Fabrication and Morphology Control of Poly(methyl methacrylate) Hollow Structures via Coaxial Electrospinning

Kok Ho Kent Chan, Masaya Kotaki

Department of Advanced Fibro-Science, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan

Received 28 May 2008; accepted 23 July 2008
DOI 10.1002/app.28994
Published online 3 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A modified electrospinning method known as coaxial electrospinning was used to fabricate poly (methyl methacrylate) (PMMA) hollow structures. In this study to understand morphology control, the effect of processing parameters such as concentration of polymer sheath solution, size of core/sheath capillaries, feed rate, and applied voltage had been evaluated. Morphological observations via scanning electron microscope (SEM) revealed that via the control of polymer concentration within the sheath solution, morphologies such as hollow particles and fibers could be obtained. With the use of fine core/sheath capillaries, micron hollow fibers with walls of less than 20 nm were obtained. This study has demonstrated how the investigated processing parameters have a direct influence on the structures and how these parameters have supported the notion that effective encapsulation process is the key to the dual layer bicomponent structures. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 408–416, 2009

Key words: coaxial electrospinning; hollow fibers; poly(methyl methacrylate) (PMMA)

INTRODUCTION

Innovative methods of electrospinning have been designed to fabricate encapsulated core–sheath structures. This includes the method commonly known as emulsion electrospinning and coaxial electrospinning. Emulsion electrospinning has been demonstrated by Angeles et al.[1] and Xu et al.,[2] using a single spinneret and mixture of two immiscible fluids, one of the fluids dispersed in drops phase within the other. With the application of high voltage, the emulsion mixture accumulated at the tip of the spinneret deforms into a Taylor cone and a fine jet consisting of core–sheath structure is emanated from the tip of the cone. Coaxial electrospinning is not unlike emulsion electrospinning, except that the former uses a spinneret which consists of two capillaries coaxially positioned within one another. Depending on the material system desired, the core capillary which is the inner capillary can be configured to host a variety of different fluids, including those which are not electrospinnable using single spinnerets. As for the sheath capillary, the outer capillary, Yu et al.[3] had highlighted that the fluid from the mentioned capillary (sheath fluid) in the encapsulation and stretching of the core fluid into fine structures. It may thus be essential that the sheath fluid is composed of an electrospinnable material.

The other unique difference between coaxial electrospinning and emulsion electrospinning is that that coaxial spinning limits any possible interaction between two different fluids to only the tip of the spinneret. In Yu et al's work, the authors mentioned that possibilities of interaction between core and sheath fluids during coaxial electrospinning is negligible due to the fact that electrospinning is a rapid process which does not provide sufficient time for the two fluids to diffuse into one another. The group has demonstrated the fabrication of bicomponent fibers with core–sheath structures using a pair of miscible core and sheath fluids. Li and Xia,[4] on the other hand, emphasized the importance of pairing the core fluid with an immiscible sheath fluid. In their experiments, they observed that reproduction of distinct core–sheath structure within fibers was not possible with the use of miscible core and sheath fluid.

Although numerous studies have been performed to demonstrate coaxially electrospun material for application purposes,[5–7] few articles have provided insight into how morphology control can be achieved via coaxial electrospinning. Unlike single nozzle conventional electrospinning, the coaxial electrospinning becomes relatively complex due to the use of dual capillaries and fluids. This article would

Correspondence to: M. Kotaki (m-kotaki@kit.ac.jp).

study the fabrication of coaxial electrospun polymeric hollow structures based on poly(methyl methacrylate) (PMMA) and through the series of investigations, derive an understanding of how processing parameters affects morphology of the resultant structure and the coaxial electrospinning process itself.

It should be highlighted that although polymeric hollow structures have been produced by various research groups,[8,9] via melt spinning using specially designed spinnerets, the fabrication process using coaxial electrospinning may prove to be useful in deriving structures of submicron and nano scale. As will be demonstrated in the later sections of the presented work, coaxial electrospinning provides the unique capability to manipulate the morphologies of hollow structures, in addition to the ability to produce sizes of less than 1 μm. Potential applications of hollow structures include its use as microfluidic channels, storage devices and even as fillers, which may increase the electrical and heat insulation of the composite material.

EXPERIMENTAL

Materials

Polymer solutions were prepared by dissolving the polymer in the respective solvents. The polymer prepared was PMMA from Kuraray (Japan). The solvents used to dissolve PMMA were chloroform and ethanol in the ratio of 3 : 1. The concentration of the solutions ranged from 4 to 20 wt %.

The core fluid used for coaxial electrospinning includes mineral oil, toluene, octane, and water. Toluene, octane, and water were used as core fluids for fabrication of hollow PMMA particles. To remove the mineral oil from electrospun fibers, the fiber mat was soaked in octane for more than 12 h.

Coaxial electrospinning

Figure 1 shows the schematic diagram of a coaxial electrospinning setup. Coaxial electrospinning was performed with varying core and sheath feed rate. Core feed rate varies from 0.1 mL/h to 1 mL/h. Two methods were used to provide for the sheath feed rate, through manual injection or with the use of an automated pump. For feed rates based on automated pump, the feed rate was kept constant at 1 mL/h.

Coaxial spinneret sizes used for this study include core/sheath capillaries of inner diameters (ID) 0.8/2.5, 0.3/2.5, 0.1/2.5, and 0.1/1.5 mm. Applied voltage was kept constant at 12 kV for most of the experiments. Distance between spinneret and collector was kept at 120 mm. The counter electrode used to collect the fibers was a grounded flat metal plate. The fibers were collected on an aluminum foils placed above the metal plate.

