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Physical Impacts of Compaction Treatments on Pet Textile Vascular Prostheses

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Abstract: Textile cardiovascular prostheses are woven or knitted structures made generally from biocompatible polyester fibres. After production, they have to undergo special treatments before packaging such as compaction. This treatment is necessary to reduce porosity especially for knitted structures, but it can modify poly(ethylene terephthalate) (PET) polymer's properties. We have studied the effect of chemical and thermal compaction process parameters on physical properties of PET with DSC and XRD techniques. The obtained results show changes of glass transition temperature according to compaction parameters. A multiple melting peaks thermograms were observed for untreated and most compacted samples indicating differences between crystallites sizes. The compaction treatment involves an increase of PET crystallites size because of molecular bonds rearrangement among the polymeric chains. With DRX, we have showed crystallites size increases for compacted samples when compared with untreated samples. This increase is particularly important in perpendicular direction to (010) crystallographic plane.

INTRODUCTION

From more than ten materials used clinically since 1954, Poly (ethylene terephtalate) has proven to be most desirable among different polymers used to manufacture porous fabric prosthesis for cardiovascular replacement [1, 2]. The polyester vascular grafts commercially available are marketed as woven and knitted. These structures have significantly different physical properties like porosity. The porosity of the synthetic prosthesis should be balanced between that necessary to provide good long-term healing characteristics and that preventing undue haemorrhaging at implantation. Since knitted structures are too porous, they have to be subjected to compaction treatment to reduce their porosity to acceptable levels. This is accomplished by either thermal or chemical treatments. The thermal process uses dry or liquid   heat.   The chemical process makes use of swelling agents or solvents or a combination of the two which causes the swelling of the yarn constituting the fabric thereby shortening, widening and reduce the spaces or gaps between adjacent yarns in the fabric [3, 4]. Literature related to compaction treatments is extremely rare. Most of researches made in this area are instigated by vascular prostheses manufacturers and results are generally kept secret for competitive reasons.

Compaction treatment is accompanied by longitudinal shrinkage and lateral swelling of PET filaments. In previous studies [5], we have demonstrated that for chemical compaction, transverse swelling and longitudinal shrinkage vary in the same way with compaction parameter (chemical agent types, immersion duration and temperature). For thermal treatment, the longitudinal shrinkage and lateral swelling increase with temperature [5]. Feldstein and Pourdeyhimi have also shown changes in the fiber morphology after chemical compaction [6]. However, the effect of thermal compaction on physical, chemical and morphological properties of the fiber has been rarely treated in the literature. Guidoin and al. have noted changes in the molecular arrangement and crystallinity degree of polymer after vascular prosthesis compaction [7].

The aim of this study is to analyse the physical and chemical structural changes of PET fibers after chemical and thermal compaction processes in order to understand fiber morphological changes related to these treatments.

MATERIALS AND METHODS

We manufactured weft knitted jersey structures by using laboratory circular jersey knitting machine (gauge E = 24). We used a biocompatible texturized multifilament PET yarns of a 110 dtex, composed of 34 filaments and

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Table 1: Chemical compaction solutions

	Compaction solutions

Temperature (25°C)	Duration (30 min)
80 % water + 20 %	Chloroform
80 % water + 20 %	Methylene chloride
80 % water + 20 %	Dichloroethane
50 % water + 50 %	Chloroform
50 % water + 50 %	Methylene chloride
50 % water + 50 %	Dichloroethane

Table 2: Thermal compaction conditions

Temperatures (°C)	120	130	140	150	180
Durations(min)	10 ; 120	10 ;120	10 ; 120	1 ; 20	0.5 ; 2

having a circular section and a 19.25 µm diameter. Samples were conditioned in the testing laboratory under standard atmospheric conditions of 20 ± 2°C and 65 ± 2% R.H. for 24 hours according to NFG 07-003 standard.

For chemical compaction, we have used three swelling agents cited by the US patent 3,853,462 [8]. The knitted samples were immersed, under agitation, in the compacting solution. Table 1 provides a description of chemical compaction solutions used in this study. After compaction, the treated samples were removed, rinsed in tap water and dried at 100°C during 5 minutes [8].

The thermal approach is based on the use of dry or wet heat at an average temperature of 120°C -155°C [3, 7]. In this study, we used different temperature ranging between 120°C and 180°C for different durations (Table 2). Knitted samples were fixed, without tension, between the tenterhooks of a ROACHES fixing stenter.

