, 1.60, and 1.65.

DSC Analysis: Perkin Elmer Sapphire II model Differential scanning calorimeter (DSC) having heat flux method were used.

Test Condition: Initial temperature 30 °C, final temperature 350 °C, heating rate 10 °C /min, purge gaseous nitrogen, sample mass approximately 10 mg, sample pan crimped aluminum pan, heating type first heating (as-received).

Results and Discussion

Untextured Yarns: It can be seen from figures 1 to 3 and table 1 that, unlike the cold crystallization peak maximum and heat of fusion of cold crystallization of POY PET yarn which decreases by increasing winding speed, real heat of fusion of melting and onset point of POY PET yarn increase. Real heat of fusion of melting was used because of eliminating cold crystallization effect. The degree of crystallinity in the semi-crystalline polymer changes the cold crystallization behavior in aspect to change in enthalpy (heat of fusion) and peak temperature[4]. Thermoplastic polymers such as PET prone to recrystallisation when it is heated in DSC analysis[11]. These four thermal behavior show that the macromolecular orientation and crystallinity ratio in the POY PET yarn increase by increasing winding speed. Melting peak maximum of POY PET yarn did not change noticeable by altering winding speed. The cold crystallization peak gets broader with increasing winding speed. Due to the difficulties of measurement of heat of fusion of cold crystallization and heat of fusion of melting properties, the effect of quenching air speed and quenching temperature on the POY PET yarn thermal behavior could not be noticed. These two properties calculated from the peak area. The area can be changed according to measurement points and these points are not fixed, and the change depends on the labor skills and measurement range. There are not identified measurement points for calculation of area.

Any significant effect could not be observed on T_g through chosen parameters. It is known that DSC technique is less sensitive to detect T_g for semi crystalline polymers [12, 13].

Table-1
DSC analysis results of POY PET

POY production parameters	T_g (^{0}C)	Cold crystallization peak maximum (^{0}C)	Heat of fusion of cold crystallization (mj/mg)	Heat of fusion of melting (mj/mg)	Onset (^{0}C)	Melting peak maximum (^{0}C)	Real Heat of fusion of melting (mj/mg)
17 ^{0}C, 0.3 m/s 1600 m/min	71.2	111.3	36.9	50.6	245.7	255.9	13.7
17 ^{0}C, 0.3 m/s 3200 m/min	71.3	102.8	22.5	54.3	247.8	255.2	31.8
17 ^{0}C, 0.3 m/s 3800 m/min	68.6	92.9	12.4	61.1	249.1	255.2	48.7
17 ^{0}C, 0.5 m/s 2600 m/min	74.4	113.1	23.4	47.1	243.1	255.4	23.7
17 ^{0}C, 0.5 m/s 3200m/min	73.6	104.1	15.7	44.1	243.2	255.9	28.4
17 ^{0}C, 0.5 m/s 3800 m/min	70.3	94.3	20.7	55.4	249.5	255.8	34.7
17 ^{0}C, 0.7 m/s 2600m/min	73.4	111.8	33.7	47.0	242.7	255.4	13.3
17 ^{0}C, 0.7 m/s 3200 m/min	73.5	106.3	28.8	48.7	244.8	255.7	19.9
17 ^{0}C, 0.7 m/s 3800 m/min	72.4	96.8	15.1	45.7	247.0	256.3	30.6
22 ^{0}C, 0.3 m/s 2600m/min	77.1	114.5	19.8	38.5	245.8	255.1	18.7
22 ^{0}C, 0.3 m/s 3200 m/min	69.9	103.1	22.4	50.2	247.0	255.0	27.8
22 ^{0}C, 0.3 m/s 3800 m/min	69.1	94.0	10.8	55.1	247.2	255.2	44.3
22 ^{0}C, 0.5 m/s 2600 m/min	72.3	111.7	24.1	48.6	244.0	255.1	24.5
22 ^{0}C, 0.5 m/s 3200m/min	73.0	104.8	26.6	51.9	243.6	255.1	25.3
22 ^{0}C, 0.5 m/s 3800 m/min	70.2	95.5	11.5	57.6	248.5	256.0	46.1
22 ^{0}C, 0.7 m/s 2600m/min	71.5	108.7	19.3	48.4	243.5	255.7	29.1
22 ^{0}C, 0.7 m/s 3200 m/min	81.3	103.1	17.4	50.2	244.7	255.6	32.8
22 ^{0}C, 0.7 m/s 3800 m/min	71.9	96.2	15.8	51.6	247.4	256.1	35.8
27 ^{0}C, 0.3 m/s 2600m/min	72.4	112.7	31.5	47.8	243.0	255.1	16.3
27 ^{0}C, 0.3 m/s 3200 m/min	76.0	106.7	16.9	44.9	243.5	255.3	28.0
27 ^{0}C, 0.3 m/s 3800 m/min	75.5	97.1	19.4	53.4	245.9	255.8	34.0
27 ^{0}C, 0.5 m/s 2600m/min	71.5	110.6	27.1	46.7	243.7	255.5	19.6
27 ^{0}C, 0.5 m/s 3200 m/min	73.3	104.9	29.4	48.2	241.0	255.3	18.8
27 ^{0}C, 0.5 m/s 3800 m/min	71.9	95.5	18.9	58.8	248.6	255.7	39.9
27 ^{0}C, 0.7 m/s 2600m/min	72.9	111.0	33.9	50.4	242.9	255.5	16.5
27 ^{0}C, 0.7 m/s 3200 m/min	71.8	102.0	33.2	49.1	244.3	255.4	15.9
27 ^{0}C, 0.7 m/s 3800 m/min	72.5	95.8	15.2	55.0	248.8	255.7	39.8