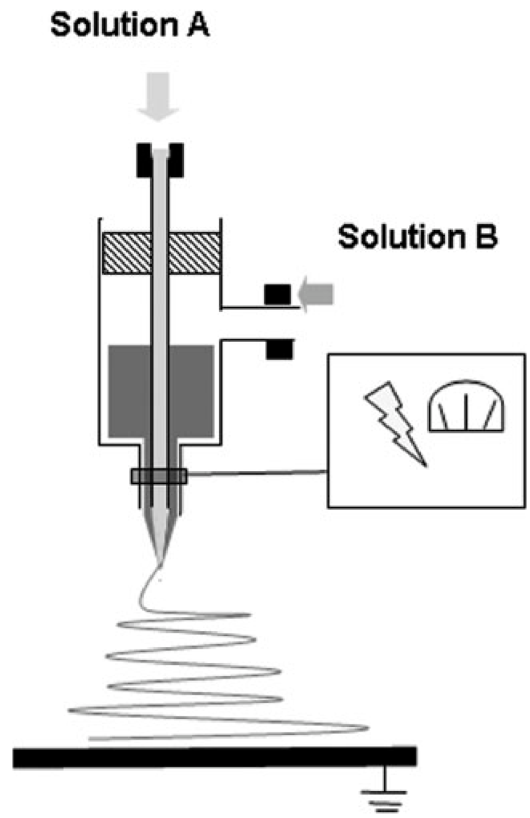

Figure 1 Schematic diagram of coaxial electrospinning setup.

For the fabrication of hollow particles, the coaxial spinneret used has a core/sheath capillary ID of 0.8/2.5 mm. In the case of these experiments, core and sheath feed rates were each kept at 0.5 mL/h. Applied voltage and distance between spinneret and collector were the same as mentioned earlier. Flat grounded metal plate was used as the counter electrode.

Characterization methods

Fiber morphologies were observed using the scanning electron microscope (SEM). Gold sputtering was performed using JEOL JFC-1100E for 6 min at 5 ampere (A). Fiber diameters and sizes were measured using image visualization software ImageJ 1.34 s.

RESULTS AND DISCUSSIONS

Solution properties effect

Selection of fluids for fabrication process

The method of hollow structure preparation is similar to that as mentioned by Li et al.,[4,10] with the use

Figure 2 Photograph showing the immiscibility between PMMA solution and mineral oil. A distinct layer of mineral oil was found above the PMMA solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of high-viscosity mineral oil as the core fluid. To minimize the interaction between the sheath and core fluid, immiscible solvent such as chloroform and ethanol were used to prepare the sheath polymer solution. It was anticipated that mineral oil, being a hydrocarbon-based compound, was to be immiscible with polar bonded chloroform and hydrogen bonded ethanol. To check the immiscibility of the fluids, mineral oil was added to the polymer solution to check for diffusion between two fluids. Figure 2 shows the distinct boundaries formed between the mineral oil and the PMMA polymer solution, an emulsion-like mixture. This is an important indication of immiscibility between the sheath and core fluid.

Concentration effect

Using a capillary of 2.5 mm as ID for the sheath capillary and a 0.8 mm as ID for core capillary (18 G), PMMA dissolved at different concentrations 4 wt %, 13 wt %, 17 wt %, and 20 wt % were coaxially electrospun with mineral oil, as core fluid. High shear viscosity was observed for PMMA solutions with the high concentrations. Based on electrospinning using conventional single spinneret, the electrospun products revealed difference in morphologies when the respective concentrations were used (details of the morphologies have been highlighted later). Study of morphological change with polymer concentrations has been performed by Tan et al.[11] For the coaxial electrospinning experiments, core feed rate was kept constant at 0.5 mL/h and sheath feed rate was manually controlled injected so as to obtain a stable Taylor cone at the tip of the spinneret.

Figure 3 shows how the morphologies of the hollow structures vary with different PMMA concentrations. Beaded and spindle-like fibers were formed at