In order to study the impact of compaction treatment on PET melting characteristics and glass transition temperature, we have used a DSC 823e differential scanning calorimetry machine. Samples were cutted in small stumps weighting less than 10 mg and were packed in perforated aluminium pans to ensure good heat diffusion. For all tested samples, we have considered the following sequence:

C   First temperature increasing from 30°C to 300°C with a heating rate of 10°C/min ;
C   Reducing temperature until 30°C with a cooling rate of 10°C/min ;
C   Second temperature increasing from 30°C to 300°C with a heating rate of 10°C/min ;
C   Reducing temperature until 30°C with a cooling rate of 20°C/min.

After the first heating, we determine the melting behaviour but not the glass transition temperature T_g. The second heating is necessary to determine the T_g.

The PET crystallites size evolutions were determined by X-rays diffraction using a PHILIPS PW 1050/37 diffractometer.

RESULTS AND DISCUSSION

DSC Analysis

Thermal Compaction: We have used weft knitted samples treated at different temperatures and durations in order to analyse the corresponding melting peak and the glass transition temperature. DSC results for all testing conditions showed the existence of multiple peaks in the melting zone. For untreated sample, we have detected two endothermic peaks with a shouldering on the left of the first peak (Figure 1). This shouldering is probably due to the existence of a third endothermic peak which appears for low temperatures.

After thermal compaction treatment (Figure 2), we have noted, for most treated samples, two endothermic peaks. These peaks appeared clearly when increasing treatment duration.

A shifting to higher temperatures was observed for the second peak. In fact, the thermal analysis of semi-crystalline polymers, indicates, generally, a multiple melting peaks or only one asymmetric peak with shouldering. In literature, many research works have noted the presence of multiple peaks in polyester melting zone during DSC tests [9-11]. Sawatari and Matsuo [12] have suggested that PET thermal treatment involves crystallites separation in two phases. They showed that the area and the position of these multiple peaks are sensible to thermal treatment temperature and duration and that peak profile modification may be due to crystalline defaults and to difference in crystallites sizes.

Le Clerc has related the existence of multiple melting peaks to crystalline morphology distribution in term of size and perfection [13].