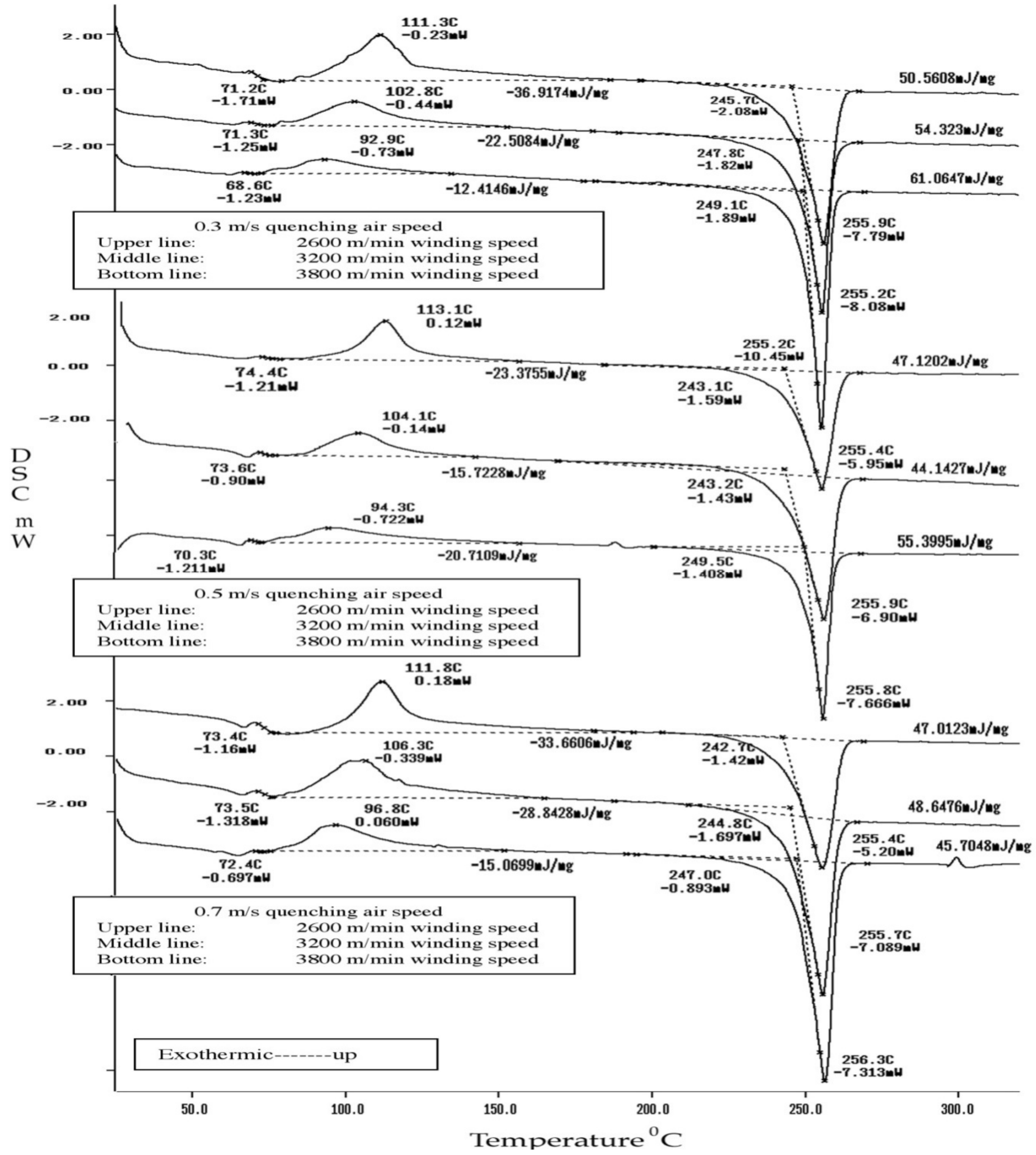

Figure-1
DSC thermograms of POY PET produced at 17 ^{0}C quenching temperature

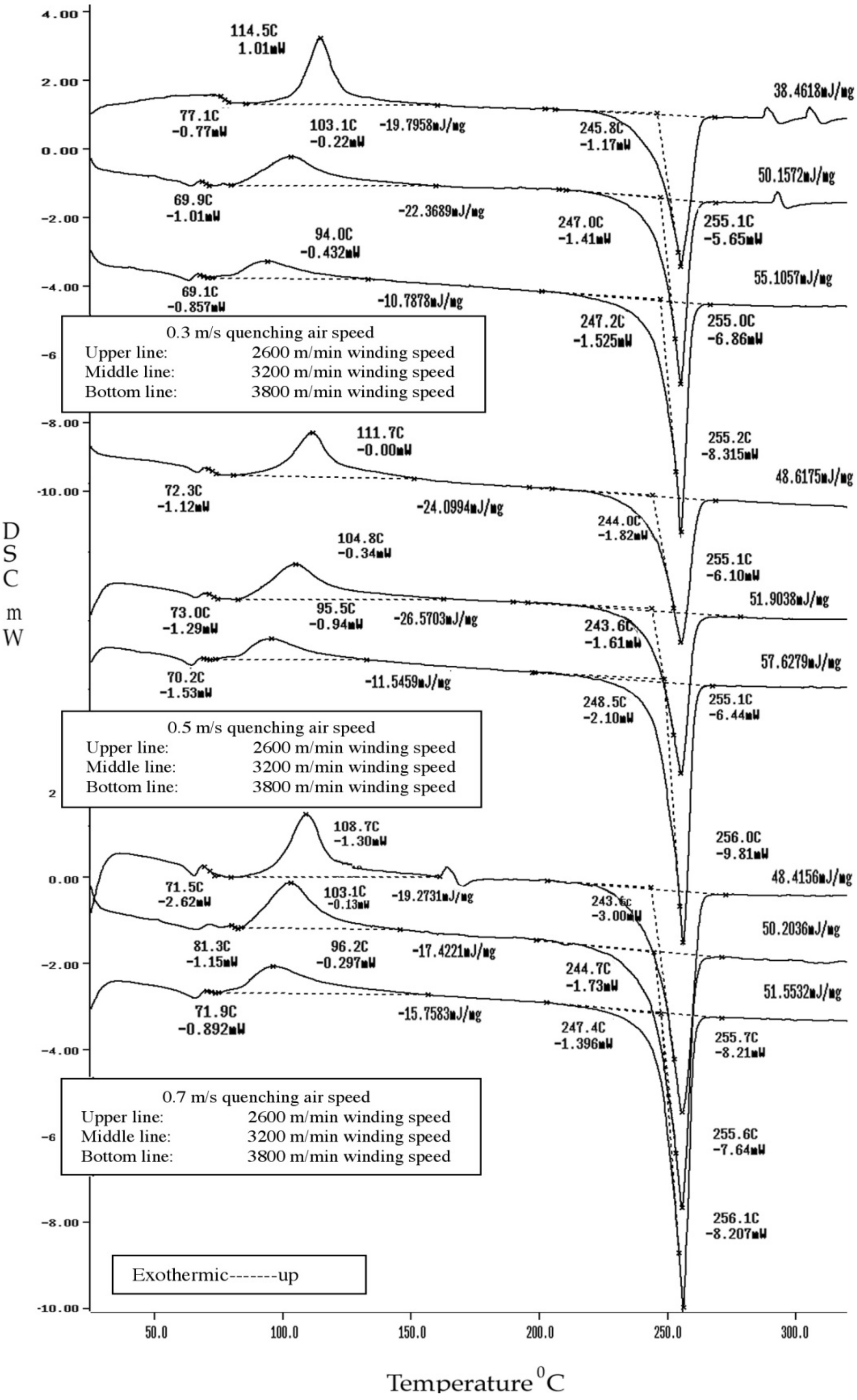

Figure - 2
