

Molecular orientation in electrospun poly(butylene terephthalate) nanofibers

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ABSTRACT

Poly(butylene terephthalate) electrospun fibers were analyzed by Thermally Stimulated Current (TSC) technique. A spontaneous current was released at near glass transition indicating dipole relaxation. Molecular orientation was also probed by birefringence analysis. Electrospun fibers showed a high level of birefringence, which extinguished upon melting.

Keywords: electrospinning, molecular orientation, nanofibers, poly(butenes terephthalate)

1 INTRODUCTION

Poly(butylene terephthalate) (PBT), a linear polyester of aromatic nature, is a thermoplastic of excellent mechanical properties. Like PET, electrospun fibers of PBT can be used in blood vessel tissue engineering applications as scaffolds for endothelial cells [1]. In this work, PBT electrospun fibers were produced by conventional electrospinning techniques, using a solution of PBT dissolved in trifluoroacetic acid. The dependence of the resulting electrospun fiber on the experimental conditions was examined.

Electrospinning is a process that converts polymer melts or solutions into fibers with diameters in the range of about 20 to 500 nm. The mechanism of the spinning process involves the injection of charge into a polymer fluid. An external electric field produces a force that is greater than the surface tension of the fluid, causing the ejection and acceleration of a polymer fluid jet. The reduction of local charge density is achieved through the creation of surface area as the cylindrical fluid jet extends to form a nanodiameter filament which deposits as a non-woven web. As with conventional spinning, the systematic variation of the extrusion and quench environments in electrospinning leads to the production of non-woven scaffolds, differing in filament diameter and morphology [2,3].

2 EXPERIMENTAL

PBT pellets (Celanex 1700A™ from Ticona®) were used as received. The solvents used were trifluoroacetic acid (Riedel) and hexafluoropropanol (Aldrich).

The electrospinning apparatus shown in Figure 1 consisted of (i) a polymer solution delivery system, (ii) a power supply to generate an electrical field and (iii) a fiber collector device. The delivery system was comprised of a 10 mL syringe fitted with an 18 or 20 stainless steel needle. The plunger of the delivery syringe was connected back-to-back to the plunger of a water filled dual syringe hydraulic system that could be remotely actuated using an infusion pump (Harvard Apparatus, Model 975). A typical electrical field of 1000 V/cm was provided by a DC power supply (Gamma High Voltage Research, Model ES30P) connected directly to the needle of the delivery syringe. The collector device was a grounded stainless steel plate positioned at a fixed distance, typically 20 cm, from the needle. The delivery syringe apparatus and ground plate were mounted inside a plastic enclosure for solvent exhaust. The infusion pump and power supply were located outside the plastic enclosure.

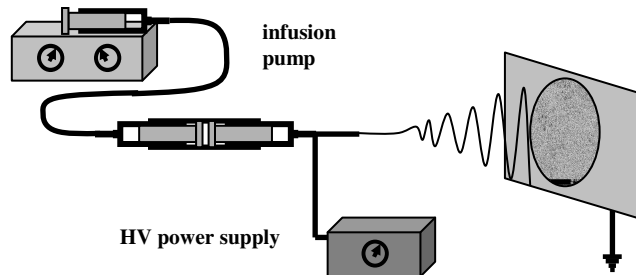


Figure 1: Electrospinning setup

Scanning electron microscopy was performed on a Leo-Zeiss Model 1525 microscope while optical microscopy was performed on a Olympus BX50 with polarizer lens attached to a Mettler Toledo FP82HT heater. Thermally Stimulated Current experiments were carried out using a TherMold TSC 9000 TSC/RMA. Conventional and modulated Differential Scanning Calorimetry experiments were performed on a TA Instruments Q100 DSC.

3 RESULTS AND DISCUSSION

Like other polyesters of the series, the PBT macromolecule contains polar structures such as the carbonyl dipole and non-polar structures such as the aliphatic butylene moiety. The flexibility of butylene segments brings to this polymer a high rate of

crystallization. Typical literature values for T_g is 45-55°C, T_m around 230°C and crystallinity of 32%.

Our own determination of T_g and T_m correlate quite well with the literature, as shown on Table 1. All measurements were taken from modulated differential scanning calorimetry (MDSC) experiments. T_g values were calculated from reversing C_p signal vs temperature, where C_p is the complex heat capacity, whereas T_m values were taken from heat flow signals vs temperature.

Sample	T_g (°C)	T_m (°C)	ΔH_f (J/g)
Ground	47.9	230.1	72.0
Electrospun	47.4	224.7	64.3
Melt-pressed	45.9	(b)	(b)
Cast	46.7	(b)	(b)

Table 1: Results from Modulated DSC^a of PBT samples
^aConditions used: ramp 1°C/min from 0°C to 250°C, modulate $\pm 1.00^\circ\text{C}$ every 60 s; ^bnot measured

It is quite clear that all samples show the same temperature for glass transition, with very subtle differences. Also, T_m seems to remain the same, with ca. 10% decrease on heat of fusion for the electrospun sample. The drop in heat of fusion, hence crystallinity, is expected in view of the rapid solidification of the fiber perhaps driven by rapid cooling due fast solvent evaporation.