We have used the Origin 8 software for DSC thermograms deconvolution and we have called Peak 1, Peak 2 and Peak 3 the three melting peaks observed in DSC thermogram. Table 3 shows temperature corresponding to each melting peak for different thermally treated samples. The comparison with untreated sample shows a shift of the melting peak temperatures T_m toward higher temperatures.
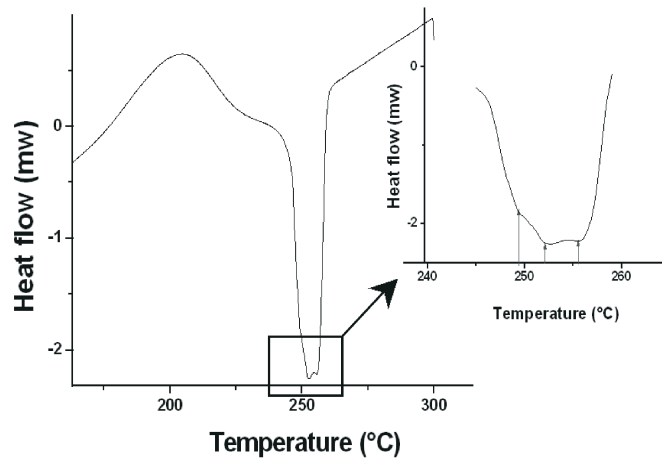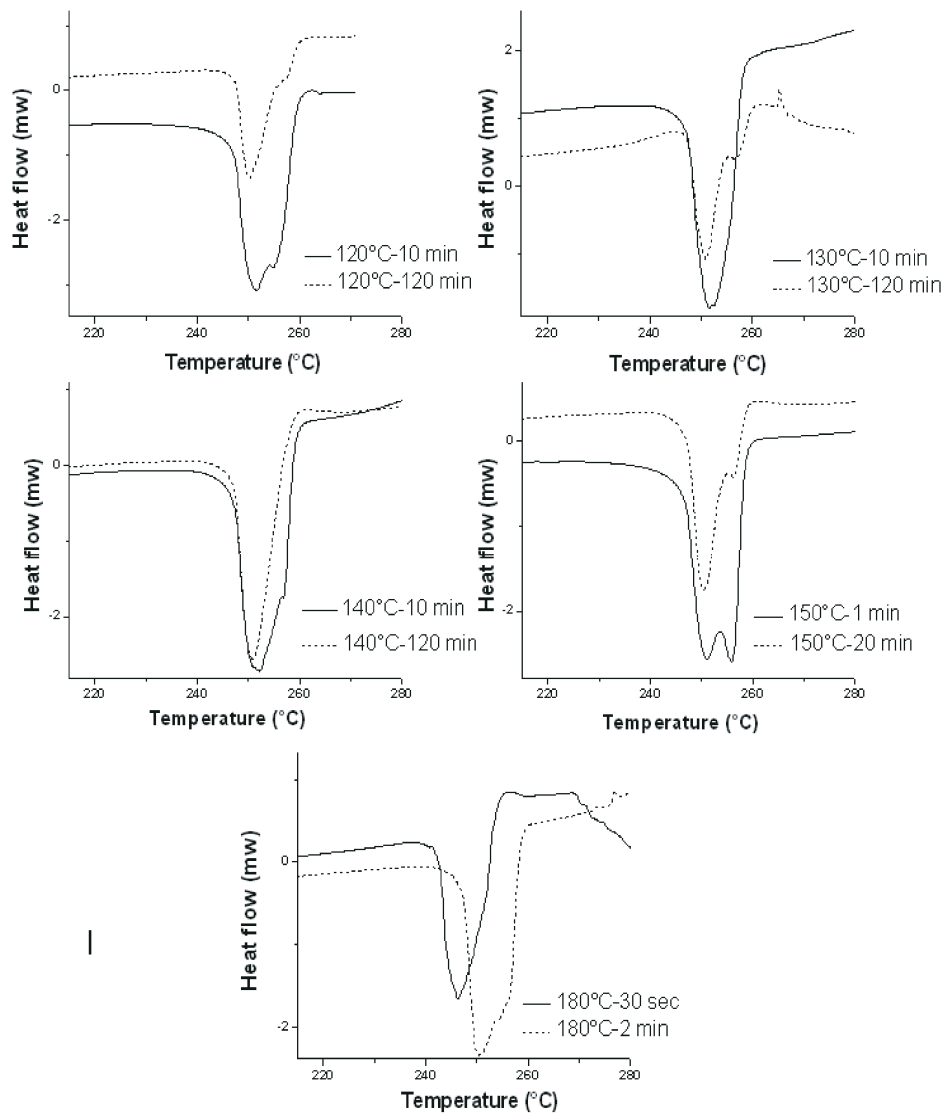
Fig. 1: Melting peak of untreated sample

Fig. 2: Melting peaks of thermal compacted samples

Table 3: Melting temperatures in thermal treatment conditions

Treatment	Peak 1 Tm (°C)	Peak 2 Tm (°C)	Peak 3 Tm (°C)(°C)
Untreated	249.5	252	255.3
120°C -10 min	251.5	254.8	-
120°C -120 min min	250.2	257.4	-
130°C - 10 min	251. 6	252.5	-
130°C - 120 min	250.9	256.5	-
140°C - 10 min	250.2	252.1	256.8
140°C - 120 min	250.7	-	-
150°C - 1 min	250.9	255.6	-
150°C - 20 min	250.2	256.1	-
180°C - 0.5 min	251.2	-	-
180°C -2 min	250.6	254.3	256.1
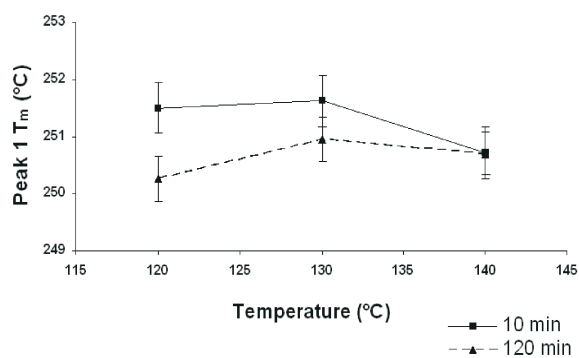
Fig. 3: Evolution of Peak 1 T_m with thermal treatment temperature
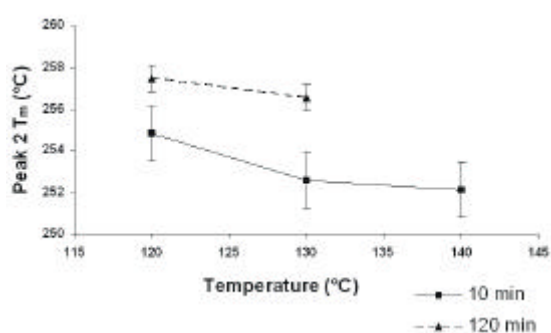
Fig. 4: Evolution of Peak 2 T_m with thermal treatment temperature

The treatment duration increase involves a light shifting of Peak 1 melting temperature toward lower temperatures (Figure 3), but induces an increase of Peak 2 melting temperature (Figure 4).

