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The thermal analysis of fibers in the twenty first century: From textile, industrial and composite to nano, bio and multi-functional

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Abstract

The one-dimensional symmetry and low linear density of fibers make them a special case for process–structure–property performance definition, simplified by the symmetry and complicated by meta-stable morphology and unwieldy sample geometry. The thermal analysis of fibers always reflects the total process history of the fiber, from synthesis through storage environment prior to sampling. Thermal analysis provides a convenient platform for quantifying fiber performance (or fabric performance) in terms of the fiber phase stability (DSC, DMA, TSC), dimensional stability (TMA), chemical stability (TGA, DSC) and mechanical property stability (DMA) as monitored under both prior history and end-use relevant conditions. Of special interest is the application of these techniques to the characterization of functional fibers, and fibers designed for in vivo use such that the resulting data is reflective of desired performance targets.

1. Introduction

The thermal analysis of fibers is the thermal analysis of oriented, semi-crystalline fibers. Fibers, defined as structures whose length to diameter ratio – aspect ratio–is greater than about 100, represent a simple one dimensional example of polyphasic polymer morphology, suitable for correlating back to process variables and forward through properties to performance. The difficulty inherent in fiber thermal analysis lies in the choice of representative samples – typical commercial fiber spinning processes run at speeds in excess of km/min – hence one must take care in the choice of samples, how one prepares samples for thermal analysis investigations and in not adding to the sample process history during sample preparation. While the thermal analysis of fibers can be used solely as a "fingerprinting tool", much more insight into the origins of the thermal analysis result can be achieved through an understanding of the process history responsible for the morphological features, giving rise to the observed response. These issues have been described by the authors in detail [1]. It is useful, however, to review the process of fiber formation as a basis for further discussion.

Fiber spinning provides a convenient form for defining the process–structure–property relationships of polymers. A simplified schematic of the spinning process is shown in Fig. 1.

Accurate control of the key spinning variables of stress, time and temperature allows the manipulation of fiber morphology, hence detailed control of structure from the nanoscale through the mesoscale, as illustrated in Fig. 2. Fig. 2 contrasts the morphologies produced by imparting molecular orientation prior to and subsequent to crystallization in a typical semi-crystalline polymer spinning process.

These routes impart significantly different performance characteristics in the fibers produced, for example, at similar mechanical property levels (equivalent average molecular orientation); fibers produced by crystallization after molecular orientation will exhibit higher dimensional stability than fibers crystallized before molecular orientation. Fibers are a convenient form for clarifying the effects of systematic morphological changes on the properties of polymers, whether the performance issues are mechanical strength or interactions with cells in vivo. It is well established that the performance characteristics of a processed polymer are as much dependent on morphology and molecular chain orientation as on backbone chemistry (see for example,

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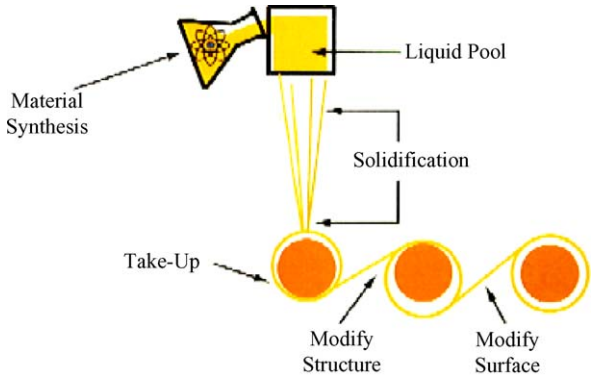


Fig. 1. Schematic of melt spinning.

