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Morphological study of electrospun polycarbonates as a function of the solvent and processing voltage

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Unlike conventional spin methods, electrospinning is capable of yielding fibers with sub-micron range diameters and high specific surface areas. In this study a Bisphenol-A polycarbonate was electrospun using two solvents: Chloroform and a 1:1 mixture of Tetrahydrofuran (THF) and Dimethylformamide (DMF). The morphological features of the electrospun polycarbonate fibers have been studied as a function of the solvent used and also as a function of the processing voltage. The studies were conducted using the SEM, TEM and Scion image analysis program. The results indicate that the morphological features of the fiber such as fiber diameter, diameter-distribution, internal structure and the Bead density variation with voltage are dependent on the solvent used. Electrospun polycarbonate fibers also exhibit a "Raisin like" puckered structure. However, such a feature is independent of the solvent used, and could enhance the functional efficiency of an electrospun material when used in an area-based application. In addition, studies on crazing of bulk polycarbonate and the surface features of electrospun polycarbonate fibers have been conducted. Results indicate that crazing of bulk polycarbonate results in surface damage and features that are also seen on the surface of electrospun polycarbonates.

1. Introduction

Electrospinning is currently being studied extensively as it holds the prospect of producing fiber based materials with a very high specific surface area that could be used in products whose functions are area based such as filters, membranes, bio-cidal gauzes, scaffolding for tissue build-up and even clothing. However the past and contemporary studies concerning electrospinning have all been conducted with the principal aim of understanding the nature of electrospun fibers as a function of process parameters [1–3] or understanding the process of electrospinning itself [4–7]. Such research has extended the frontiers of knowledge and understanding on electrospinning. However only in recent times has there been a concern on issues that play an equally important role in shaping the advantages and features of such electrospun materials into actual practical applications. Research into the use of electrospun materials as Protective Clothing, Energy, Aerospace and Medical applications [8–12] or research issues such as electrospinning of a plastic, especially polycarbonate or any polymer that is suited for developing practical applications in terms of its mechanical strength, surface texture or surface activity will supplement the already growing understanding and interest in electrospinning. Such properties are vital in bringing electrospun fiber-mat based applications to reality.

Bisphenol-A polycarbonate has been commercially available since the 1960s. It possesses a broad range of physical properties that enable it to replace glass or metal in many products. Polycarbonate offers a combination of good heat resistance, moisture absorption capability, impact strength, rigidity, and toughness that helps prevent potentially life-threatening material failures. In addition, it provides good visual clarity. As a result of such properties polycarbonate is used in load bearing applications, armored vehicles, rail cars and architectural applications. Polycarbonate is also available in grades that fulfill biocompatibility-testing standards such as ISO 10993-1 and USP Class VI [13]. Such features make the use of polycarbonate in the medical industry products such as IV connection components, cardiac surgery products, surgical instruments and renal dialysis, possible. However polycarbonate has poor scratch resistance, as a result modified polycarbonate is being used in applications such as optical lenses. But in general it is a well known fact that polycarbonate is a very popular engineering material offering good mechanical properties with the advantage of a low weight. However the action of solvents on plastics can cause crazing, and this may lead to failure. Since electrospinning of polycarbonate produces fibers that can have traces of solvent, it is essential to study the effect of such residual solvents on the fiber

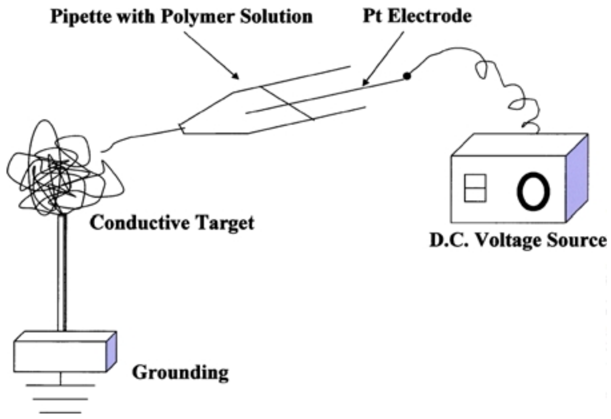

Figure 1 Illustration of a typical electrospin apparatus.

surface in evaluating polycarbonate as an electrospun material.