Table 4 presents the values of T_g for untreated and thermal treated samples. It appears clearly that glass transition temperature has increased for all thermal treated samples when compared to virgin sample. This can be explained by the fact that, for treated samples,

Table 4: Glass transition temperatures in thermal treatment conditions

Treatment	Tg (°C)
Untreated	76.23
120°C - 10 min	79.55
120°C - 120 min	79.87
130°C - 10 min	79.21
130°C - 120 min	79.51
140°C - 10 min	79.28
140°C - 120 min	79.53
150°C - 1 min	80.62
150°C - 20 min	81.17
180°C - 0,5 min	79.80
180°C - 2 min	79.29

the molecules of the amorphous phase are better oriented along the fiber axis and consequently a higher energy level is necessary to release cooperative movements of molecular chains.

Chemical Compaction Treatment: After chemical treatment with swelling solvents, a modification of melting peak profiles was obtained (Figure 5).With 20% chloroform solution, only one melting peak with shouldering was observed. This indicates the possible existence of second melting peak. In fact, a second peak appeared with the increase of chloroform proportion. The same observations can be formulated for samples compacted with dichloroethane. With 20% of methylene chloride solution, only one asymmetric melting peak was observed. This asymmetry disappears with the increase of dichloromethane proportion.

Table 5 shows obtained melting temperatures. The melting temperatures of all chemical treated samples have increased when compared with untreated sample. This is probably due to a major change in polymer crystalline structure. This will be investigated by XRD analysis.
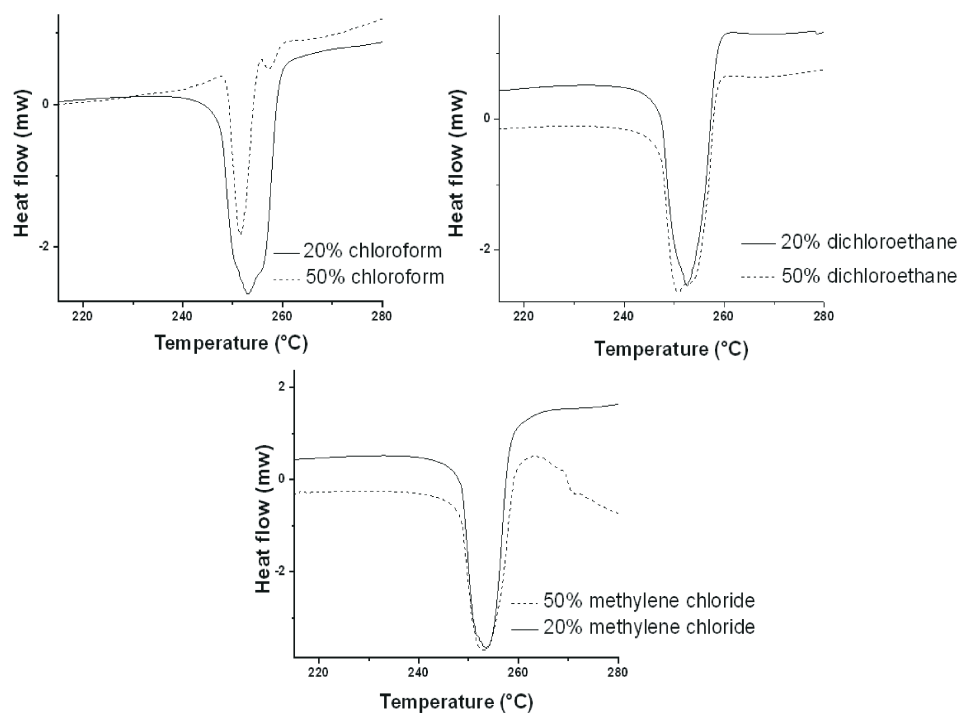
Fig. 5: Melting peaks of chemical compacted samples

