Contact Angles of Polymer Solutions on Anodized Aluminum Oxide Templates and their Effect on Nanostructure Morphology

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Abstract

The synthesis of a variety of nanostructures is currently the focus of society due to their many possible applications. Of the various techniques to produce nanostructures, template assisted fabrication is of interest as a cost effective method to produce nanotubes and nanorods. This research focused on the fabrication of polystyrene (PS) and poly(methyl methacrylate) (PMMA) nanostructures by polymer solution infiltration of anodized aluminum oxide (AAO) templates. The correlation between contact-angles of polymer solutions on AAO templates and Berry's number was investigated. The findings of this work shed light on the nanostructure morphology control, which will allow specific applications of interest to society to be addressed.

Acknowledgments

We would like to thank Professor Shivkumar for his continuous support of our research. We will always remain grateful for his accommodation of our project amidst his numerous other commitments.

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1. Introduction

Nanotechnology, sometimes referred to simply as ‘nanotech,’ refers to the manipulation of matter on the nanometer scale. Derived from the word ‘nano,’ meaning ‘dwarf’ in Greek, the particles in the nano-range typically vary from 0.1 nm to 100 nm (2). One nanometer is a billionth of a meter or 10^{-9} of a meter. To give some perspective to this very small scale, one sheet is newspaper is about 100,000 nanometers thick (4). Although particles on the nano-level have been used for many centuries, the term "nano-technology" was not coined until 1974 by Norio Taniguichi (2). Since these structures are too small to see, even with regular laboratory microscopes, more powerful instruments are necessary. Around 30 years ago, devices such as the scanning tunneling microscope (STM) and atomic force microscope (AFM) were development, allowing nanoparticles to be seen and better studied (4).

Nanostructures are structures on the nanoscale, larger than molecular and smaller than microscopic. The main categories of nanostructures are classified by the number of dimensions on the nanoscale: nanotextured surfaces have one dimension on the nanoscale; nanotubes/nanorods have two dimensions on the nanoscale; nanoparticles have three dimensions on the nanoscale. All of the varying nanostructures can be synthesized in a variety of ways and be made up of a variety of materials such as carbon, ceramics, and polymers. Depending on the specifications of these nanostructures, a variety of applications are possible.

With the vast amount of applications for the varying types of nanostructures, it is important for researchers to understand all types as much as possible. However, it is impossible for one single research group to fully study every type of possible nanostructure. Therefore, for the purpose of this research, the only nanostructures studied were polymer nanotubes/nanorods synthesized using anodized aluminum oxide (AAO) templates.

Looking at AAO template assisted nanofabrication; two polymer-solvent systems (poly methyl methacrylate in acetone and polystyrene in tetrahydrofuran) were studied. For each system, an array of solutions was made with varying molecular weights and concentrations. For each solution, contact angles were measured with a goniometer. Using the collected contact angle data, trends were analyzed and compared to known polymer classifications tools such as the Mark-Houwink constant and Berry number. The performed analysis gave insight into how polymer nanostructures were formed in AAO templates.

2. Background

2.1. Benefits and applications of nanostructures

There has been a vast amount of research conducted in recent years on nanotechnology benefits and applications. From sunscreens and cosmetics to stain-free fibers to polymer films for laptop displays, products developed with nanotechnology are already commercially available (8). After many years of research, nanotechnology applications are benefiting society and are expected to be even more promising in future years (3). Some areas in which nanotechnology has been introduced are: medicine, electronics and information technology, sustainable energy, environmental remediation, transportation, and everyday materials and processes.

Medicine

The health care industry will receive many early benefits from nanotechnology due to the fact that "biological structures are within the scale the researchers are now able to manipulate and control" (1). With the aid of nanotechnology, a variety of procedure and tools will be cheaper, safer, and more personalized. Some of these medical advances include (2):

- Quantum Dots: These nanocrystals enhance biological imaging for medical diagnostics. Compared to currently used dyes, they offer optical detection up to 1,000 times better for tests such as MRIs.

- Gold Nanoparticles: These particles have been used to detect Alzheimer's disease in its early stage.

- Growth of Nerve Cells: Nanotechnology may soon be able to spur the growth of nerve cells, e.g., in damaged spinal cord or brain cells.

