



SYNCHROTRON SCATTERING OF THERMOTROPIC POLYMER

Synchrotron scattering and nanoindentation of heat treated high performance thermotropic polymer

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A multi-scale analysis, ranging from μm \rightarrow nm \rightarrow \AA -scale on the influence of thermal treatment on the thermotropic copolyester based on 60 mol% (1,4)-hydroxybenzoic acid (B), 5 mol% (2,6)-hydroxynaphthoic acid (N), 17.5 mol% terephthalic acid (T) and 17.5 mol% biphenol (BP) - COTBP- was carried out. The \AA and nm -scale structure was investigated by synchrotron scattering (WAXS and SAXS). Extruded tapes ca. $30\ \mu\text{m}$ thick were annealed at $300\ ^\circ\text{C}$ under air, without tension. WAXS revealed fibre-like structure with crystalline order, whereas SAXS patterns exhibited diamond-shaped diffuse scattering and discrete meridional scattering elucidating structures along the fibre axis and periodic crystallites. Heat treatment produced roughness reduction, and WAXS patterns showed reflections sharpening indicating an improvement of molecular register and packing (molecular alignment and degree of crystallinity χ increased). Thermal treatment increased the thermal stability, melting transition and tensile Young's modulus, E , along extrusion axis, whereas nanoindentation showed decrease of hardness and elastic modulus. Hence, a thermally-induced self-reinforcing effect was evidenced, with microstructure reorganization correlating with improved thermo-mechanical properties.

Introduction

The pioneering research by the Celanese of America R&D scientists on wholly aromatic thermotropic LCs rapidly demonstrated that these materials were effectively high-performance thermoplastics. This opened applications into automotive, aerospace,

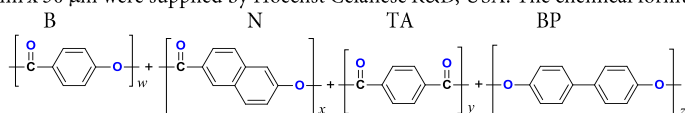
microelectronics, and more recently in medical devices. Thermotropic LCPs easily meet the challenge of complicated mould designs, tight dimensional tolerances, autoclaving resistance, and flame retardancy^[1, 2]. The thermal decomposition temperatures exceed 450°C, hence these materials can hold modulus of the order of 1 GPa above the glass transition temperature. These LCPs also exhibit resistance to acid, bases and corrosion, making them suitable for soldering microcomponents, high temperature and harsh environments^[1]. A key advantage of thermotropic LCPs over lyotropic LCPs is the ability to be processed by extrusion, injection and blow moulding machinery^[1, 2].

Thermal treatment carried out close to the melting transition is quite effective to modify physical properties of LCPs^[2-5]. Aramid, Kevlar fibres are heat treated under tension, promoting molecular rearrangements^[2, 5]. Thermotropic LCPs, annealed close to the solid-to-nematic transition temperature ($T_{s \rightarrow n}$), increased molecular weight and degree of crystallinity. This promoted higher chemical resistance, increase of thermo-mechanical properties^[1, 3, 4]. Here, the influence of heat treatment on physical properties of extruded copolyester COTBP has been studied^[4, 7]. A multi-scale structure analysis was carried out, from the μm -scale through the Å- and nm-scale.

Experimental

Materials

The thermotropic random copolyester consisted of: 66 mol% 1,4-hydroxybenzoic acid (B), 5 mol% 2,6-hydroxynaphthoic acid (N), 17.5 mol% of terephthalic acid (TA), and 17.5 mol% of biphenol (BP), termed COTBP^[4]. Extruded tapes 10 mm x 30 μm were supplied by Hoechst Celanese R&D, USA. The chemical formula is



Tape sets ca. 50 mm long were placed in Petry dishes and annealed at 300°C under dry air for up to 300 min, without tension.

Methods

Synchrotron wide-angle and small-angle X-ray scattering (WAXS and SAXS, respectively) experiments were carried out at the X27C beamline in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) (Upton, NY,

USA). A 3-pinhole collimation system, wavelength of 1.366 Å, and a beam of 600 μm diameter were used. The WAXS patterns were recorded on Fuji image plates, sample-to-detector distance of 60 mm, and 3 s exposure. The SAXS patterns were recorded with a MAR CCD X-ray detector (MARUSA), 512x512 pixels resolution (pixel size=158 μm). The sample-to-detector distance was 1.70 m, 10 s exposure, and calibrated with silver behenate. The patterns were analysed using POLAR v2.6 (Stonybrook Technology Inc., USA). The morphology was investigated by small-angle light scattering (SALS) optical and atomic force microscopy (AFM). For AFM the Dimension Icon DS100 microscope (Veeco Instruments Inc.) was utilized. Images were acquired in contact mode, scanning 80 x 80 μm² analysing with NanoScope Analysis v. 1.5.