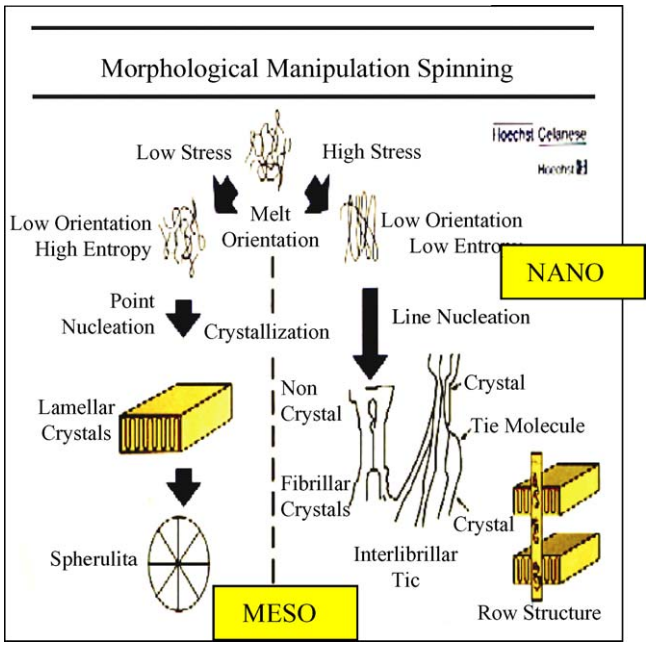
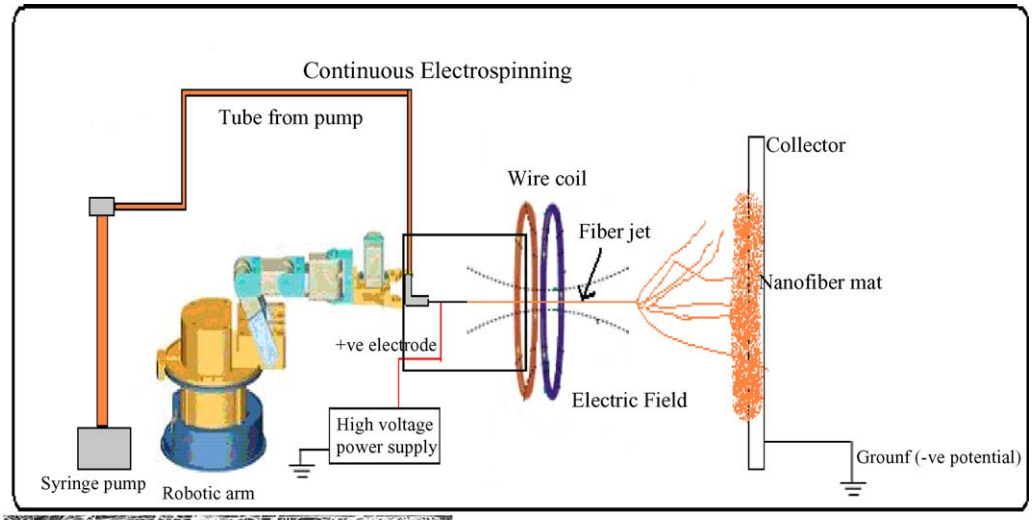
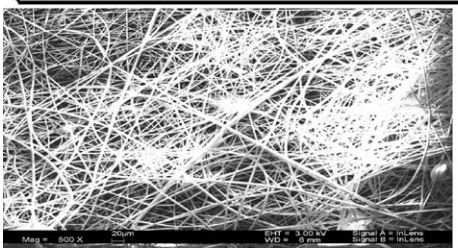


Fig. 2. Morphology development during fiber spinning.

the recently published book of Ward on [2] orientation effects in polymers). Fibers themselves are conveniently assembled into multidimensional arrays (fabrics, composites, tissue engineering scaffolds, etc.). Fiber-based structures allow the control of surface area through fiber cross-section and porosity through control of fabric or non-woven parameter space, while allowing the three dimensional design of mechanical performance through control of filament orientation and filament tie-points.

The thermal analysis of fibers in the 21st century differs from earlier studies not in the nature of the studies but in the focus. Over the past few years the textile fiber industry has been declared mature, consolidated significantly and moved from the developed to the developing countries (China, India). The focus in fiber science has, as in the field of materials overall, moved to specialty areas with large, upside performance potential. Examples of these areas are bioerodable polymers for in vivo use, nanofibers produced by electrospinning, higher performance fiber chemistries (including reconstituted silk and genetically modified silk protein) and "smart fibers", i.e. fibers that are able to sense their environment. In this paper we will focus on two areas, fibers in biology and the characterization of electrospun nanofibers.





50/50 PLGA Nonwoven Mat

Concentration 14%

Diameter range 300nm-2micron

Density208±.02 gm/cm^3

Fig. 3. Schematic representation of the electrospinning process, scanning electron micrograph of the resulting fiber mat.

2. Experimental

2.1. Biorelevant analysis

Conventional thermal analysis involves the monitoring of a material characteristic of interest as a function of temperature. The well known advantages of thermal analysis as a technique include the large amount of information that can be obtained from relatively simple and fast experiments, coupled with the low cost and availability of TA instrumentation. Extensive studies document the effects of heating rate, measurement atmosphere, additives and isothermal effects as a function of time [1]. In biorelevant testing of polymers, the temperature of interest is limited to 37 °C ±3, and it is often the time effects in aqueous environment containing biological molecules that are critical. Utilization of TA platforms to develop data relevant to performance under the above boundary conditions defines Biorelevant Analysis (BA). While at temperatures significantly higher than 37 °C, proteins denature and direct biological relevance may be lost, the plasticizing and chemistry/structure degrading effects of the biological environment may offer routes other than temperature alone to accelerate, thus understand, in vivo phenomena of interest. The study of biorelevant polymers has become a popular area of study, there is little emphasis yet in the literature, in the structural or thermal analytic characterization of such materials.