DSC thermograms of POY PET produced at 22 ^{0}C quenching temperature

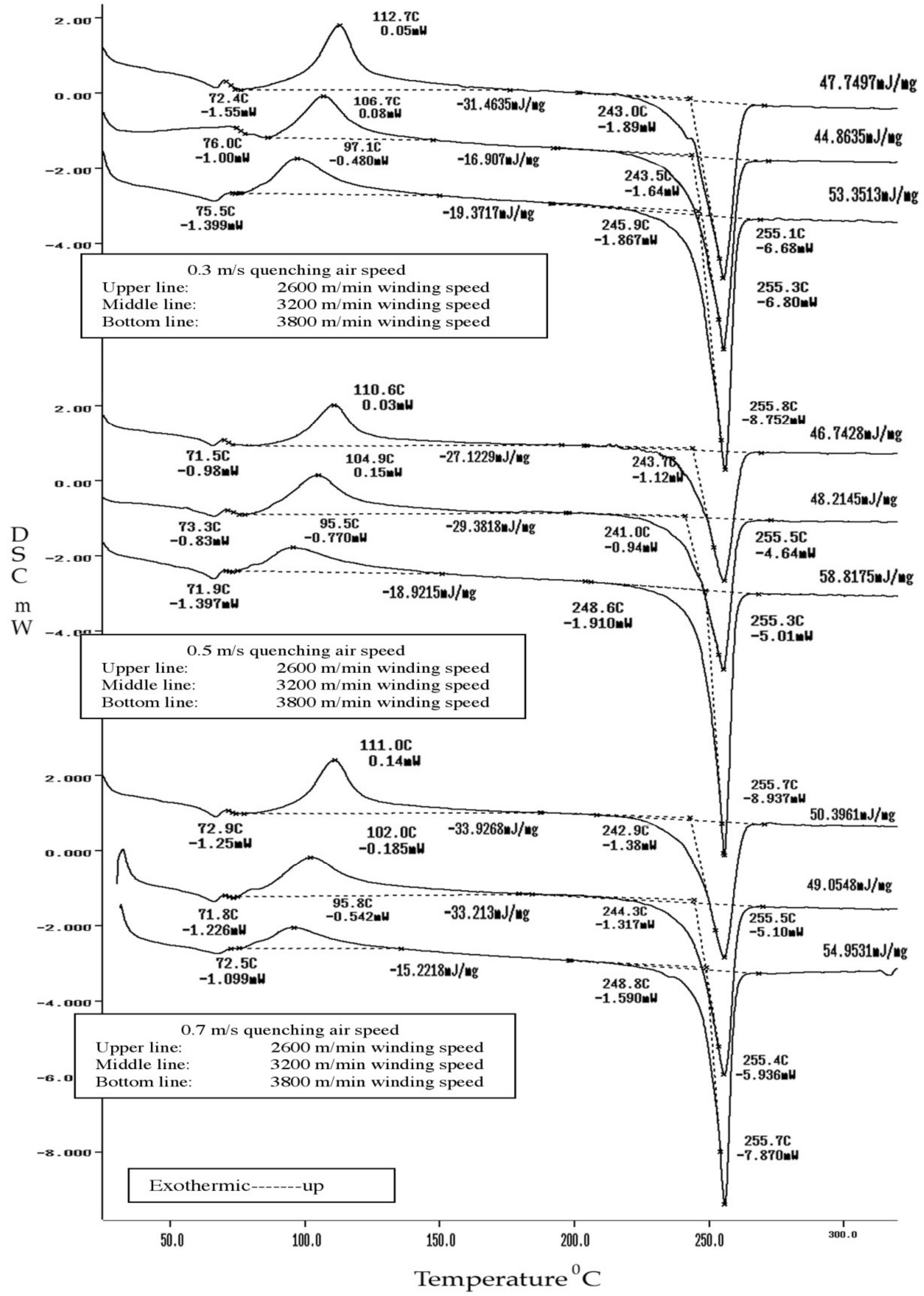

Figure - 3
DSC thermograms of POY PET produced at 27^{0}C quenching temperature

Textured Yarns: According to thermograms of textured PET yarns shown in figures 4-6 and table 2, all three production parameters did not have any significant effect on onset point and real of heat of fusion of melting.