Results and discussion

The molecular structure at Å-resolution by WAXS is shown in Figure 1(a, b). The lower half of the WAXS patterns were contoured for easy visualization of crystalline reflections. The presence of meridional reflections in the WAXS patterns (a and b) is highly unexpected considering that COTBP consist of four monomers, and the position along the meridian is aperiodic^[2,4,d]. After heat treatment at 300°C the reflections of COTBP tapes sharpened (clearly appreciated in the contour plots) and the intensity of off equatorial reflections increased, Figure 1(b). The reflections are indexed according to an orthorhombic unit cell with dimensions $a=7.96$ Å, $b=5.69$ Å and $c=12.54$ Å.

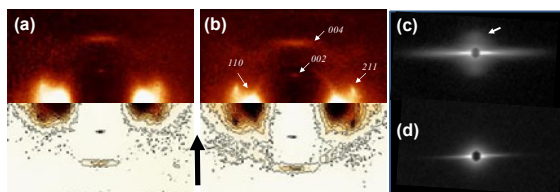


Figure 1. Synchrotron wide-angle and small-angle X-ray scattering patterns of extruded tapes of COTBP: (a, c) as-received, and (b, d) heat treated at 300°C for 300 minutes. Black vertical arrow indicates extrusion axis.

The SAXS pattern of the as-extruded tape, Figure 1(c), exhibits diamond-shaped intensity streaks along the equatorial axis. Strikingly, there is also discrete scattering along the meridional axis associated to spatially periodic nm-sized structures, i.e. crystallites. Transmission electron microscopy (TEM) confirmed this result^[7]. Figure 1(d) shows that

after 300 min heat treatment at 300°C the discrete scattering along the meridional axis is not detected (i.e., it has shifted to smaller q range, into the beam stop) and the angular spread of the diamond-shaped equatorial scattering has been greatly reduced (azimuthally and radially) indicating nanostructure alignment along extrusion axis. The SAXS intensity maximum indicates an average long-spaced structure $L=2\pi/q_{max}$ of 43.9 nm.^[7]

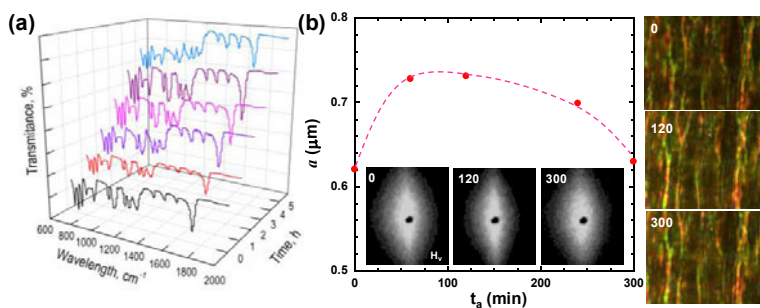


Figure 2. (a) FTIR spectra of COTBP annealed at 300°C. (b) Correlation length a as a function of time t , annealing at 300°C. SALS patterns and polarized optical micrographs (POM) of tapes at 300°C obtained at the times indicated. He-Ne laser and H_v polarization.

Analyses of the X-ray scattering patterns^[5-7] revealed increase of crystallinity and degree of molecular alignment P_2 with heat treatment time. Furthermore, the Young's modulus E (uniaxial tension mode) increased over 150%.^[4]

The thermal annealing did not degrade the specimens, as verified by infrared spectroscopy, Figure 2(a). The morphological changes, also probed by SALS and POM, are shown in Figure 2(b). The correlation length a was extracted from the equatorial streaks of the SALS patterns and plotted as a function of heat treatment time t_a . Note that the thermal treatment first induced an increase of correlation length and then gradually decreased.

The POM micrographs of the tape, right side of Figure 2, exhibit aligned defect texture responsible for the equatorial streaks in the SALS patterns. The optical morphology revealed by SALS and POM was correlated with AFM topographic variations consisting of hills and valleys, with average hill-to-hill distance $l=7$ μm in the as-extruded tape. After thermal annealing the topographic defects were reduced, and smoother surfaces were produced. Height profiles showed that after 60 min l increased to ca. 9 μm, and after 300 min $l=17$ μm. These results revealed an increase of l with heat treatment time, correlating with increase of P_2 and roughness reduction. The heat treatment significantly reduced the surface roughness, from ~120 nm at $t_a=0$ to ~45 nm at $t_a=300$ min.