Electronics and information technology

Faster, smaller, high storage, and portable systems are possible for many computing and electronic systems because of advances in nanotechnology (2). Some of these applications include:

- Transistors: Transistors are now produced on the nanoscale and are faster, energy efficient and more powerful.

- Magnetic Random Access Memory (MRAM): MRAM is made possible by "nanometer-scale magnetic tunnel junctions that can quickly and effectively save even encrypted data during a system shutdown or crash, enable resume-play features, and gather vehicle accident data" (2).

- Organic Light-Emitting Diodes (OLED): Displays for various electronic devices now incorporate nanostructured polymer films called OLED screens. These screens offer brighter images in a flat format, as well as wider viewing angles, lighter weight, better picture density, lower power consumption, and longer lifetimes.

- Other products: Flash memory chips; ultraresponsive hearing aids; antimicrobial/antibacterial coatings on mouse/keyboard/cell phone casings; conductive inks for printed electronics for RFID/smart cards/smart packaging; more life-like video games; and flexible displays for e-book readers.

Sustainable energy

"The difficulty of meeting the world's energy demand is compounded by the growing need to protect our environment. Many scientists are looking into ways to develop clean, affordable, and renewable energy sources, along with means to reduce energy consumption and lessen toxicity burdens on the environment" (2).

- Solar Panels: prototypes that include nanotechnology are more efficient than standard designs. Nanostructured solar cells already are less expensive in more installation friendly because they can be processes and can be made in flexible rolls rather than discrete panels. Newer research suggests that future solar converters might even be "paintable."

- Batteries: batteries that use nanotechnology are less flammable, charge faster, weigh less, and can hold an electrical charge longer.

- Thin-film Solar Electric Panels: these panels are used to power mobile electronic devices and will eventually be to fit onto woven material such as computer cases and clothing. Energy will be generated using heat, friction, and light.

2.2. Nanotechnology and society

Responsible development of nanotechnology is one of the goals of the National Nanotechnology Institute, a government run organization. The various ethical, legal, and societal implications of nanotechnology are continuously taken into consideration. As nanotechnology research continues, additions aspects to be considered include: introduction of new applications into society, transparency of decision, public trust of new technologies, and all potential ethical, legal, and social issues yet to be addressed (6).

The U.S. Food and Drug Administration (FDA) currently regulates a wide range of products, including cosmetics, drugs, food, veterinary products, and tobacco products which utilize nanotechnology or contain nanomaterials (7).

2.3. Template assisted nanofabrication:

Nanostructures require guidance or masks during the fabrication process to attain the desired geometry and morphology. Templates that could be dissolved after the structures are fabricated have been utilized for the last decade or so as cost effective methods to produce nanostructures. The templates are mainly substrates that have surface features – e.g. pores – that guide the fabrication of the nanostructure with the desired properties – nanorods or nanotubes.

Anodized aluminum oxide (AAO) templates are the most ubiquitous templates in the nanofabrication field. Their ease of production, uniformity and cost effectiveness made them suitable for research

purposes. AAO templates are porous templates with pores on the order of 10 – 300 nm, these pores are excellent for nanotube and nanrod fabrication. They can be infiltrated to produce ceramic nanowires in a sol-gel method or can be infiltrated by polymer solutions to produce polymeric nanostructures.

Polymeric nanotubes and nanorods have been of interest to the scientific community for their utility in many fields such as drug delivery and biomaterials. Therefore, much work has been done on fabricating these nanostructures using AAO templates. Polystyrene (PS) and polymethyl methacrylate (PMMA) are few of the many polymers that have been studied to produce these nanostructures. Polymer solution infiltration method is the most common, where the AAO templates are infiltrated by a polymer solution (0.5 – 10wt%) by dipping them in solutions for various lengths of time. The templates then are dissolved in sodium hydroxide solution leaving a suspension of nanostructures.

There has been much work to control the morphology of the nanostructures fabricated (eg. nanotubes vs. nanorods), and has been found that many factors affect the morphology. These include concentration of solution, molecular weight of polymer and dipping time. However, surface interactions between polymer solutions and AAO templates have not been addressed thoroughly.