2.2. Electrospinning

Electospinning is a modification of dry spinning (spinning fiber from a high vapor pressure solvent directly into a solid fiber), where an electric field is introduced into the polymer, giving rise to excess charge and forces which result in filaments and filamentary mats with diameters as low as 50 nm to be produced [3]. With the increased interest in nanotechnology in recent years, the process has received a great deal of attention in the scientific literature [3]. The fibers so-produced do not present a consistent structural state and there are special handling problems associated with the small diameters and low mechanical properties of such samples. A representation of the electrospinning process and an Scanning Electron Micrograph of a typical electrospun mat are shown in Fig. 3.

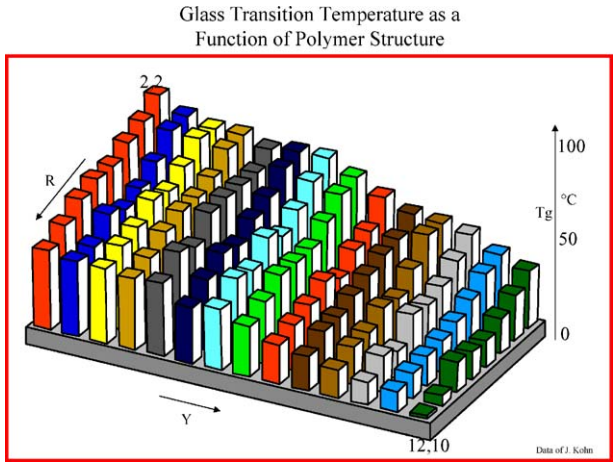


Fig. 4. Variation of Tg with chemical structure for a combinatorial library of bioerodable polyester amides data represents second heating DSC results [8].

3. Results and discussion

3.1. Biorelevant behavior of bioerodable polyarylate fibers

Bioerodable polymeric biomaterials are polymers designed for safe in vivo use as medical devices. Kohn [4] has produced a combinatorial library of regularly alternating polyester amide copolymers based on a dimer of the amino acid tyrosine, with the advantage that by simple changes in backbone and sidechain chemistry, regular changes in glass transition and surface water contact angle can be produced. Fig. 4 illustrates the published glass transition data, generated by taking Tg values from a second heating DSC experiment. It was noted that when a high Tg composition (sidechain and mainchain linkage short—poly(desaminotyrosylethyladipate)) was utilized in vivo, significant shrinkage occurred, rendering the material unsuitable for the application. As illustrated in Fig. 5, Jaffe et al. [5] were able to demonstrate that the shrinkage was enabled by the

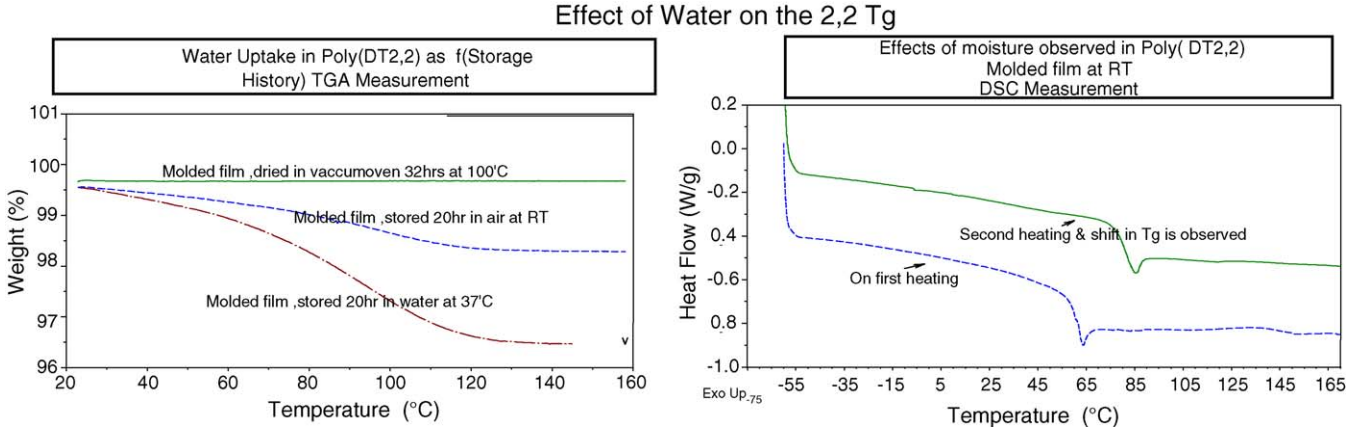


Fig. 5. The water uptake of poly(desaminotyrosylethyladipate) as measured by TGA and the effect of the absorbed water on the glass transition as measured by DSC.