2. Experimental details

The polymer used is a Bisphenol-A polycarbonate with an 8–10g/10 min melt flow index. Two typical polycarbonate solutions are used to study the effect of the solvent on the morphology of electrospun Polycarbonate fibers. The two solutions are as follows:

(i) Polycarbonate dissolved in chloroform. (*Which will be referred to as* PC-CH *hereafter*)
(ii) Polycarbonate dissolved in an equi-weight percentage mixture of dimethyl formamide and tetrahydrofuran. (*Which will be referred to as* PC-MIX *hereafter*)

Dissolution of polycarbonate in the solvents was assisted by mechanical agitation using an ultrasonic vibrator maintained at about 42–44°C. The solvents—chloroform, tetrahydrofuran (THF) and N,N di-methyl formamide (DMF) are 99.9% HPLC grade, and are from Sigma-Aldrich. Typical polycarbonate concentrations in the solutions are 14% and 15% by weight. The pipette from which the solutions are spun has an orifice dimension of about 1.2 mm. The tip to target distances was generally maintained between 80–120 mm. Electrospinning voltage was varied from 6 kV to 30 kV. A Pt electrode was used to induce charge into the solution. Fig. 1 shows the electrospin equipment set up. The electrospun fiber morphology was studied using an AMRAY AMR model 1000 SEM and a Philips EM 400 T TEM. The image processing and analysis to study variation of bead density as a function of processing voltage was performed using Scion Image, an image processing and analysis program for a PC, based on the popular NIH product *Image* for a MacIntosh. PC solution viscosity measurements were made using a Brookfield viscometer with a TB92 spindle. Table I shows the viscosity data. Electrospun fiber cross-sections were obtained using an Ultramicrotome.

3. Results and discussions

3.1. Solvent v/s fiber morphology

Electrospinning a PC-CH solution yields fibers that have diameters ranging from just under a micron to fibers with diameters up to a few tens of microns. However, a large fraction of the fibers have diameters around 2–3 microns. All fibers with diameters above 3–5 microns appear as collapsed or flattened cylinders. These large diameter fibers also exhibit "twisting". Electrospinning a PC-MIX solution yields fibers that have diameters in the sub-micron range. The diameters of the fibers range from 100 nm to 500 nm. But almost all fibers have diameters in the narrow range of 150–200 nanometers and do not exhibit any flattening or twisting. Figs 2 and 3 shows this difference in the two

TABLE I Viscosity data

Solution	Polycarbonate concentration (wt%)	Viscometer reading	Viscosity (centipoise)
PC in Chloroform	14	0.1	80
PC in Chloroform	15	0.1–0.2	80–160
PC in (THF:DMF)	14	0.3–0.4	240–320
PC in (THF:DMF)	15	0.5–0.6	400–480

Viscosity measurement made with Brookfield Viscometer, Spindle number HA 6 @ 100 rpm.

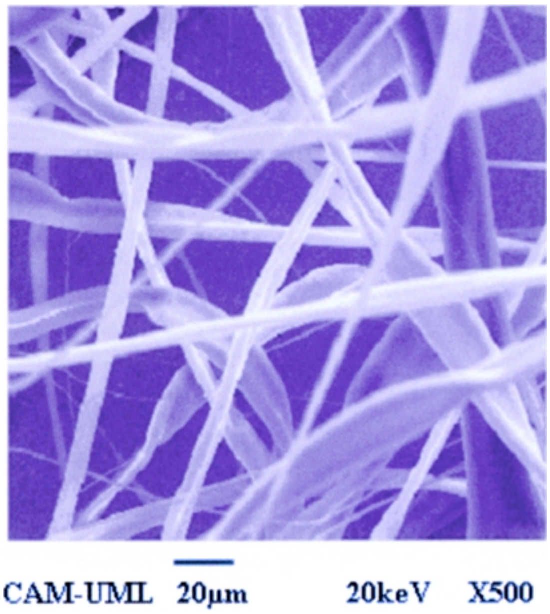

Figure 2 14% PC-CH based electrospun fiber-mat.

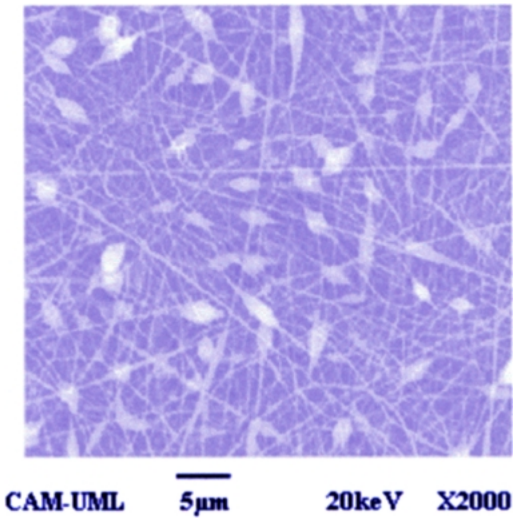

Figure 3 14% PC-MIX based electrospun fiber-mat.