Table 5: Melting temperatures in chemical treatment conditions

Treatment	Peak 1 Tm (°C)	Peak 2 Tm (°C)	Peak 3 Tm (°C)(°C)
Untreated	249.5	252.7	255.3
20 % chloroform	250.4	252.9	-
50 % chloroform	251.4	256.9	-
20 % methylene chloride	253.3	-	-
50 % methylene chloride	253.3	-	-
20 % dichloroethane	252.3	-	-
50 % dichloroethane	250.8	252.7	-
-	No Peak obtained		

Table 6: Glass transition temperatures in chemical treatment conditions

Treatment	Tg (°C)
untreated	76.23
20 % chloroform	77.96
50 % chloroform	79.8
20 % methylene chloride	79.82
50 % methylene chloride	-
20 % dichloroethane	79.22
50 % dichloroethane	78.59

Table 6 presents the values of glass transition temperature for untreated and chemical treated samples. The chemical treatment involved an increase of glass transition temperature. This can be explained by the fact that for chemical compacted samples, molecular chains became more difficult to move since the T_g marks the onset of segmental mobility of the polymer. Indeed, the preferential interaction of these solvents with either aromatic or aliphatic ester residue in PET, can allow a new internal structural rearrangement of macromolecular chains in amorphous zone [14].

XRD Analysis: The differences between melting peaks profiles and melting temperatures of untreated sample and compacted samples allowed to suppose that the two compaction treatments have induced modifications in crystallites size. The X-ray diffraction would confirm this hypothesis.

Table 7:Crystallites size in thermal treatment conditions

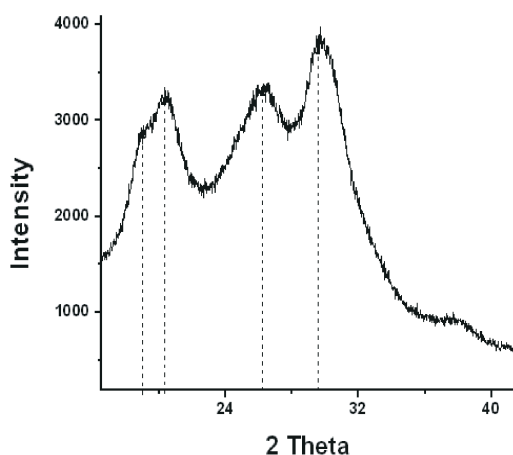|	Temperature (°C)	Duration (min)	Crystallites size (Å)	
			d_{010}	d_{100}
Untreated sample			32.95	31.43
	120	10	38.45	35
	130140		38.45	35.77
	140		41.43	35.76
Compacted samples	120	120	38.44	34.99
	130140		37.55	35
	140		42.5	36.56
	150	120	39. 38	41.4
		20	36.55	36.55
	180	0.5	42.5	40. 38
		2	37. 39	32.91

Fig. 6: Diffractgram of untreated sample

Thermal Compaction: The diffractogram of the untreated sample shows four peaks corresponding to the following reticular planes: , $(0\bar{1}1)$,(010), $(\bar{1}10)$ and (100). These planes correspond respectively to the following 2θ values: 18.88°; 20.37°; 26.32°; 29.65° (Figure 6). These peaks were also detected in treated samples diffractograms.

A variation of crystallites size in all perpendicular directions to reticular planes was observed. We focused on (010) and (100) directions because they allow to calculate the crystallites size in the direction of a and b cristallographics axes (Table 7).These directions correspond respectively to the interactions directions between dipoles and ð electrons [13, 15].

Figure 7 represents the size of the crystallites in planes perpendicular, respectively, to (010) and (100). We can observe an increase of a crystallites size for all thermal compacted samples comparatively to untreated sample.

This is probably due to the fact that thermal compaction, which happens quite over the glass transition temperature, induces changes in the orientation of molecular chains and consequently changes in crystallites size. Indeed, the main effect of a heat treatment on polymers structure is the rearrangement of bonds among the polymeric chains due to increased thermal motion. Roldán and al. analyzed the effect of temperature on the polymers structure. They associated the increase of crystallites size to the rupture of molecular bonds and their rearrangement for morphology of minimum conformation energy [16]. For the untreated sample, the crystallites middle height width is higher than that of treated samples. This indicates the existence of imperfect crystals. Dieval and al. [17] explained that thermal treatment, over glass transition temperature, makes molecular chain segments aligned and closer to each other.

The crystallites size is lower in the (100) direction because of the PET molecular interactions. According to literature, dipole-dipole interactions of the adjacent ester groups along the fiber axis are more significant than interactions of aromatic electrons ð in a direction. Polymer recrystallisation takes place in the direction of the strongest interactions minimising then the energy of the system [17].