Recent work in the Shivkumar Group (unpublished) has shown that the morphology of the fabricated nanostructure is dependent on the contact-angle between the polymer solution and the template. Solutions with low contact-angles resulted in nanorods while solutions with high contact –angles resulted in nanotubes. Our work investigates the contact-angles of two polymer solutions PMMA in acetone and PS in tetrahydrofuran (THF) on AAO templates. It also studies the correlations between contact-angles and Berry's number which is a dimensionless product of the intrinsic viscosity of a polymer solution and its concentration. This work sheds light on some of the cohesive and adhesive forces in the AAO template pores and their equilibrium, which ultimately affect the morphology of the nanostructure.

3. Methodology

3.1. Materials

Table 1: Polymers used

Polymer	M_w	Vendor
PMMA	996,000	Aldrich Chemistry
PMMA	120,000	Aldrich Chemistry
PS	1,045,000	Scientific Polymer
PS	350,000	_
PS	18,000	Scientific Polymer
PS	10,000	Scientific Polymer
PS	4,130	Scientific Polymer

THF, HPLC grade, was obtained from Aldrich Chemistry.

Acetone, HPLC grade, was obtained from Pharmco.

The templates used were Whatman Anodisc filter membrane, 47 mm diameter, 0.2 μm pore size.

3.2. Preparation of solutions

Four solutions of PMMA in acetone were made

Fifteen solutions of PS in THF were made

Table 2: Solutions made

Polymer	Concentration wt%	Mass of polymer (g)	Mass of solvent (g)
PMMA 996,000	5	1.5	28.5
PMMA 996,000	0.5	0.15	29.85
PMMA 120,000	5	1.5	28.5
PMMA 120,000	0.5	0.15	29.85
PS 1045000	5	0.05	0.95
PS 1045000	2	0.02	0.98
PS 1045000	1	0.01	0.99
PS 350000	5	0.05	0.95
PS 350000	2	0.02	0.98
PS 350000	1	0.01	0.99
PS 18000	5	0.0125	0.2375
PS 18000	2	0.005	0.245
PS 18000	1	0.0025	0.2475
PS 10000	5	0.05	0.95
PS 10000	2	0.02	0.98
PS 10000	1	0.01	0.99
PS 4130	5	0.05	0.95
PS 4130	2	0.02	0.98
PS 4130	1	0.01	0.99

3.3. Measurement of contact-angles

Contact angles were measured using ramé-hart goniometer. A template was placed on a glass slide which in turn was placed on an aluminum platform. The platform was between the light source and the camera. A drop size of 10 µl was used each time. Three drops were measured for a given solution and three measurements were recorded for each drop and the average was read. A 10 µl drop of 5 wt% of PMMA (M_w=996,000) in acetone on AAO template is shown in Figure 1. A 10 µl drop of 2 wt% of PS (M_w=350,000) in THF on AAO template is shown in Figure 2.