plasticization of the resultant fiber by water at 37 °C from over 80 °C to below the body critical temperature of 37 °C. Water uptake was monitored by TGA and shown to greater than 3% and analysis showed that the drop in Tg with water uptake d Tg/d[water] was 14.5 °C/%. As surprising a resulted observation was that fibers from a composition with a published Tg of less than 15 °C showed no shrinkage at 37 °C when used in vivo. DSC investigation indicated that the stability of these fibers was due to long range order, subsequently confirmed by X-ray diffraction and infrared spectroscopy studies [6,7]. The DSC results are illustrated in Fig. 6. These results illustrate the importance to experimental conditions when analyzing samples for biomedical applications, especially the importance of testing under biorelevant conditions. All of the thermal history of the sample, including the sterilization of medical devices prior to implantation and the presence in biological fluids are relevant to performance in the designated end use.

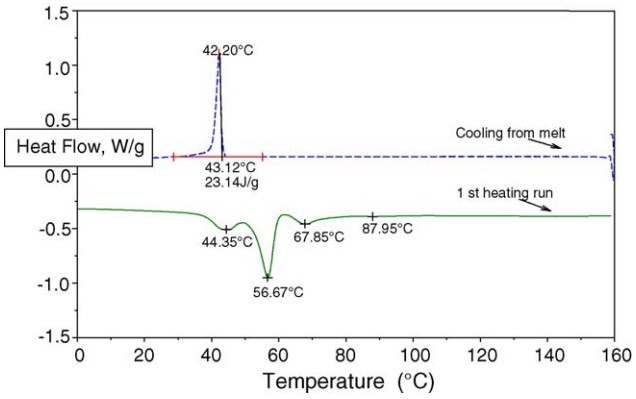
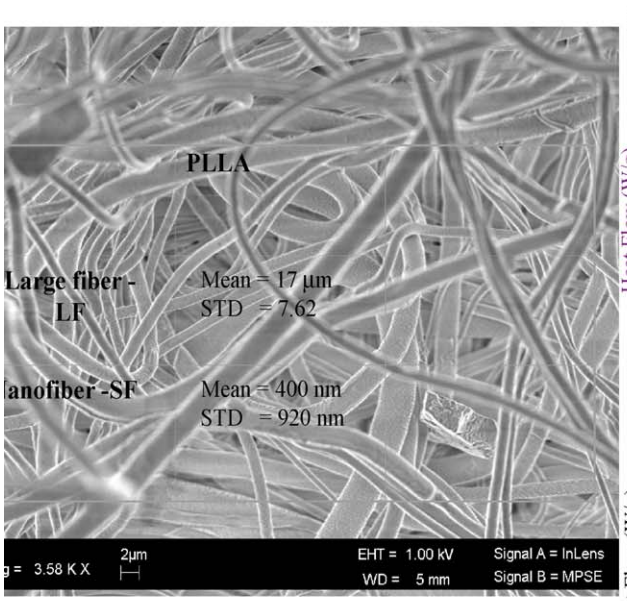
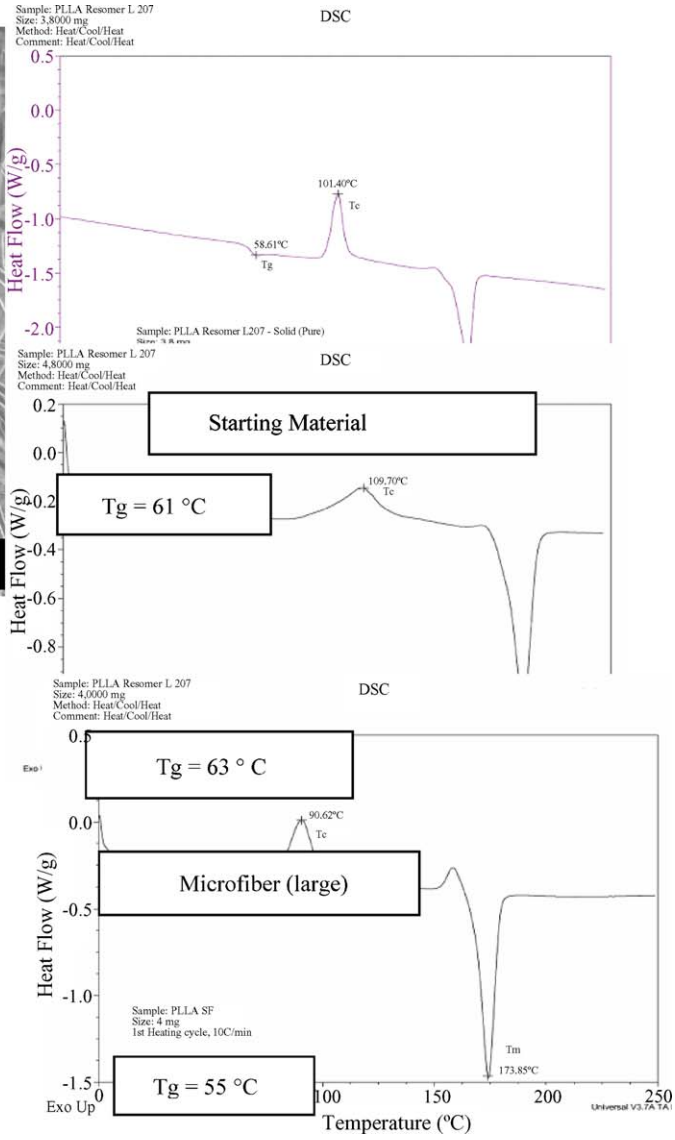