Chemical Compaction: Figure 8 shows an increase of crystallites size for all chemical compacted samples in perpendicular directions to (010) and (100) planes. We suggested that the interaction between PET fiber and solvents induces nucleation of crystallites and consequently crystallites size increase. Statton and al. tried to characterize chain folding in PET fiber.
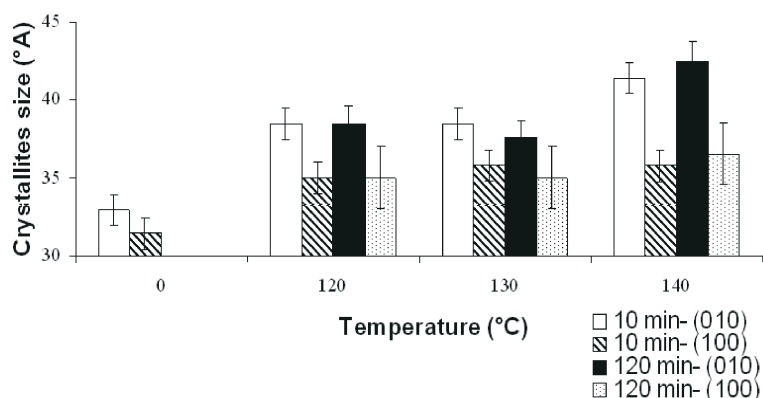
Fig. 7: Crystallites size evolution in perpendicular directions to (010) and (100) planes with thermal treatment temperature
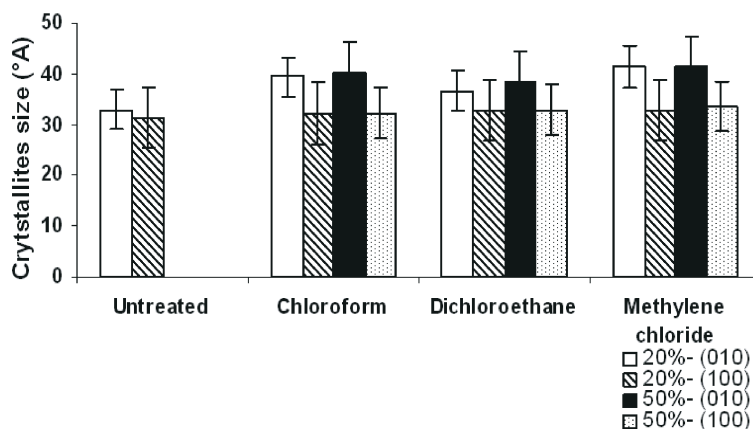

Fig. 8: Crystallites size evolution in perpendicular directions to (010) and (100) planes for different solvents proportions

They noticed that for PET fiber treated in strong plasticizing solvents at room temperature appears to be that nucleation of small crystals of short fold length is occurring, similar to crystallization during low-temperature (< 175°C) annealing [18]. The crystallites size increase is more significant in the perpendicular direction to (010) plane. It appears also that swelling agent proportions do not induce considerable modification of crystallites sizes. The crystallites sizes were more affected by the nature of swelling agent because the interactions between polymer and solvent.

We have demonstrated in previous works [5] that all compaction treatments induce a longitudinal shrinkage and lateral swelling for compacted samples. The physical and chemical changes of PET fibers observed in this study let us suggest that morphological changes and crystals formation and growth occur in separate process. In fact, Wilson [19] used infrared techniques to follow the crystallization stage. He noted that shrinkage occurs first and the onset of crystallization occurs subsequently,

causing little or no additional length changes. The crystallization process is therefore a secondary process which at low temperatures does not inhibit the shrinkage process.

CONCLUSION

The aim of this study was to determine the effect of thermal and chemical vascular prostheses compaction on physical and chemical properties of PET fibers. The DSC technique showed that all compaction systems induced a glass transition temperatures increase for different compaction parameters. The analysis of the melting behaviour permitted to conclude that melting temperature depends on treatment conditions and that the DSC thermograms show clearly two or more melting peaks indicating the existence of different crystallites sizes. The XRD technique allowed to evaluate crystallites size increase, after compaction, in the two crystallographic perpendicular directions to (010) and (100) planes.

This increase is more significant in the first direction because of the nature of molecular interactions. These obvious changes in the structure of PET yarns have an influence on grafts life time in the human body. Consequently compaction conditions have to be rigorously chosen during grafts manufacturing.

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