

Fabrication of polymer nanofiber arrays using thermal nanoimprint lithography

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Controlling the molten polymer flow in anodic aluminum oxide templated thermal nanoimprinting produces polymer nanofiber arrays with reproducible well-defined fiber lengths and aspect ratios.

The modification of polymer surfaces to produce materials with desirable properties is a research area that attracts considerable attention, largely owing to the potential applications for these materials in a wide range of fields, including optical, electrical, automotive, and medical. Polymers are not typically adhesive, but through surface modification to produce arrays of polymer nanofibers, they can become smart surface materials with properties such as dry adhesion, friction, and the ability to self-clean.¹ An important nature-inspired example has these features: polymer nanofiber arrays (PNFAs), which mimic the adhesive abilities of gecko feet.

A number of methods are currently available to prepare PNFAs. However, a lot of research in recent years has gone into making the current methods faster, cheaper, higher quality, less toxic, and more scalable. Here, we present the results of our investigation into an alternative fabrication method for PNFAs, using a combination of nanoporous anodic aluminum oxide (AAO) templating and thermal nanoimprint lithography.²

Nanoporous AAO templating is widely used with either melt-wetting or chemical-wetting to produce nanostructured materials. However, both of these methods are slow and use harsh chemicals. Our method uses thermal nanoimprint lithography instead, resulting in a faster, greener process. Furthermore, we can control the length and aspect ratio of the polymer nanofibers, which are significantly affected by the flow properties of the molten polymer, by adjusting the process (e.g., AAO pore size, imprint time, pressure, temperature).

We produce the nanoporous AAO templates using a two-step anodizing process, resulting in a honeycomb-like structure containing 50 or 100nm diameter pores: see Figure 1(a). We insert the template into a thermal nanoimprint press and use this system to nanoimprint

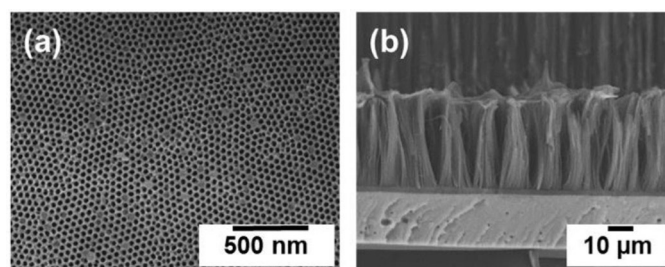


Figure 1. Scanning electron microscopy images of a (a) 50nm diameter nanoporous anodic aluminum oxide (AAO) template and (b) polystyrene nanofiber array.

films of polystyrene (PS) and polypropylene (PP) at high temperature and pressure. The AAO template is removed by chemical etching, leaving a PNFA: see Figure 1(b).

Our results show that the length of the PS nanofibers greatly depends on the flowing ability of the molten polymer in the AAO pores. We are able to control the polymer flow, and hence the fiber length, in a number of ways. For example, increasing the press time (from 10 to 90min) produces longer nanofibers: see Figure 2(a). However, press times over 30min cause only slight increases in fiber length, a result of resistance attributed to residual air effects in the pores.

Longer nanofibers are also obtained by increasing the pressure of the thermal nanoimprint press (from 1.0 to 5.0MPa) or increasing the temperature (from 160 to 200°C): see Figure 2(b)–(d). We found that press temperatures above 200°C and pressures above 5.0MPa have insignificant effects on the nanofiber length, because the high pressure and/or polymer fluidity causes the polymer to splash out of the AAO pores. Using the Hagen-Poiseuille equation (a physical law that defines the flow of a fluid through a tube) we established that the viscosity of PS in the AAO template is lower than the Newtonian viscosity.³ This reduced viscosity increases the flowing ability of the polymer, and

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may be a result of shear rate, wall slip, and/or the pressure used in the imprinting process.

The length and aspect ratio of the nanofibers are also highly dependent on the type of polymer used. We found that over a range of temperatures, PP gave significantly longer fibers with higher aspect ratios than PS with the same melt flow rate: see Figure 3(a). In general, the interfacial surface tension between the fluid and the walls of a cavity plays a key part in capillary flow. In this case, longer fibers are formed with PP because the interfacial tension with the AAO pore surface is lower, resulting in a lower contact angle and better wetting of the surface: see Figure 3(b). The contact angle can be lowered further by coating the AAO pore walls with a thin layer of platinum. This coating decreases the interfacial surface tension by reducing the pore surface roughness on the nanoscale, increasing fiber length with both PS and PP.