fiber-mats. The difference in the diameters of the PC-CH fiber and the PC-MIX fiber, electrospun under identical concentration and processing conditions like voltage and tip to target distance can be explained only in terms of the differing solvent induced properties such as rates of evaporation and viscosity. The application of a voltage to the polymer solution through the platinum electrode generates electrostatic charges within the polymer solution. The repulsion between these like electrostatic charges is responsible for drawing of the polymer solution into a jet from the tip of the pipette. This is analogous to the mechanical drawing force applied in conventional spinning. Hence though the diameter that a liquid polymer solution jet attains depends on the applied kV, the viscosity of the PC solution determines the ease with which the final solid polymer cylindrical fiber is formed. When the solution is very viscous, it is difficult to bring about rapid changes in the shape of the jet and hence higher electrostatic forces are required to draw the jet out into a fine fiber. When we consider electrospinning of two solutions with very different viscosities, the solution with higher viscosity will result in fibers much thicker than the low viscosity solution, provided the concentration, voltage and time of flight, which is determined by the tip to target distance and the material flow rate, are identical. PC-CH solutions are more viscous than PC-MIX solutions. Thus PC-CH electrospun fibers would have to be thicker than PC-MIX electrospun fibers.

3.2. Raisin like structure

When examined at high magnifications the PC fibers are puckered or wrinkled and have an appearance similar to that of a raisin. In the case of chloroform-based electrospun PC, the raisin like structure is evident in both the large sized fibers as well as the beads. Figs 4 and 5 show the puckering in a fiber and a bead respectively. Fig. 6 shows a relatively lower degree of puckering in a fine sized fiber, when compared to the degree of puckering in a larger fiber as shown in Fig. 4. In the case of THF:

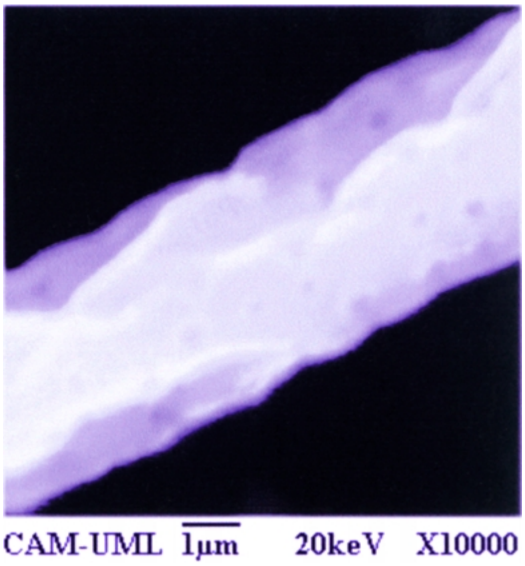

Figure 4 Puckering in 14% PC-CH electrospun fiber.

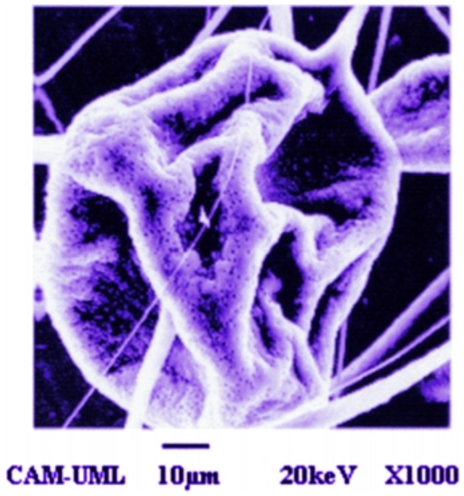

Figure 5 Raisin like structure of 14% PC-CH electrospun bead.

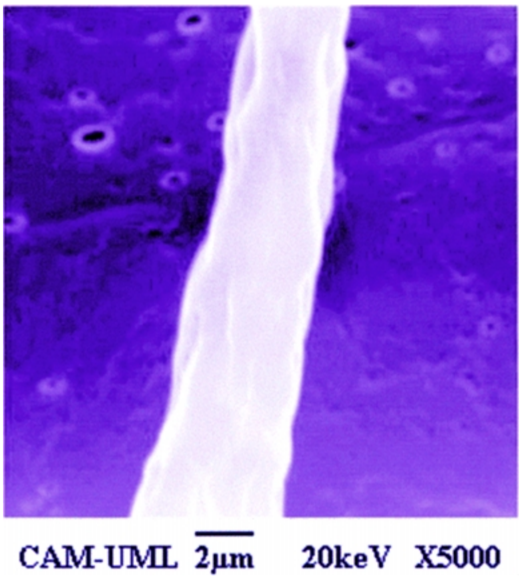

Figure 6 Lower degree of puckering in a fine, 14% PC-CH electrospun fiber.