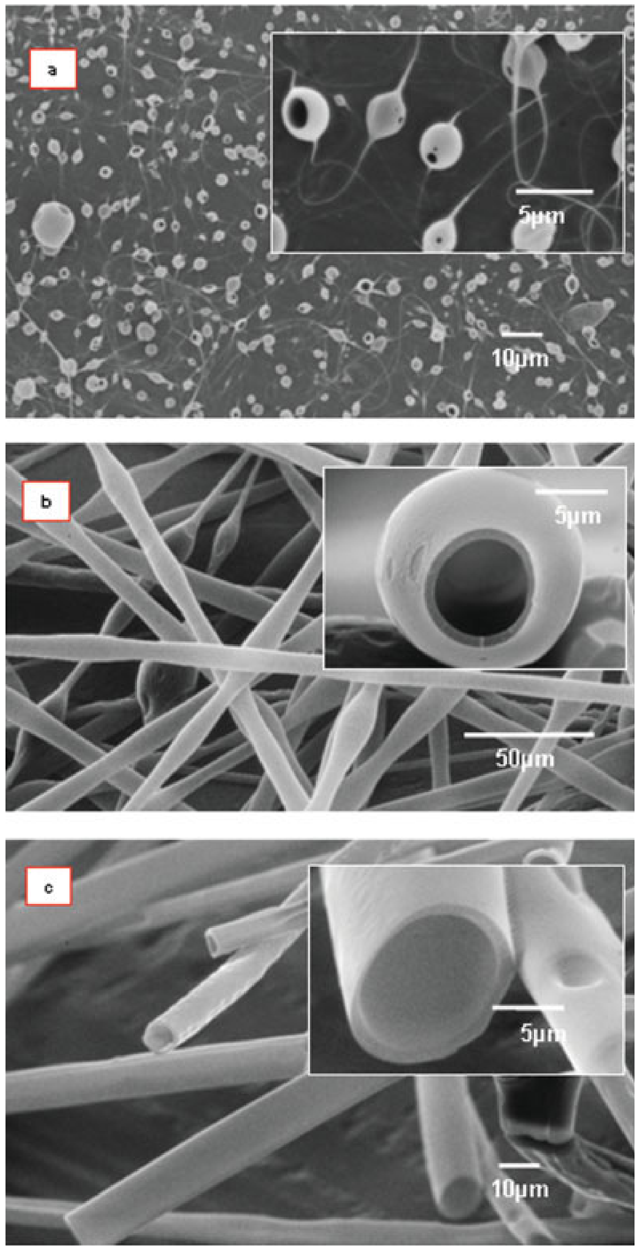

Figure 3 SEM micrographs show the effect of PMMA concentration on coaxial electrospun hollow fibers, (a) 4 wt %, (b) 17 wt % and 20 wt % (core/sheath ID = 0.8/2.5 mm).

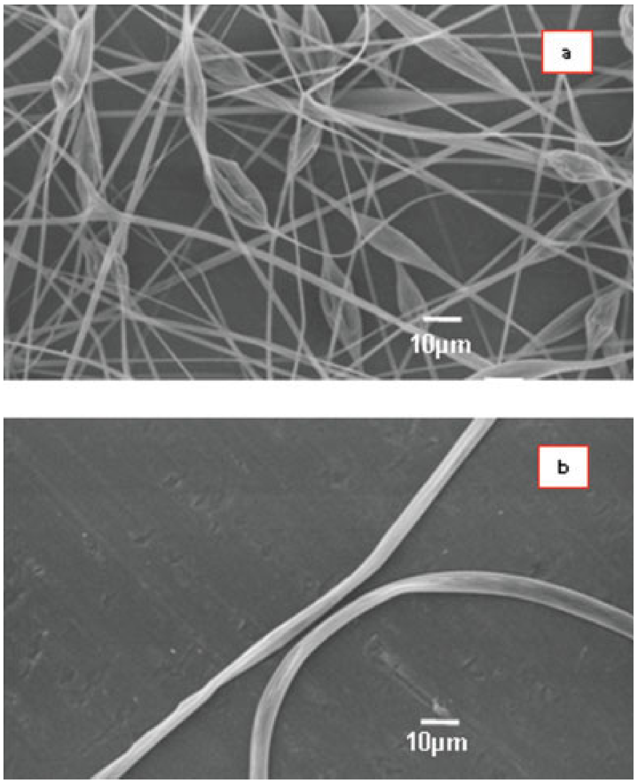

Figure 4 SEM micrographs of PMMA fibers electrospun from concentrations of 17 wt % and 20 wt %, using 2.5 mm (ID) single spinneret.

concentrations of 13 wt % and 17 wt %, respectively. On the other hand, hollow particles of PMMA attached to fine fibers were observed at 4 wt % concentration as observed in Figure 2(a).

Large beads with partially collapsed surfaces were observed on 13 wt % PMMA coaxial electrospun structures. The increase in concentration to 17 wt % resulted in a spindle-like fibers with hollow cores. Uniform tubular PMMA structures were obtained at 20 wt %. IDs of these structures range from 5 to 10 μm. The average outer diameter was calculated to be about 9 μm. Analysis based on one of the fiber cross-sectional areas revealed that the cavity is about 8 μm in diameter, and the walls are about 700 nm in thickness.

SEM micrographs in Figure 4 show the morphology of fibers spun from PMMA 17 wt % and 20 wt % solution using single 2.5 mm (ID) spinneret. Observations revealed similarities in morphologies between those of coaxial electrospun and those of electrospun with single spinnerets, the micrographs indicated that fibers electrospun from 17 wt % from both coaxial and single spinneret are beaded in nature. This demonstrated that the morphology of the hollow fibers can be manipulated by changing the properties of the sheath solution.

The crosssection of spindle-like structure as indicated in SEM micrograph found in the inset of Figure 3(b), shows that the hollow interior resembles a "parallel" morphology to the exterior sheath. This observation suggests that sheath morphology plays an important influence on the core structure.

Processing conditions effect

Feed rate effect

The feed rate regulates the flow rate of fluid exiting from the spinneret tip. In this experiment, coaxial electrospinning was conducted using core and sheath capillaries with ID of 0.8 and 2.5 mm, respectively. The sheath capillary feed rate was kept constant at 1 mL/h, whereas the core capillary feed rate was varied from 0.1 to 1 mL/h. It should be noted that the control of core fluid (mineral oil) feed rate, varies the ratio of mineral oil to polymer solution within the emulsion located the tip of the spinneret. In a way, it also determines the flow rate of at which mineral oil is being drawn into fibers by the viscous drag force exerted by the PMMA solution.

Figure 5 indicates the relationship between core feed rates and hollow fiber morphologies. The feed rate of 0.6 mL/h was the optimum feed rate for the fabrication of hollow structures. A gradual change of morphology was observed when the core feed rates were increased.