PBT was successfully electrospun from trifluoroacetic acid and hexafluoropropanol as solvent. Figure 2 shows an example of a non-woven mat produced.

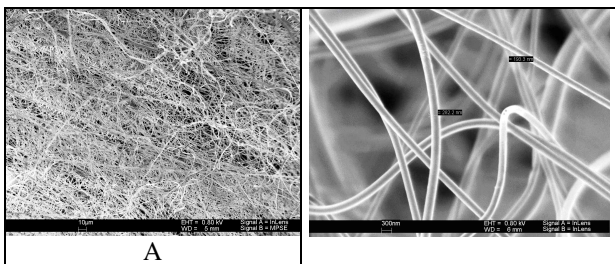


Figure 2: SEM pictures of PBT fibers electrospun from TFA solution. (A) Mag = x1,000; (B) Mag = x40,000

Final fiber diameter was shown to be dependent on polymer concentration (Figure 3), solution flow, needle diameter, electrical field (Figure 4), distance between spinnerette and take-up, solvent, etc. This behavior is typical of what is observed in other electrospinning processes [4].

We have also attempted to analyze molecular features of the electrospun fibers. PBT is known to produce two types of crystalline phases: the α phase where the butylene group sits on a gauche-trans-gauche conformation (therefore, found on relaxed samples) and β phase, where the butylene group presents an extended all trans conformation (found on stressed samples) [5].

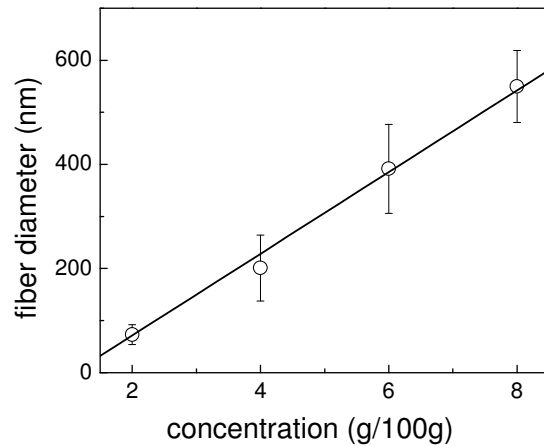


Figure 3: Fiber diameter dependence on concentration of PBT in TFA solution

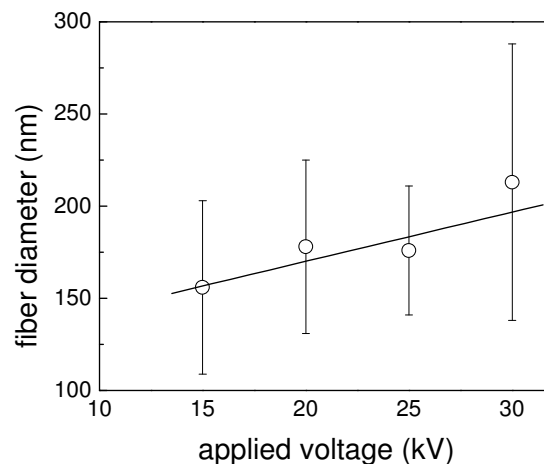


Figure 4: Fiber diameter dependence on concentration of PBT in TFA solution

PBT electrospun fibers showed a high level of birefringence (Figure 5), which extinguished upon melting. Direct measurement of the birefringence was precluded by the small size of the fibers.

This anomalous behavior has only been observed in wet-spun fibers [6] as a dependence of network drawn ratios, but with no relation on the proportion of the two predominant α and β crystalline phases, suggesting an amorphous phase orientation phenomena

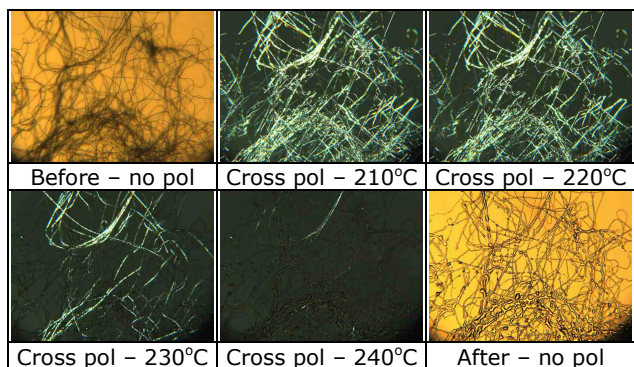


Figure 5: Birefringence observed in PBT electrospun mats using polarization microscopy

Thermally Stimulated Current (TSC), a dielectric technique, was used to probe for dipole orientation and free charge mobility. A spontaneous current was released near the glass transition indicating dipole relaxation for a non-equilibrium, oriented state, which was not observed in control melt-pressed and cast film specimens (Figure 6). Control experiments using a Teflon layer between the sample and the electrodes demonstrate that the observed current is not due space charges, but due a true dipole relaxation.