Table - 2
DSC analysis results of textured PET

Texturing production parameters	Heat of fusion of cold crystallization (mj/mg)	Heat of fusion of melting (mj/mg)	Onset (^{0}C)	Melting peak maximum (^{0}C)	Real Heat of fusion of melting (mj/mg)
150 ^{0}C, 1.5 D/Y 1.55 draw ratio	7.0	70.0	248.0	253.8	63.0
150 ^{0}C, 1.5 D/Y 1.60 draw ratio	7.3	69.4	248.1	254.4	62.1
150 ^{0}C, 1.5 D/Y 1.65 draw ratio	4.3	64.5	249.2	255.0	60.2
150 ^{0}C, 2.0 D/Y 1.55 draw ratio	4.9	64.9	248.1	253.7	60.0
150 ^{0}C, 2.0 D/Y 1.60 draw ratio	7.5	65.1	249.7	254.7	57.6
150 ^{0}C, 2.0 D/Y 1.65 draw ratio	7.1	64.2	248.8	253.7	57.1
150 ^{0}C, 2.5 D/Y 1.55 draw ratio	5.5	67.2	248.6	254.4	61.7
150 ^{0}C, 2.5 D/Y 1.60 draw ratio	4.3	68.0	248.4	254.0	63.7
150 ^{0}C, 2.5 D/Y 1.65 draw ratio	2.9	60.9	248.9	254.6	58.0
190 ^{0}C, 1.5 D/Y 1.55 draw ratio	4.9	68.3	249.0	253.7	63.4
190 ^{0}C, 1.5 D/Y 1.60 draw ratio	5.2	69.2	248.3	254.3	64.0
190 ^{0}C, 1.5 D/Y 1.65 draw ratio	5.5	65.0	248.4	255.1	59.5
190 ^{0}C, 2.0 D/Y 1.55 draw ratio	4.3	63.0	248.8	254.3	58.7
190 ^{0}C, 2.0 D/Y 1.60 draw ratio	7.9	64.6	248.1	254.4	56.7
190 ^{0}C, 2.0 D/Y 1.65 draw ratio	6.6	60.4	248.2	254.5	53.8
190 ^{0}C, 2.5 D/Y 1.55 draw ratio	5.3	58.6	248.9	254.0	53.3
190 ^{0}C, 2.5 D/Y 1.60 draw ratio	4.0	65.9	248.6	254.0	61.9
190 ^{0}C, 2.5 D/Y 1.65 draw ratio	6.3	68.0	250.6	254.7	61.7
230 ^{0}C, 1.5 D/Y 1.55 draw ratio	5.5	63.2	248.3	254.0	57.7
230 ^{0}C, 1.5 D/Y 1.60 draw ratio	4.3	62.1	249.4	254.5	57.8
230 ^{0}C, 1.5 D/Y 1.65 draw ratio	5.0	63.3	248.3	254.1	58.3
230 ^{0}C, 2.0 D/Y 1.55 draw ratio	5.8	65.7	248.4	254.0	59.9
230 ^{0}C, 2.0 D/Y 1.60 draw ratio	6.0	56.4	248.5	253.7	50.4
230 ^{0}C, 2.0 D/Y 1.65 draw ratio	4.6	65.1	249.2	254.1	60.5
230 ^{0}C, 2.5 D/Y 1.55 draw ratio	11.1	68.2	248.2	254.3	57.1
230 ^{0}C, 2.5 D/Y 1.60 draw ratio	5.9	63.3	248.6	253.1	57.4
230 ^{0}C, 2.5 D/Y 1.65 draw ratio	3.6	64.6	249.7	254.1	61.0