At 0.1 mL/h, well-defined hollow cores were absent when the fibers' cross-sectional areas were observed. The surfaces of the fibers were rough and wrinkled; indicating that collapse of the PMMA structures has taken place. Some of the fibers also indicated undulating surfaces; the interior of the fibers was suspected to be consisted of short solid fiber segments. A similar morphology had been obtained by Li and Xia,[4] using TEM for low core feed rate (Fig. 6). Wang et al.[12] had earlier suggested that when the feed rate was low, the high-viscous stress subjects the core material to break down into small individual segments.

When the feed rate was increased to about 0.4 mL/h, semicollapsed fibers could be observed, as seen in Figure 5(b). This morphology was recognized by most articles (Koombhongse et al.[13]) as ribbon structures. From the SEM micrographs, it could be observed that these ribbon-like fibers run over a few microns in length. The ribbon-like structures are formed due to the massive PMMA sheath being unable to support the small hollow interior, resulting in the collapse of the PMMA walls over the cavities. Further increasing the feed rate to 0.6 mL/h indicated the formation of long PMMA tubular structures.

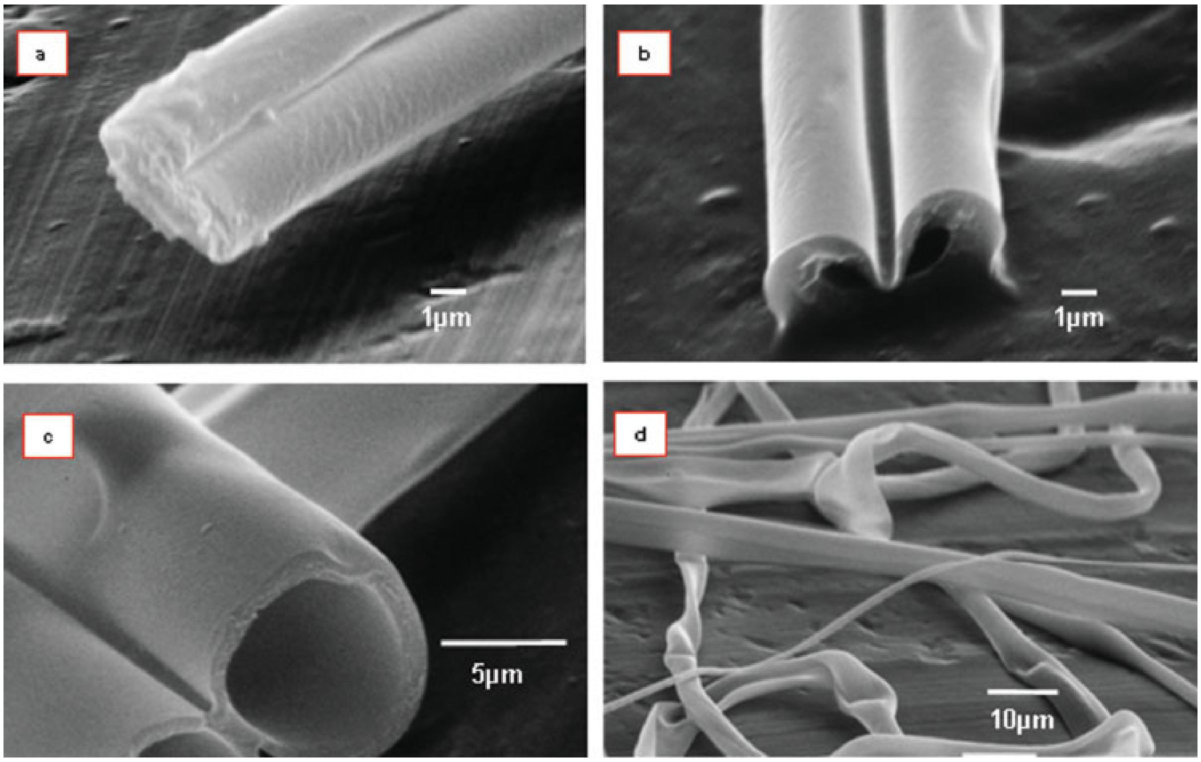

Figure 5 SEM micrographs of etched PMMA 20 wt % coaxial electrospun with core/sheath ID = 0.8/2.5 mm with different mineral oil feed rates (a) 0.1 mL/h, (b) 0.4 mL/h, (c) 0.6 mL/h and 1 mL/h, PMMA sheath solution feed rate fixed at 1 mL/h.

At core feed rate of about 1 mL/h, wet fibers coated with mineral oil as mentioned by Diaz et al.[14] were observed. This may be explained by the fact that the encapsulation process has been disrupted, resulting in the mineral oil and polymer solution being diffused together at the spinneret tip. Similar phenomenon has been demonstrated in emulsion electrospinning. Both Xu et al.[2] and Angeles et al.[1] observed that large sizes of the drop phase within emulsions had resulted in poor encapsulation of the phase during the electrospinning process.

In addition, flat and irregular-shaped fibers were also observed after etching was carried out on the samples. The fibers were relatively thin in thickness, and they may have been formed after the removal of the thick mineral core from the bicomponent fibers [Fig. 5(d)].

Spinneret size effect

This part of the experimental investigation aims to derive an understanding of the effect of capillary sizes on the fiber diameters and morphologies. Although a handful of articles (Zhao et al.[15]) have identified the effect of spinneret sizes on fiber diameters, few studies have been performed to demonstrate the effect of spinneret sizes on a coaxial spinneret. As mentioned, it should be anticipated that the presence of two capillaries makes the study of spinneret size slightly more complex. In this experiment, spinnerets of 2.5 mm sheath capillary were used with inner capillaries ranging from 0.8 mm (18 G), 0.3 mm (23 G) and 0.1 mm (27 G).