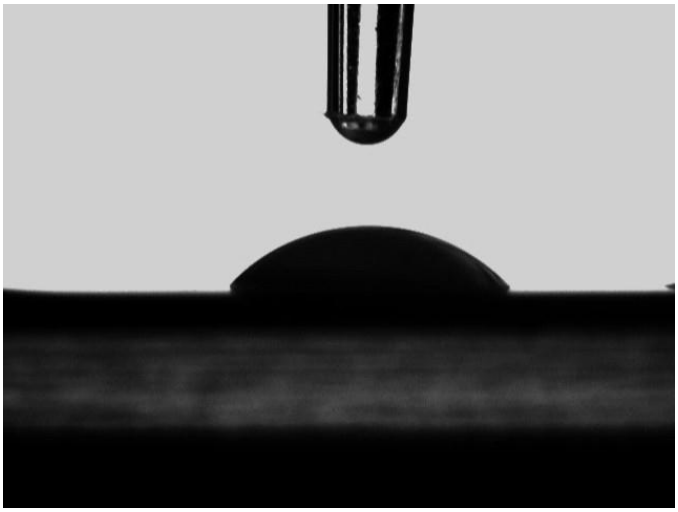

Figure 1: A droplet of 5% PMMA Mw=996,000 on AAO template

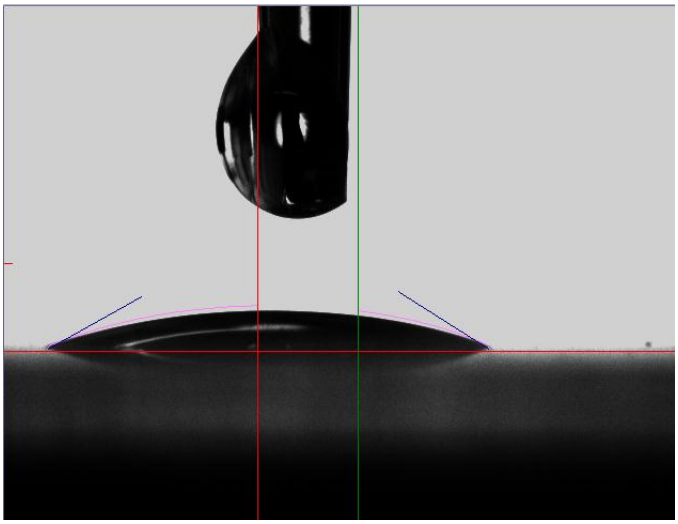

Figure 2: A droplet of 2% PMMA Mw=350,000 on AAO template

3.4. Template infiltration

Small pieces of templates were dipped for 30 mins total in small vials containing the solutions. After which the pieces were left to dry for 24 hrs before further work.

3.5. TEM sample preparation

Each of the dipped templates was fractured into a few small pieces and placed in a 4ml vial. The vials were filled with 100ul 0.1M NaOH and templates were allowed to dissolve over 72 hrs. Ethanol (900ml) was added to the vials and these were sonicated for 10 minutes. The vials were the centrifuged and the supernatants were removed. This cycle of adding ethanol, sonicating, centrifuging and removing the supernatant was repeated two more times. Three 8ml droplets of the remaining solution from each vial were placed on carbon coated TEM grids for TEM analysis.

4. Results and Discussion

The intrinsic viscosities of all the polymer solutions were calculated using the Mark-Houwink equation and constants:

$$[\eta] = KM_w^a$$

Where M_w is the molecular weight of the polymer and K and a are constants that depend on the polymer and the solvent. The constants, shown in Table 3, were obtained from the Polymer Handbook (4th Edition):

Table 3: Mark-Houwink constants

Solution	K (ml/g)	a
PMMA/ acetone	6.76E-03	0.71
PS/ THF	1.10E-02	0.725

Berry's Number (Be) was calculated from the intrinsic viscosity and the concentration:

$$B_e = c[\eta]$$

Where *Be* is dimensionless and the concentration *c* has units of (g/ml). The units of concentrations were converted from wt% to g/ml using the following equation:

$$c_{\left(\frac{g}{ml}\right)} = \frac{c_{(wt\%)}\rho_{solv}}{100 - c_{(wt\%)}}$$

Where ρ_{solv} is the density of solvent in g/ml ; $\rho_{acetone}$= 0.793 g/ml and ρ_{THF}= 0.889 g/ml. This conversion does not take into consideration the volume contribution of the solute. This is not a very accurate assumption, but can be considered valid at the concentrations being investigated.The results obtained from the contact-angle measurement experiments of polymer solutions on AAO templates are summarized in Table 4. The anomalous data were omitted.

Table 4: Berry's numbers and contact-angles

Solute	Solvent	Mw (g/mol)	Concentration wt%	Concentration g/ml	K (ml/g)	a	[η] (ml/g)	B_e	θ (°)
PMMA	Acetone	120,000	0.5	3.98E-03	6.76E-03	0.71	27.30	1.087E-01	12.6
		996,000	0.5	3.98E-03	6.76E-03	0.71	122.66	4.885E-01	14.5
		120,000	5.0	4.17E-02	6.76E-03	0.71	27.30	1.139E+00	17.2
		996,000	5.0	4.17E-02	6.76E-03	0.71	122.66	5.116E+00	31.3
PS	THF	4,130	5.0	4.68E-02	1.10E-02	0.725	4.60	2.154E-01	15.1
		10,000	1.0	8.98E-03	1.10E-02	0.725	8.74	7.848E-02	15.0
		10,000	2.0	1.81E-02	1.10E-02	0.725	8.74	1.586E-01	15.0
		10,000	5.0	4.68E-02	1.10E-02	0.725	8.74	4.089E-01	16.0
		350,000	1.0	8.98E-03	1.10E-02	0.725	115.04	1.033E+00	16.4
		350,000	2.0	1.81E-02	1.10E-02	0.725	115.04	2.088E+00	21.6
		350,000	5.0	4.68E-02	1.10E-02	0.725	115.04	5.384E+00	29.3
		1,000,000	1.0	8.98E-03	1.10E-02	0.725	246.26	2.212E+00	18.9
		1,000,000	2.0	1.81E-02	1.10E-02	0.725	246.26	4.469E+00	23.5
		1,000,000	5.0	4.68E-02	1.10E-02	0.725	246.26	1.152E+01	37.9