Interestingly, we found that fabrication of the nanofibers causes a change in molecular orientation in the polymers. For example, a PS PNFA with 50nm diameter, 50 μ m length fibers has a higher glass transition temperature (T_g)—the temperature at which a material changes from a hard ‘glassy’ state to a rubber-like state—than a 40 μ m film of the same polymer (see Figure 4). This temperature increase is a result of nanoconfinement of the polymer, which increases the polymer chain packing density and, therefore, T_g . A similar effect is observed with PP PNFA.

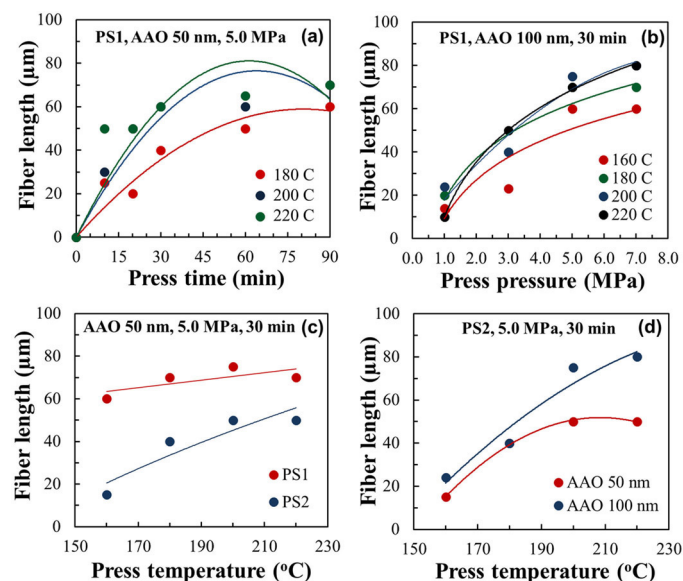


Figure 2. The effect of changing various thermal nanoimprint lithography parameters (namely, time, pressure, and temperature) on the polymer nanofiber length. PS1, PS2: Polystyrenes with glass transition temperatures of 87 and 100 $^{\circ}\text{C}$, respectively.

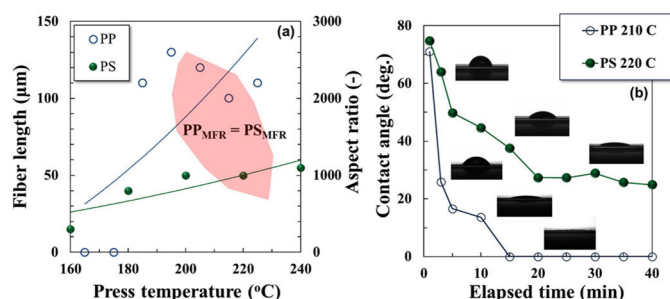


Figure 3. (a) The effect of polymer type on nanofiber length. The colored area indicates the region in which PP and PS have the same melt flow rate (MFR). (b) Droplet contact angles of molten polypropylene (PP) and polystyrene (PS) with the AAO pore surface.

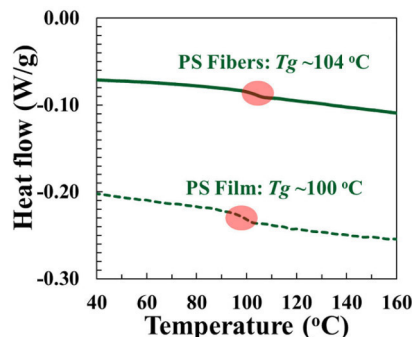


Figure 4. Differential scanning calorimetry curves showing the glass transition temperatures (T_g) of a PS nanofiber array and a PS film.

In summary, we have fabricated a range of PNFA using thermal nanoimprint lithography with a nanoporous AAO template. We can control the flowing ability of the molten polymer by adjusting the AAO pore size, imprint time, pressure, temperature, polymer type, and polymer/AAO surface interaction. This control enables us to reproducibly prepare PNFA with different fiber lengths and aspect ratios. Our future work in this field will include modifying the PNFA surfaces to be porous rather than smooth. This modification will significantly increase the potential applications for these materials.



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