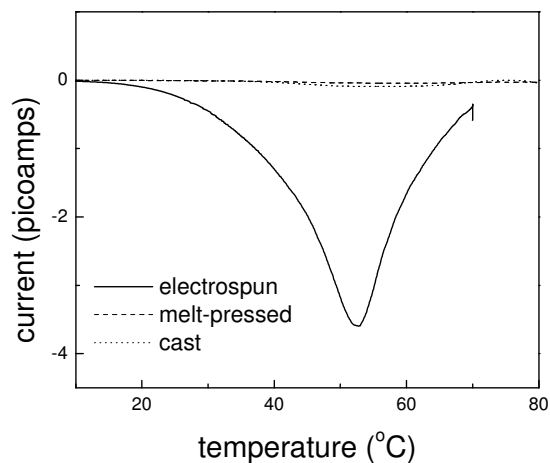


Figure 6: Thermally stimulated relaxation current spectra of PBT near glass transition

We propose that this dipole orientation is a result of the working electric field used in the electrospinning process upon the microstructure of the fiber. In the presence of the field, this microstructure develops during evaporation of the solvent and results in a non-random disposition of these dipoles at the take-up device.

Orientation of such dipoles seems to be strictly dependent on the field orientation. Figure 7 shows that the signal of this relaxation current is dependent on the position of the sample on the TSC electrode pair. By flipping the faces of the samples an opposite direction of the current is observed.

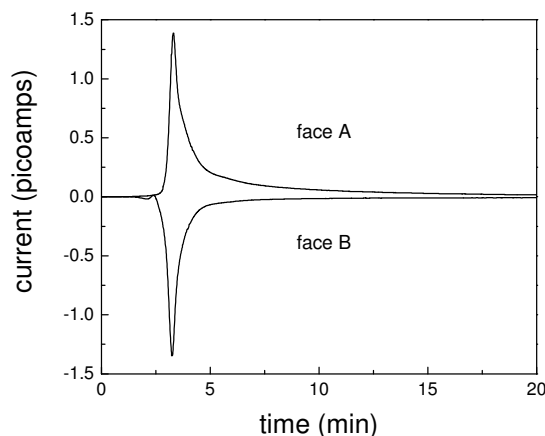


Figure 7: Thermally stimulated relaxation current kinetics of PBT upon heating at 60°C.

Lastly, the same technique has shown a large amount of space charge trapped at the polymer surface, which is released near melting (Figure 8). This signal, up to 40,000 times more intense than that of relaxation, is totally suppressed when a Teflon layer is placed between the sample and the electrodes.

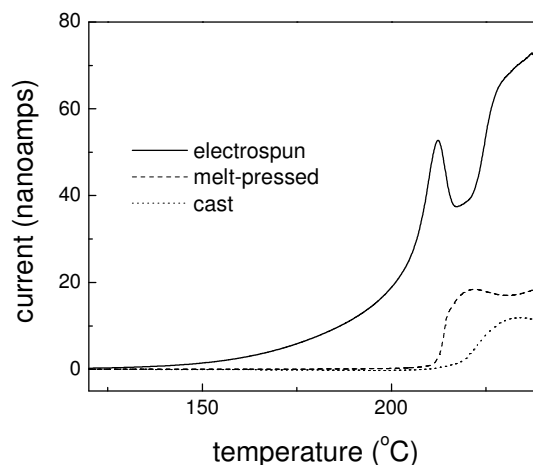


Figure 8: Thermally stimulated relaxation spectra of PBT near melting

This phenomenon is quite general and was also observed in our laboratory for other polymeric systems as

well (results not shown). The simplest explanation is that the charge placed onto the surface of the internally localized fibers can not discharge due lack of contact with the take-up device. Owing to the dielectric character of the material, the charge will remain in place.

CONCLUSIONS

Electrospun fibers present unexpected molecular and crystalline orientation. This orientation is likely to be a result of the high electrical field at which the forming fibers are subject throughout its formation event. Both facts could be of some benefit in the growth of dipolar cells. Nervous cells, for instance, is known to present a dipolar structure [7]. Spinal implants, typically made of biodegradable polyesters, depend on the ingrowths of such cells through porous materials [8].

The presence of large amounts of space charge is a reflex of the high specific area of the formed mats, generated by the electrospinning process. This charge is trapped in the surface of the inner fibers and may represent a problem for many electrospinning applications. Therefore, processes to release this charge prior to use must be developed.

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