Measured average diameters of hollow fibers electrospun with these capillaries are 8.7 μm, 4.6 μm, and 4.7 μm, respectively. The feed rates to obtain these structures using mentioned capillary sizes are as follows 0.6, 0.4 and 0.5 mL/h. For similar feed

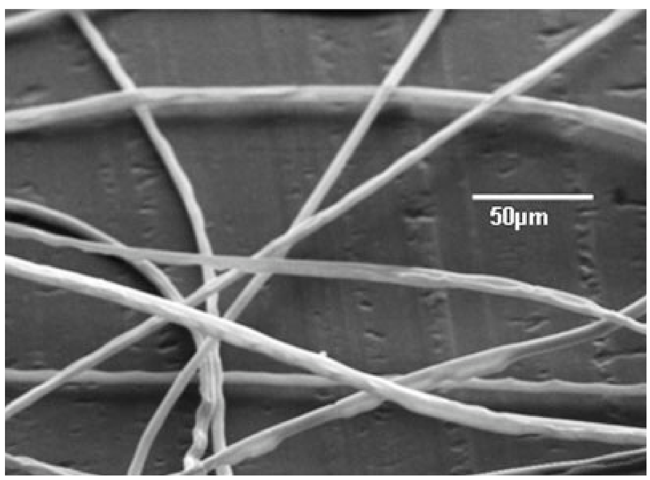

Figure 6 SEM micrograph showing PMMA fibers with undulating surfaces, consisting of short solid segments.

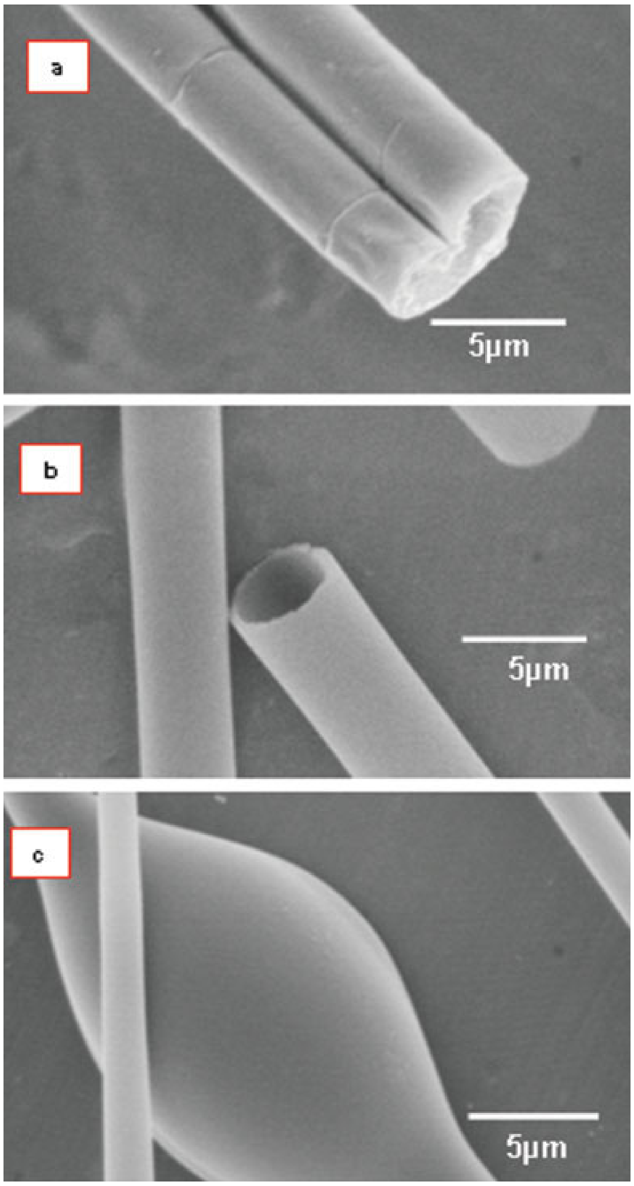

Figure 7 SEM micrographs of etched PMMA 20 wt % coaxial electrospun with core/sheath ID = 0.1/2.5 mm with different mineral oil feed rates, (a) 0.4 mL/h, (b) 0.6 mL/h and 0.8 mL/h, PMMA sheath solution feed rate fixed at 1 mL/h.

rate, it has been demonstrated that the core capillary size controls the core size within the electrospun fibers. Hollow tubular structures fabricated from a 0.1 mm (ID) core capillary revealed fibers with core diameters of 4 μm and PMMA wall thickness of about 500 nm, as shown in Figure 7(b). On the other hand, the fibers fabricated by 0.8 mm core capillary indicated 9 μm core diameters and 700 nm sheath wall thickness.

The ratio of core to sheath IDs for 18 G, 23 G, and 27 G capillaries are 0.32, 0.12, and 0.04, respectively. Electrospinning with spinnerets of small sheath capillaries such as 0.3 and 0.1 mm with high core feed rate did not result in formation of oil-stained fibers. Instead, after the etching process, it was observed that some of the fibers were linked together by "pockets of oil" as indicated in Figure 7(c). This clearly demonstrates that the use of a fine core capillary, or rather a small core to sheath ID ratio, is able to confine mineral oil more effectively and this encourages the encapsulation of mineral oil within the sheath. It should be highlighted that the fibers between "pockets of oil" did not feature hollow interiors. It was suspected that the high core feed rate resulted in the rapid accumulation of oil within the PMMA solution, located at the tip of the spinneret. This resulted in droplets of oil, encapsulated in PMMA solution, dripping off from the spinneret more rapidly that the PMMA sheath solution could draw it together to form fibers.