Fig. 6. DSC of poly(desaminotyrosyldodecyldeconate) showing clear endotherm on heating and exotherm on cooling, indicative of long range order.





Poly(l-lactic acid)

Material	Tg °C	Tc °C	Tm °C
start	61	100	175
large	63	103	172
small	55	92	172

Fig. 7. Melting behavior of electrospun mats of poly(l-lactic acid) fibers as a function of fiber diameter and process history.

3.2. Melting of electrospun mats of poly(l-lactic acid)

Poly(l-lactic acid) was electrospun from room temperature chloroform such that mats of about 400 nm average fiber diameter and 17 μm average fiber diameter were reduced at essentially the same mat density. The purpose of this experiment was to study the growth of mesenchymal stem cells as a function of the fiber diameter of the substrate or scaffold [8]. Results indicated that the stem cells preferred the smaller diameter fibers, indicating that cellular response is sensitive to the physical nature of the substrate. A representative micrograph of poly(l-lactic acid) fiber mat is shown in Fig. 7. Also shown in Fig. 7 are the first heating DSC traces of the starting material, the larger diameter fibers and the smaller diameter fibers, respectively. Comparison of the data from the three samples indicates the smaller diameter fibers show a significantly lower Tg and Tc than either the starting material or the large diameter fiber mat, suggesting a less stable (more rapidly quenched) structure is present in the nanoscale diameter mat. The melting points of all three samples are essentially the same, indicating that after cold crystallization all three samples reach the same state of physical perfection. It is not surprising that the very rapid solvent removal from the submicron fibers would be the equivalent of a significantly different quench history of the resultant fibers, as shown by the DSC result. This leads to the possibility that the observed differences in cell behavior may a function of different molecular chain conformation in the nanofiber diameter mat, rather than the diameter itself. Such differences could be eliminated by control of process history, i.e. slowing the solvent evaporation rate or annealing above Tc but below Tm of the nanofiber mat. Thermal analysis is sensitive to these subtle (sometimes not so subtle) differences in fiber structure often not recorded in complex biomedical or other end-use investigations in which such fibers are often utilized.

4. Conclusions

The importance and strength of thermal analysis as a tool for the characterization of fibers has not changed and will not change in the future. Principles described decades ago [1] are still valid, understanding the process history of fibers is still the critical factor in understanding the results of fiber thermal analysis and, in cases where this is not present, significant information about the chemical and morphological state of the fibers can still be deduced. What is changing in the 21st century is the emphasis on nano, bio, high performance and smart and this introduces new problems and new opportunities for the thermal analyst. At a time when instrument design and computers make the generation of thermal analysis data easier, the chances for the misunderstanding of the data also increases. It is up to the thermal analysis community to learn the origins of the problems presented to them by becoming familiar with the underlying science and technology, thus to insure that the powerful thermal analysis tool continues to grow in utility.

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