The physical significance of Berry's number is in indicating the presence or absence of entanglements in a polymer solution. Unlike in polymer melts, the entanglement in polymer solutions is not only affected by the molecular weight of the polymer i.e. their chain lengths, but also by the concentration of the solution. Berry's number is smaller than one (B_e<1) in the absence of entanglement and greater than one (B_e>1) in the presence thereof. In dilute solutions of even high molecular weight polymers B_e hardly approaches unity. A clear example of this is the second line of Table 4; PMMA of M_w=996,000 g/mol at 0.5 wt% concentration has B_e = 0.49. This means that the solution is dilute enough that the long chains of polymer molecules are too far to entangle.

There is a clear trend between the Berry's number and the contact-angle (Figure 3 and Figure 6). As B_e increases the contact-angle increases. However the correlation of this trend in the region B_e<1is different than the correlation in the region B_e>1. It is clear that the correlation between the contact-angle and the Berry's number in the absence of entanglement is exponential (Figure 7) or has a higher slope than the general trend (Figure 4). However, in a polymer solution with B_e>1 the correlation is mainly linear, shown in Figure 5 and Figure 8.

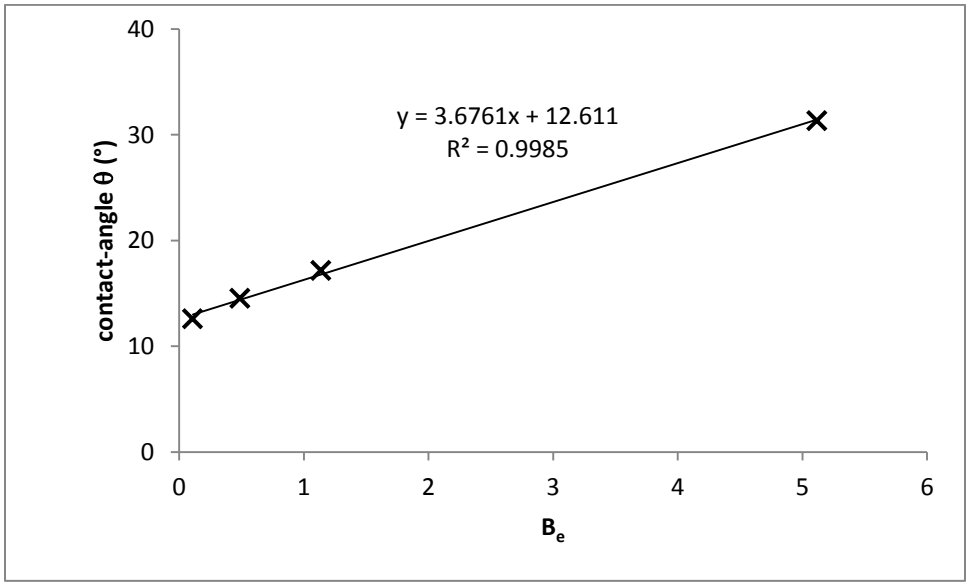

Figure 3: Contact-angles of PMMA-acetone solutions at all B_e

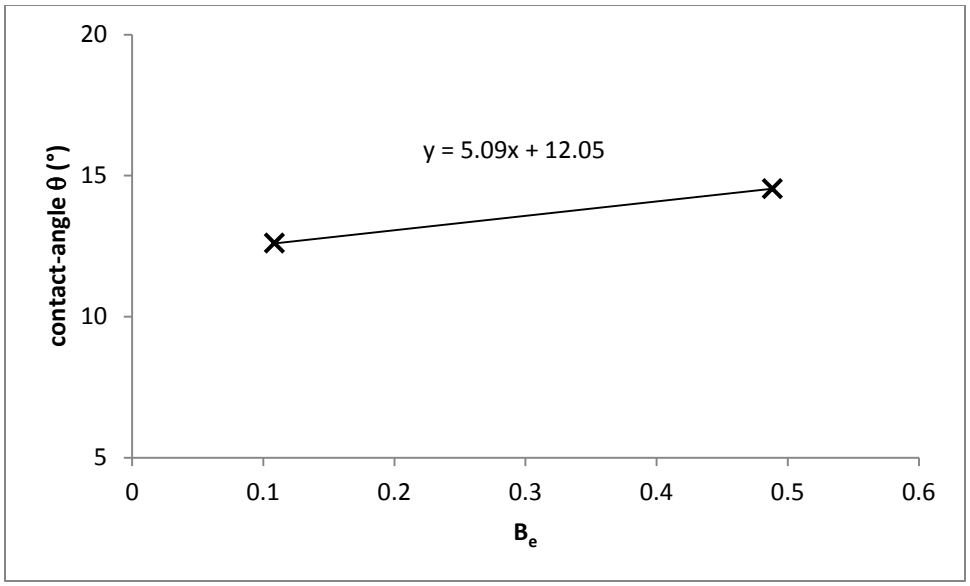

Figure 4: Contact-angles of PMMA-acetone solutions at B_e<1

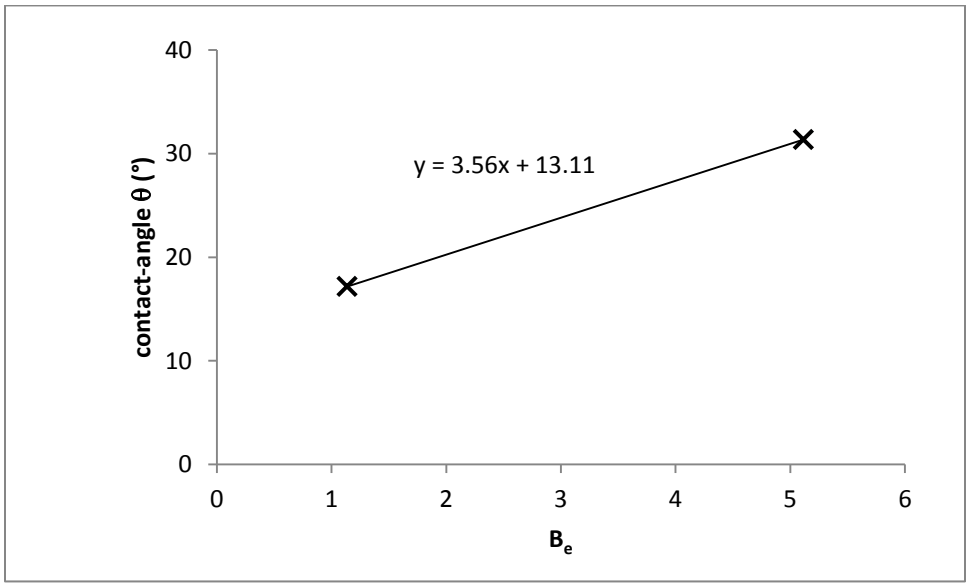

Figure 5: Contact-angles of PMMA-acetone solutions at B_e>1

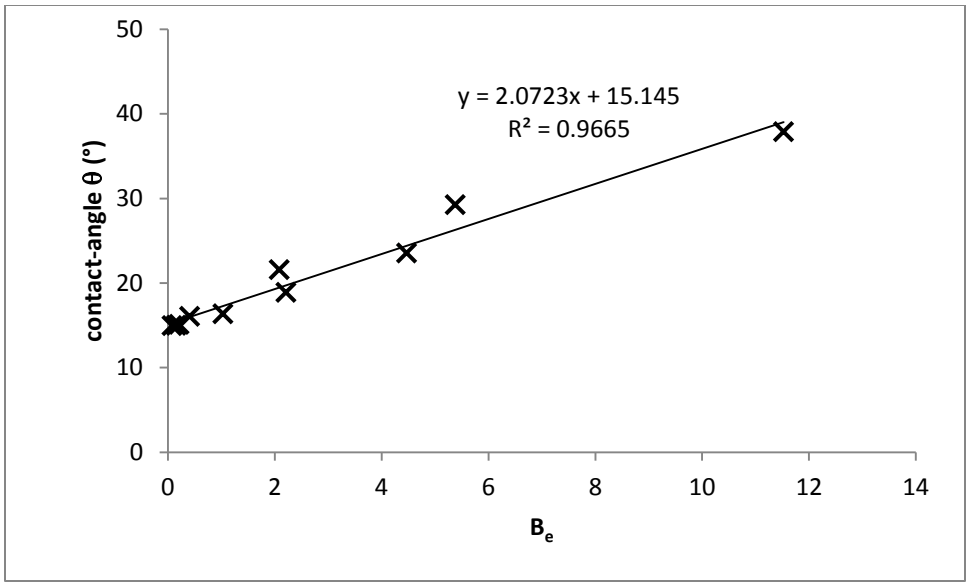

Figure 6: Contact-angles of PS-THF solutions at all B_e

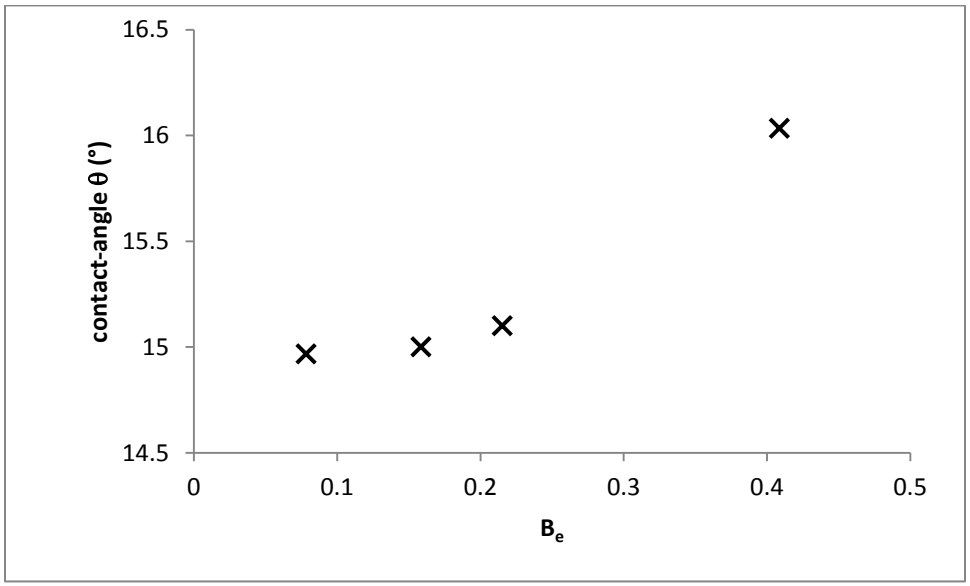

Figure 7: Contact-angles of PS-THF solutions at $B_e<1$

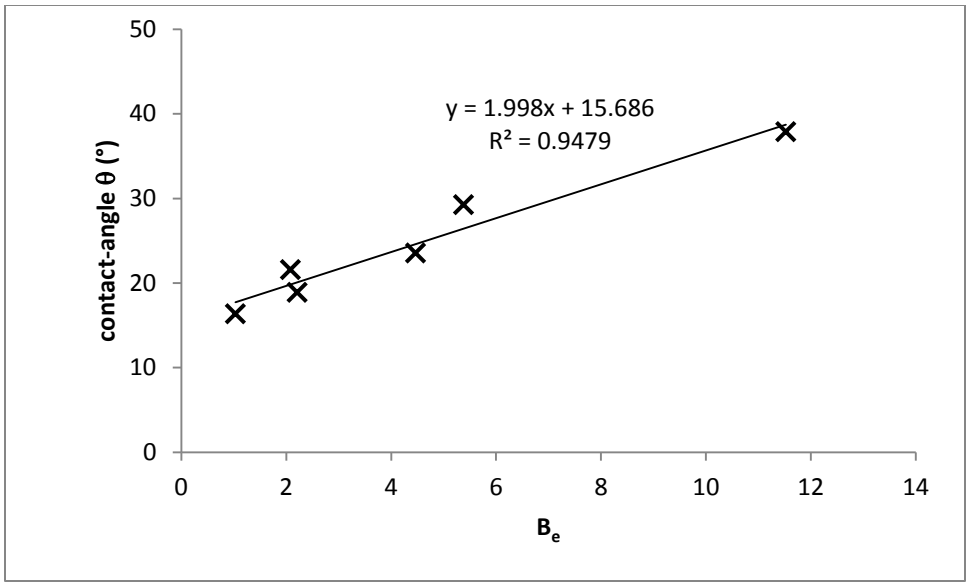

Figure 8: Contact-angles of PS-THF solutions at Be>1

Unfortunately, advancing and receding contact-angles were not recorded because of the difficulties posed by the uncontrolled environment which allowed fast solvent evaporation and the viscous polymer solutions. Nevertheless, these measurements will be made in the near future to have an insight on contact-angle hysteresis. Contact-angle hysteresis is caused by surface roughness; therefore it will be invaluable for our analysis to have a set of hysteresis data to complement the study since AAO templates are rough surfaces. There are two models that tackle the problem of surface roughness: Wenzel's model which describes the homogeneous wetting regime (Figure 9) and Cassie-Baxter model which describes the heterogonous wetting regime (Figure 10) which is more complex.