To obtain fine hollow fibers of submicron sizes, a 0.1 mm core capillary and 1.5 mm sheath capillary were used. Hollow fibers of about 1 μm could be obtained from this spinneret configuration. The fiber wall was relatively thin and could not be measured via observation from SEM; the estimated sheath wall thickness was about 14 nm (Fig. 8). The observation regarding relationship between fiber diameter and

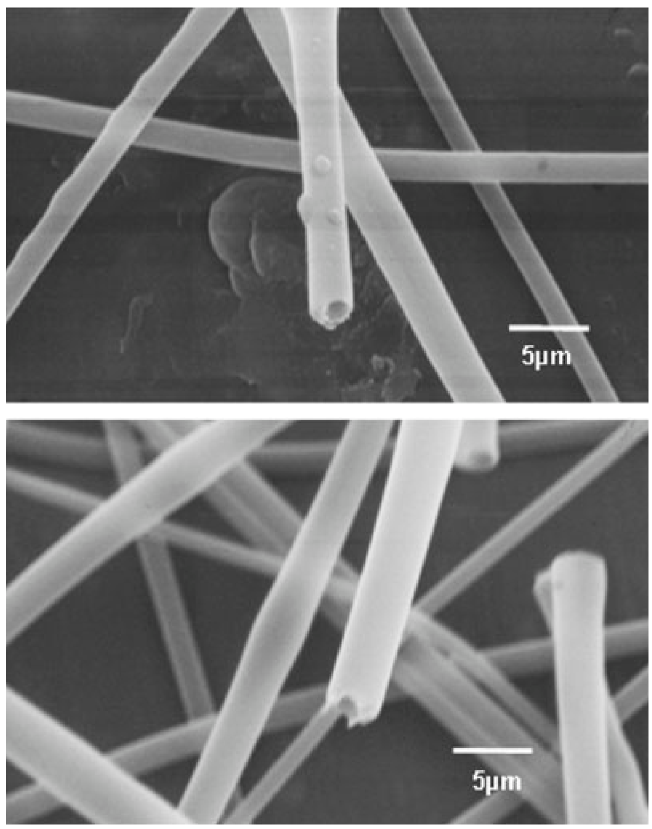

Figure 8 SEM micrographs indicating fine PMMA hollow nanofibers after etching fabricated using coaxial electrospinning. Core/sheath ID = 0.1/1.5 mm, core sheath feed rate = 1 mL/h.

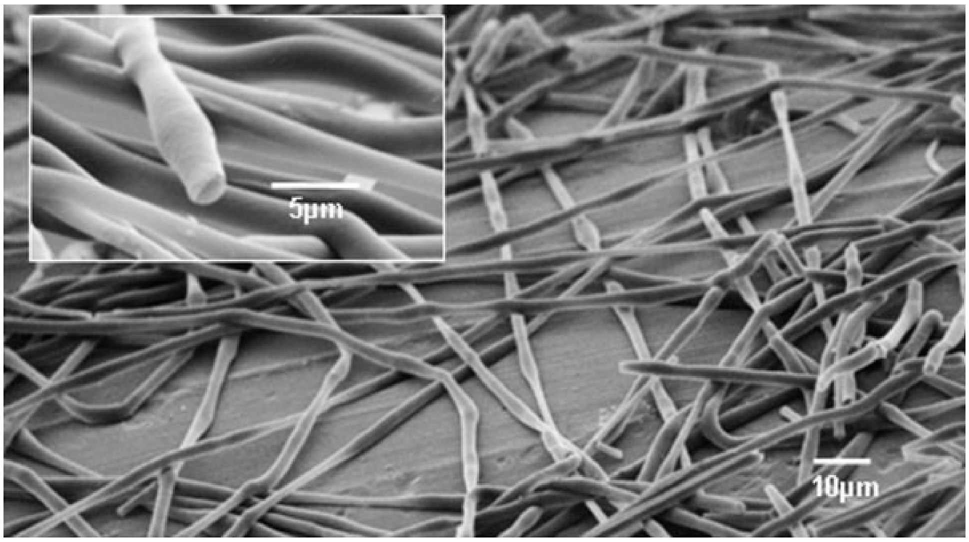

Figure 9 SEM micrographs of etched PMMA coaxially electrospun fiber, the applied voltage is at 18 kV (core/sheath ID = 0.1/1.5 mm).

spinneret size coincides with findings mentioned in most articles about the use of small capillary sizes being able to encourage the fabrication of fine fibers.

Applied voltage effect

By maintaining the feed rates constant, it was observed that when applied voltage was increased to 18 kV, the Taylor cone became unstable with the surface of the fluid meniscus subsiding rapidly into the inner walls of the spinneret. This event can be understood by the fact that at higher voltages, the electric field draws the fluid at the tip of the spinneret at a relatively fast rate and when the feed rate of the pump is unable to supply sufficient fluid to meet the rate at which the fluid is drawn; the meniscus subsides and breaks down within the inner walls of the spinneret. The smaller menisci residing at the inner walls of the spinneret continue to eject short cones which accounts for what is observed of multiple jets. It should be noted that the etched fibers, in this case, did not possess any hollow cores, neither do they possess collapsed structures nor most of them were of irregular shapes. Chen et al.[16] had reported of similar instability in the coaxial (compound) Taylor cone when they increased the voltage applied, they had described this phenomenon as the "multijet mode." The authors had added that the observation of the cone revealed a disruption in interface between the core–sheath components. SEM micrograph in Figure 9 shows the presence of irregular structured fibers obtained at 18 kV, after etching the bicomponent mineral oil/ PMMA bicomponent fibers with octane. From this analysis, it may be concluded that the formation of stable Taylor cone (single jet mode) is essential for the efficient encapsulation of the core fluid, if core–sheath structures within the fibers are desired.