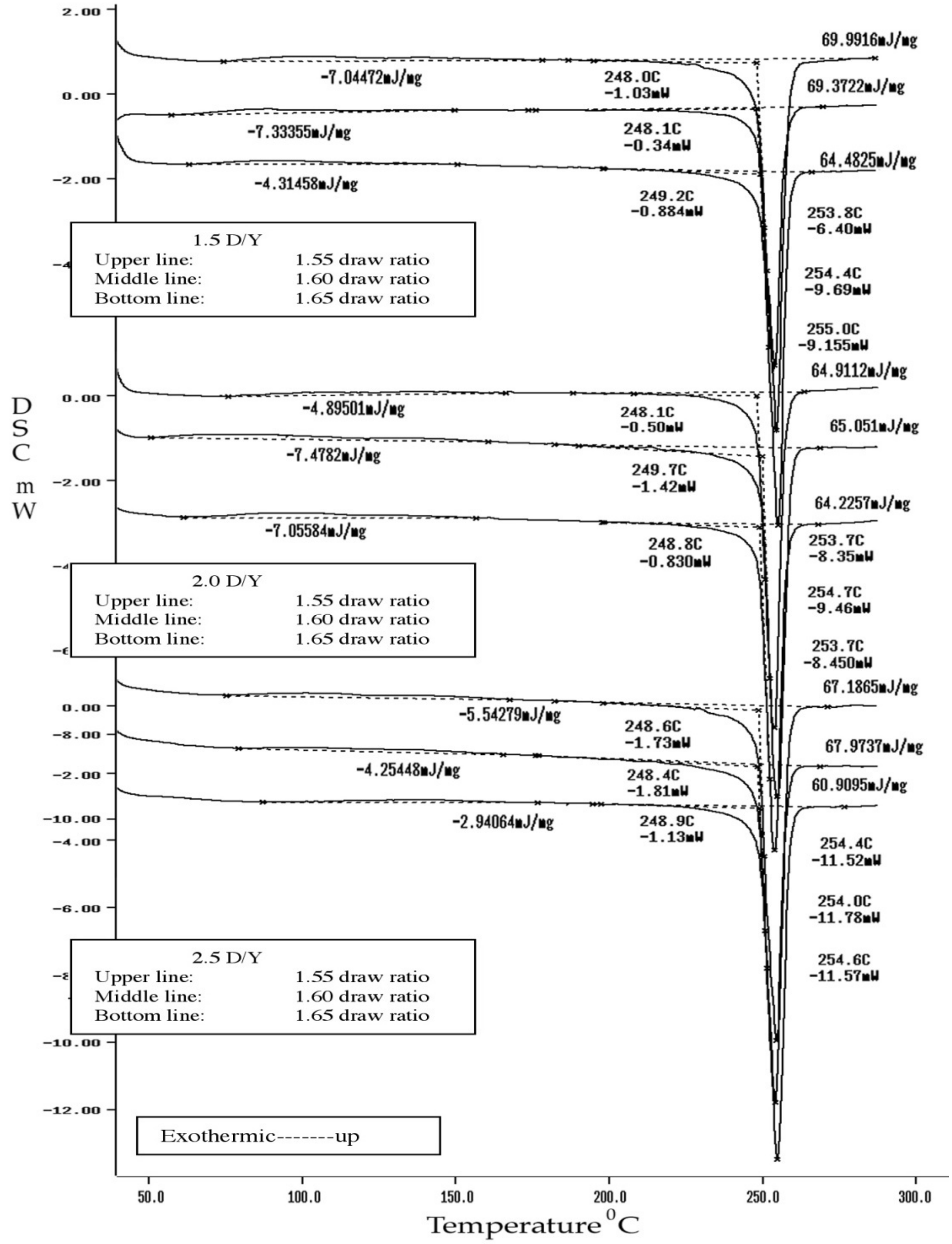

Figure - 4
DSC thermograms of PET textured at 150^{0}C first heater temperature

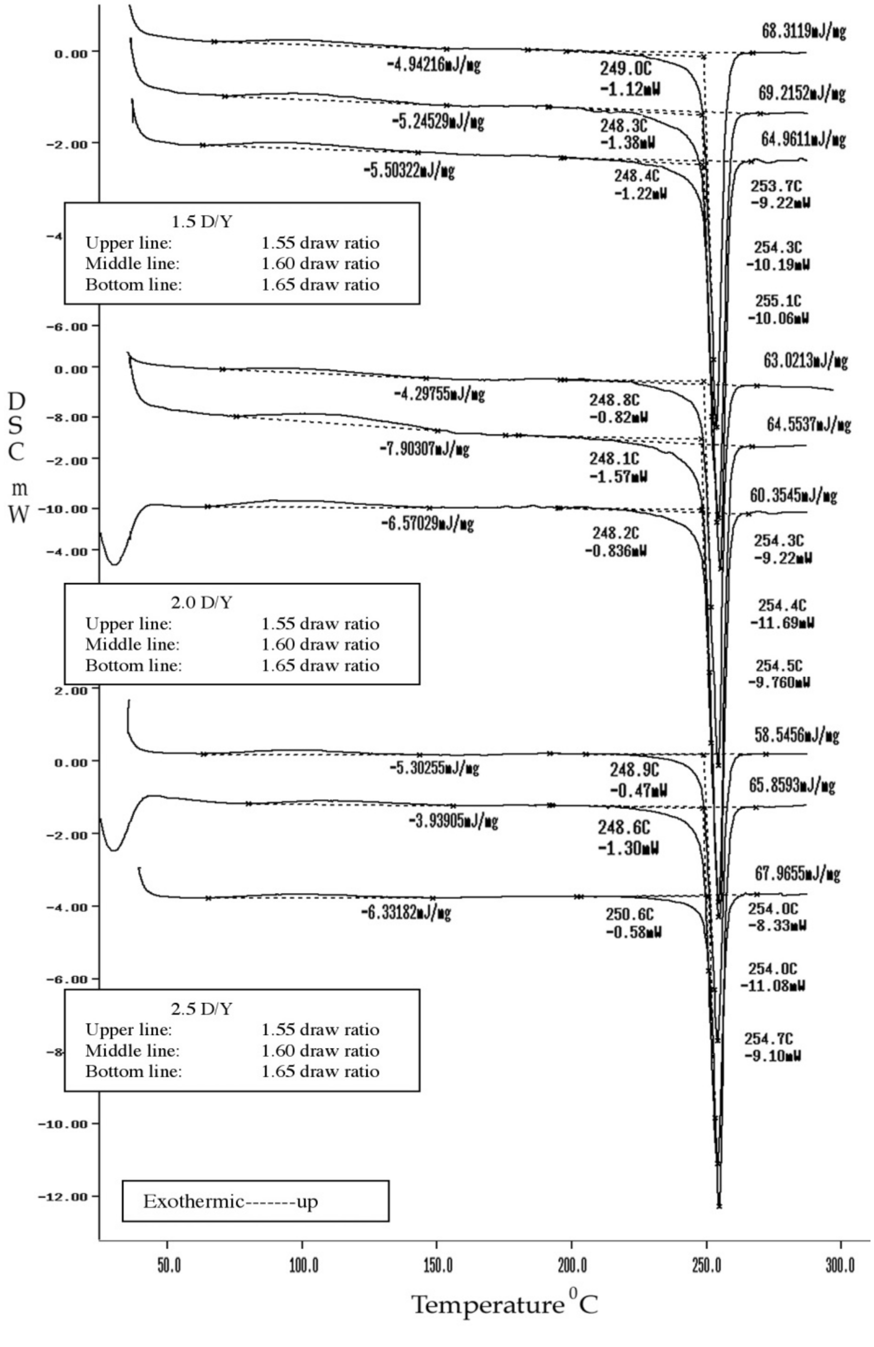

Figure - 5
DSC thermograms of PET textured at 190 ^{0}C first heater temperature

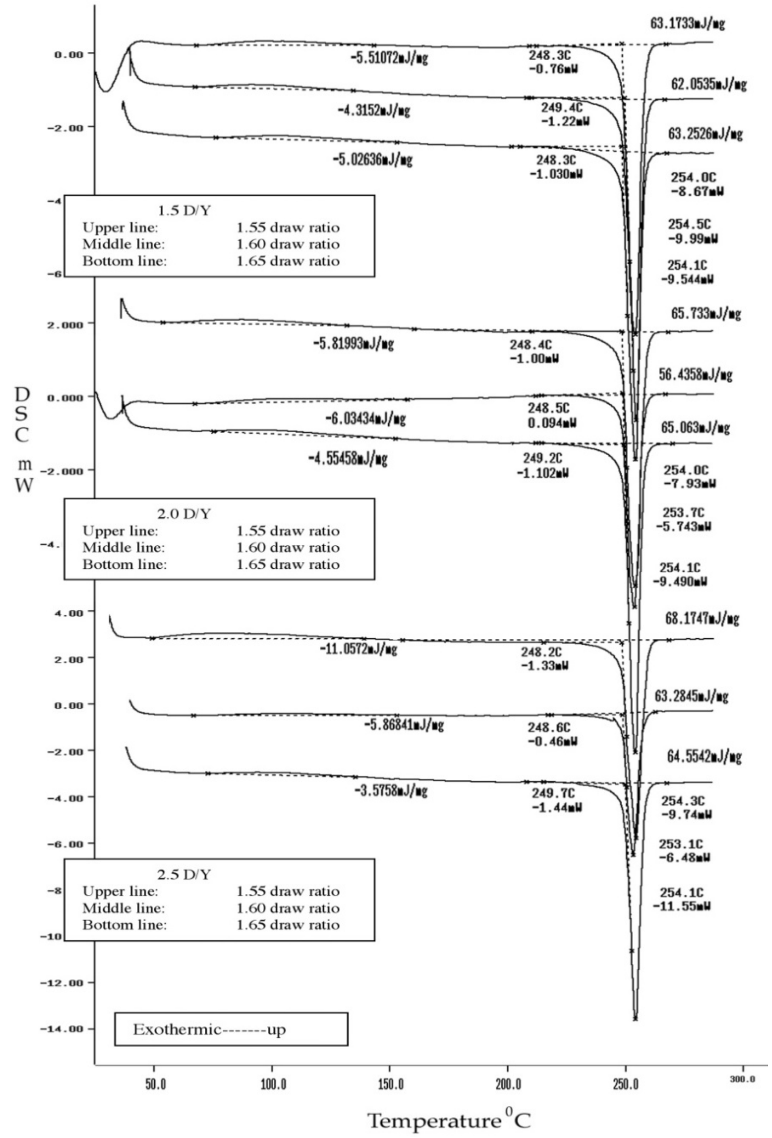

Figure - 6
DSC thermograms of PET textured at 230 ^{0}C first heater temperature

Contrary to untextured PET yarn thermograms which have huge heat of fusion of cold crystallization peak, there was not noticeable heat of fusion of cold crystallization peak on the thermograms of textured PET yarn. Heat of fusion of melting peak area on the textured PET yarn thermograms was greater than the heat of fusion of melting peak area on the POY PET yarn. There was no noticeable difference between POY and textured PET yarn thermograms in aspect to onset point. Heat of fusion of melting peak of the POY PET yarn was broader than that of the textured PET yarn. The width of the heat of fusion of melting peak is related