Nanoindentation studies were carried out by AFM in penetration mode, as shown in Figure 3, using the AFM Cypher S (Asylum Research) with a probe AC160TM-R3 (Olympus) of 7 nm diameter. The force vs. penetration curves are shown in Figure 3. Strikingly, after 300 min thermal treatment the force curve decreased denoting lower modulus M and hardness H . The mechanical properties were quantified fitting the elastic portion of the force traces and using the Hertz model suitable for spherical probes,^[8] the results are shown in Figure 3. Note the considerable reduction of surface mechanical properties with heat treatment, correlating with increased molecular alignment and reduction of nm-sized defects. The experimental error based on at least three indentations, on different region each time, was determined to be within 10%.

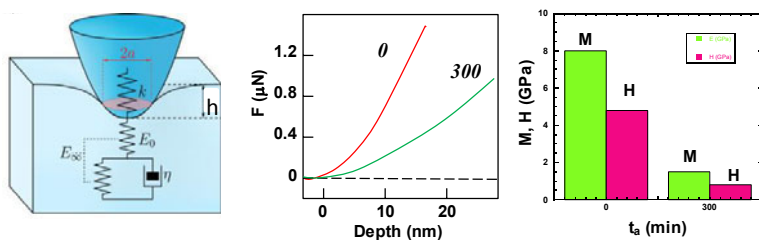


Figure 3. AFM force as a function of indentation depth for COTBP tapes heat treated at 300°C for 0 and 300 min in air. Modulus M and hardness H as a function of treatment time t_a .

The structural changes and mechanical properties induced by thermal annealing were further investigated by analysing fractured specimens by scanning electron microscopy, SEM. The SEM micrographs of the as-extruded and thermally annealed tapes are shown in Figure 4(a, b). Interestingly, the as-extruded tape revealed plastic deformation whereas the annealed tape exhibited brittle fracture (wood-like morphology), consistent with an increased tensile modulus.

Conclusions

A multi-scale analysis of heat treated tapes of thermotropic copolyester COTBP was carried out. Heat treatment induced an increase of molecular alignment, reduction of surface defects and reduction of roughness. Heat treatment also increased the crystallinity and the nanovoids increased in length, were laterally compressed and the misorientation angle was reduced. The structural changes correlated with increase of tensile modulus. The WAXS patterns revealed aperiodic meridional reflections suggesting that COTBP forms

non-periodic layer crystals (npl). The crystallites were sufficiently spatially correlated along the chain axis, hence SAXS exhibited discrete scattering. The heat treatment was carried out without tension; hence the results also revealed a self-reinforcing effect. Strikingly, nanoindentation revealed a reduction of hardness and modulus at the surface, consistent with highly aligned macromolecules.

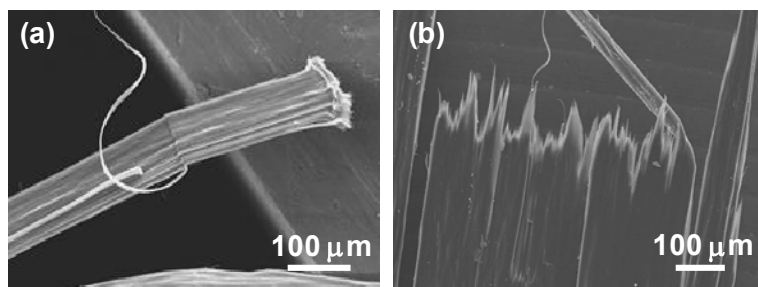


Figure 4. SEM micrographs of COTBP tapes: (a) as-received, and (b) heat treated at 300°C for 300 min in air.

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References

- [1] G. W. Calundann, M. Jaffe, Anisotropic polymers, their synthesis and properties. Proc Robert A. Welch Conf. Chem. Res. XXVI. *Syn. Polymers* **2**, 247-285 (1982).
- [2] A. M. Donald, A. H. Windle, S. Hanna, *Liquid Crystalline Polymers*, 2nd edition, Cambridge University Press, United Kingdom (2005).
- [3] S. Salahshoor-Kordestani, S. Hanna, A. H. Windle, *Polymer* **4**, 6619-26 (2000).
- [4] A. Reyes-Mayer, B. Alvarado-Tenorio, A. Romo-Uribe, M. Jaffe, *Polym. Adv. Techn.* **24**, 1029-1039 (2013).
- [5] S. Ran, D. Fang, X. Zong, B. S. Hsiao, B. Chu, P. M. Cunniff, *Polymer* **42**, 1601-1612 (2001).
- [6] A. Reyes-Mayer, B. Alvarado-Tenorio, A. Romo-Uribe, R. Benavente, M. Jaffe, A. Molina-Ocampo, *Polym. Adv. Techn.* **27**, 748-758 (2016).
- [7] A. Romo-Uribe, A. Reyes-Mayer, M. Calixto-Rodriguez, R. Benavente, M. Jaffe, *Polymer* **153**, 408-421 (2018).
- [8] E. H. Yoffe, *Phil. Mag.* **A 50**, 813-828 (1984).