Coaxially electrospun hollow particles

The fabrication of bicomponent particles was carried out using coaxial spinneret with a low concentration of PMMA 4 wt % as the sheath fluid and mineral oil as the core. The etching process was conducted using octane. Figure 10(a) shows hollow PMMA particles fabricated using the mentioned process. Loscertales et al.[17] had demonstrated the fabrication of bicomponent particles via the use of a similar method, based on a pair of immiscible pair of fluid, water and oil.

As a mean to eliminate the tedious process of etching the cores out from the bicomponent particles, to obtain hollow structures, the article suggests the use of volatile liquid as the core fluid.

For these series of experiments, octane, water and toluene have been used as core fluids. These fluids have low-viscosity profiles and may not be suitable material for the fabrication of continuous cores within hollow fiber structures. In the experiments performed by McCann et al.,[18] they reported the inability to form continuous hollow structures from TiO_2-PVP when they substituted octadecane over the higher viscosity mineral oil as the core fluid. It was explained that octadecane, compared with oil, would be more prone to a varicose breakup when subjected to stretching processes, and this had resulted in the formation of compartmentalized domains of octadecane within coaxially electrospun fibers.

SEM micrographs in Figure 10 revealed that when octane and water were used as core fluids, fine fibers were observed on the surface of the particles.

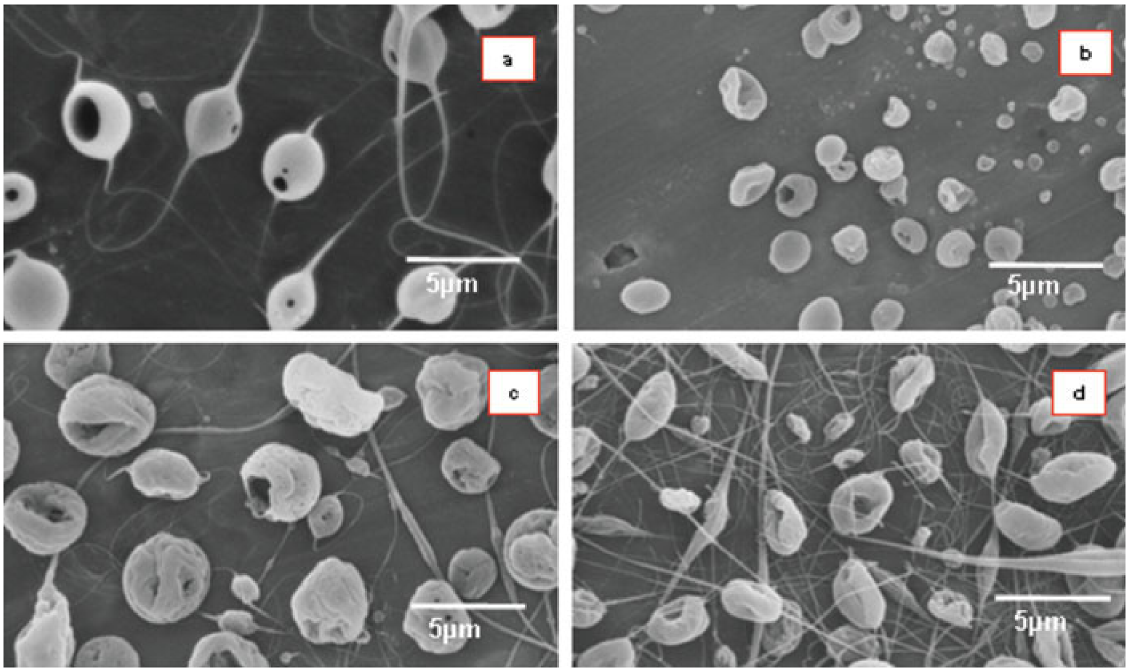

Figure 10 SEM micrographs showing PMMA 4 wt % coaxial electrospun with (a) mineral oil, (b) toluene, (c) octane, and (d) water.

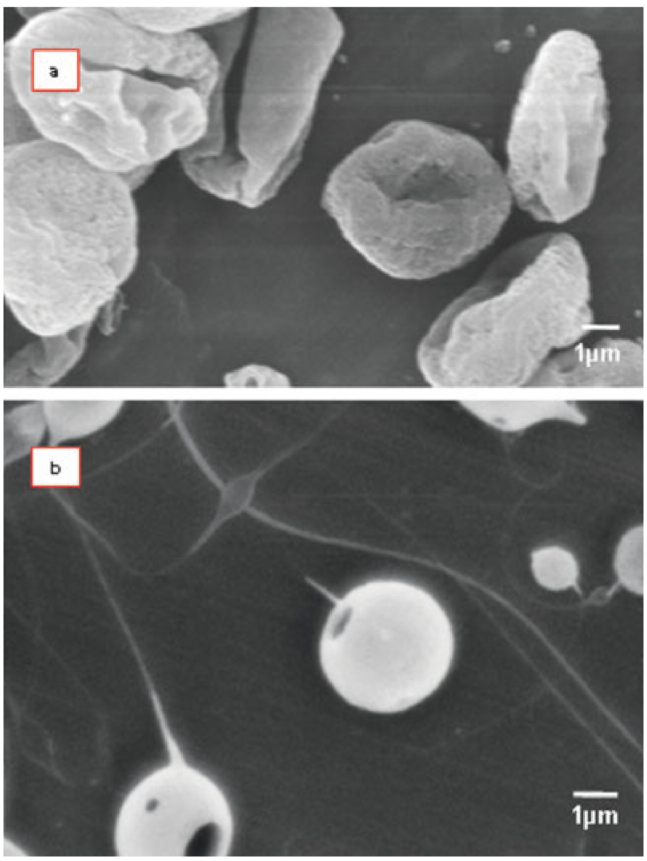

Figure 11 SEM micrographs showing (a) PMMA 4 wt % solution electrospun with 2.5 mm capillary (b) PMMA 4 wt % coaxial electrospun with mineral oil (core/sheath ID = 0.8/2.5 mm).