to crystallinite size distribution[11]. This phenomenon indicates that in the texturing process small crystallites are converted to big crystallites and the crystallite size distribution gets narrower. Unlike indium which contains single crystal, polymers involve range of crystals of varying stability that melt over a broad range[14]. It can be seen from thermograms of POY PET that there is a significant exothermic and endothermic activity; on the contrary generally endothermic activity can be seen on textured PET's thermograms. POY PET thermograms include small endothermic heat of fusion about 60°C, however textured PET's thermograms do not have. We assumed that, this small endothermic heat of fusion resulted from melting of the surface oligomers [3] on the POY. During texturing process oligomers on the filaments surface can be removed by the action of friction of discs, therefore endothermic heat of fusion could not be observed on the textured PET's thermograms.

Conclusions

Thermal behavior of POY and textured PET yarns analyzed using DSC technique. Although a noticeable difference could not be observed between POY and textured yarns at onset points; heat of fusion of melting peak area on the textured PET yarn thermograms was greater than that of POY. Any significant change could not be observed on T_g both of the yarns.

Increasing winding speed made larger the heat of fusion of melting peak area due to alteration in molecular orientation. Altering the quenching air temperature and speed could not effect drastically the heat of fusion of melting peak area. It can be concluded that the DSC technique is not sensitive to detect the change of fiber thermal properties when altering quenching air temperature and speed on present experimental conditions.

Texturing yarns and flat yarns could be differentiating via DSC thermograms based on the cold crystallization peak and heat of fusion of melting peak area width.

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