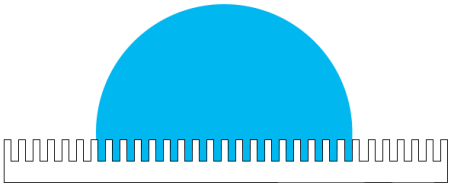

Figure 9: Wenzel model

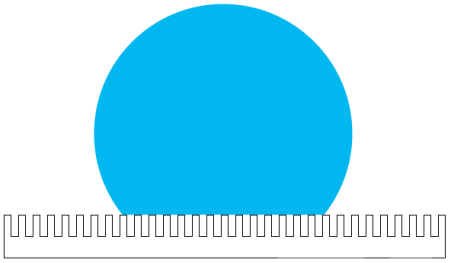

Figure 10: Cassie-Baxter model

Organic materials and solvents are generally considered low surface energy materials with respect to their surface energy (Van der Waals forces of interaction), while inorganic materials are known to have high surface energy (ionic in the case of AAO templates). Low energy liquids spread rapidly on high energy surfaces (9). Thus, it can be safely assumed that the low energy polymer solutions spread rapidly on the high energy AAO surface. Based on the strength of interaction with the walls of the pores, strong adhesive forces (lower contact-angle solutions) will allow full immersion of the pores. While strong cohesive forces (higher contact-angle solutions) will first wet the walls and the equilibrium of pore immersion will require longer times to be reached. This is in agreement with the results of previous work in the Shivkumar Group. Where low contact-angle solutions result in the formation of rods while higher contact angle solutions result in the formation of tubes, for a dipping time of up to 12 hours. However, for prolonged dipping times, rods are formed in all cases because enough time is provided for the equilibrium to be established and pores all fully immersed.

5. Conclusions

Through our studies, the data we collected and analyzed yielded new information that can further be used to understand polymeric nanotube/nanorods fabricated with AAO templates. Using our research methods, further experiments can be carried out to study other nanostructures such as those made of a different polymer. As more studies are performed, nanostructures will be better understood and our society will be able to utilize more beneficial nanotechnology applications.

Our work has shown that polymer solutions with high Berry's number (B_e) have larger contact-angles with AAO templates than solutions with lower B_e. Solutions with large contact-angles have large cohesive forces compared to their adhesive forces. This resulted in a slow establishment of equilibrium of forces and wetting of pore walls rather than full immersion of the pores, subsequently forming nanotubes. On the other hand, solutions with small contact-angles have large adhesive forces compared to their cohesive forces. This resulted in almost immediate immersion of the pores and the formation of nanorods. Therefore, our findings were in agreement with the results of previous work.

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