On the other hand, the fiber fabricated with PMMA soluble solvent, toluene showed only separated particles, without the presence of fibers. The surfaces of the particles were relatively smooth, and toluene was suspected to be trapped in some of these particles.

Although nonpolar octane and water are immiscible with polar-based chloroform, the interaction between these solvents and PMMA solution causes the polymer to undergo a mild solidification process, resulting in the formation of fiber-like structures (Figs. 10 and 11). This morphological observation has indicated signs of interaction between the core and sheath fluid. Despite coaxial electrospinning being described as a rapid process, it should be noted that to some extent, it may be of significance to select core–sheath fluids with consideration, to eliminate undesirable interaction effects.

CONCLUSIONS

This study has demonstrated the feasibility of using coaxial electrospinning to fabricate hollow structures based on polymer, PMMA. On the basis of the morphological observation and analysis on etched coaxially electrospun material, we have acquired useful understanding with respect to the relationship between core–sheath structure control and several processing parameters of coaxial electrospinning. The studied parameters included the control of sheath concentrations, spinneret sizes, core feed rate and applied voltage.

Investigation into sheath concentration effects revealed that electrospun PMMA hollow structures evolved from particle-like to uniform circular fiber structures with increasing polymeric concentrations, from 4 wt % to 20 wt %. The core structures were observed to be "parallel" to that of the sheath, an indication that core morphologies can be modified via the manipulation of the sheath solution properties.

Sheath and core capillaries with fine IDs are able to encourage the formation of fibers with fine outer diameters. Fabricated hollow fibers with outer diameters of about 10 μm had been shrunk to submicron size using sheath and core capillary of smaller IDs. To facilitate efficient encapsulation of the core fluid, the use of core capillaries with fine IDs would be more ideal candidates for the process. Unlike conventional single spinneret electrospinning, coaxial electrospinning has demonstrated itself to be relatively complex with the need to take into account the interaction between core–sheath components (capillaries and fluids) during the spinning process. Applied voltage and feed rate should be selected with consideration so as to maintain a stable compound Taylor cone, with minimum disruption to the core–sheath interface during electrospinning.

It should be highlighted that the key process to the fabrication of electrospun core–sheath bicomponent fibers via coaxial electrospinning lies in the successful encapsulation of the core via the sheath fluid and processing parameters should be selected for in consideration to the mentioned process.

References

1. Angeles, M.; Cheng, H.; Velankar, S. Polym Adv Technol 2007, 19, 728.
2. Xu, X.; Zhuang, X.; Chen, X.; Wang, X.; Yang, L.; Jing, X. Macromol Rapid Commun 2006, 27, 1637.
3. Yu, J. H.; Fridrikh, S. V.; Rutledge, G. C. Adv Mater 2004, 16, 1562.
4. Li, D.; Xia, Y. Nano Lett 2004, 4, 933.
5. Jiang, H.; Hu, Y.; Li, Y.; Zhao, P. J Controlled Release 2005, 108, 237.
6. Zhang, Y. Z.; Venugopal, J.; Huang, Z. M.; Lim, C. T.; Ramakrishna, S. Bio Macromol 2005, 6, 2583.
7. Greiner, A.; Wendroff, J. H.; Yarin, A. L.; Zussman, E. Appl Microbiol Biotechnol 2006, 71, 387.
8. Rwei, S. P. J Appl Polym Sci Vol 2001, 82, 2896.
9. Rovere, A. D.; Shambaugh, R. L. Polym Eng Sci 2007, 41, 7.
10. Li, D.; McCann, J. T.; Xia, Y. Small 2005, 1, 83.
11. Tan, S. H.; Inai, R.; Kotaki, M.; Ramakrishna, S. Polym 2005, 46, 6128.
12. Wang, M.; Jing, N.; Kameoka, J.; Chou, C. K.; Huang, M. C.; Chang, K. A. Appl Phys Lett 2006, 88, 0033106.
13. Koombhongse, S.; Liu, W.; Reneker, D. H. J Polym Sci 2001, 39, 2598.
14. Diaz, J. E.; Barrero, A.; Marquez, M.; Loscertales, I. G. Adv Funct Mater 2006, 16, 2110.
15. Zhao, S. L.; Wu, X. H.; Wang, L. G.; Huang, Y. J Appl Polym Sci 2004, 91, 242.
16. Chen, X.; Jia, L.; Yin, X.; Cheng, J. Phys Fluids 2005, 17, 032101.
17. Loscertales, I. G.; Barrero, A.; Guerrero, I.; Cortijo, R.; Marquez, M.; Ganan-Calvo, A. M. Science 2002, 295, 1695.
18. McCann, J. T.; Marquez, M.; Xia, Y. Nano Lett 2006, 6, 2868.