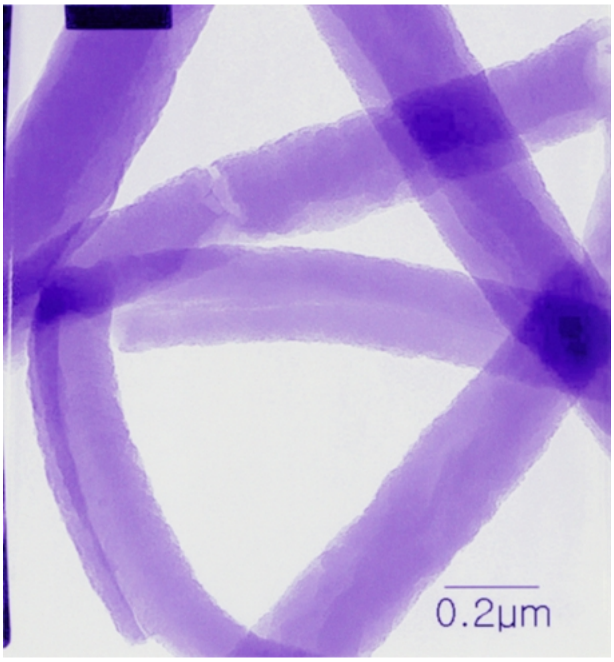

Figure 7 TEM image showing puckering in PC-MIX electrospun fibers.

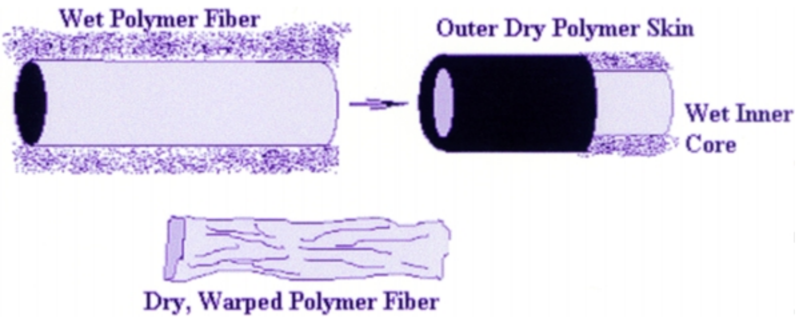

Figure 8 Illustration of the hypothetical "Dry Skin" model to explain puckering of electrospun polycarbonate fibers.

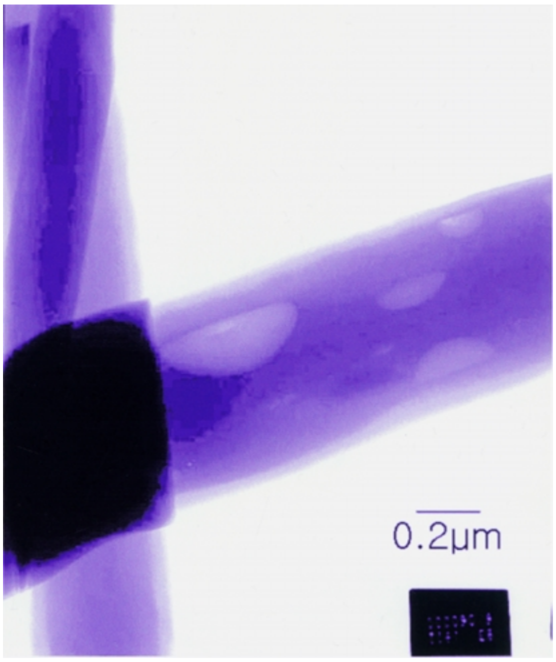

Figure 9 TEM image of a PC-CH electrospun fiber showing internal, random, rarified regions.

DMF based electrospun PC, the raisin like structure is seen in both the fibers and beads. However, because of the fine size of these fibers, TEM imaging is a better tool in revealing the puckered nature of the fibers as compared to SEM imaging. Fig. 7 demonstrates this aspect. The appearance of the raisin like structure is related to the relative rates of evaporation of the solvent from the surface of the polymer solution jet and the rate of evaporation at the core of the fiber, during electrospinning. Consider a cylindrical jet of the polymer solution in flight, between the tip and the target. The solution is essentially a polymer dissolved in a volatile solvent, which in our case is either chloroform or an equi-weight percentage mixture of tetrahydrofuran and dimethylformamide. As the polymer solution jet is drawn out by the electrostatic forces on its surface, the cylindrical jet elongates and by the principle of conservation of mass its diameter begins to decrease. This results in an increase in the specific surface area of the polymer solution jet. The increase in surface area enhances the rate of evaporation of the volatile solvent from the solution jet. This evaporation of the solvent from the polymer solution jet eventually results in a charged, solid polymer

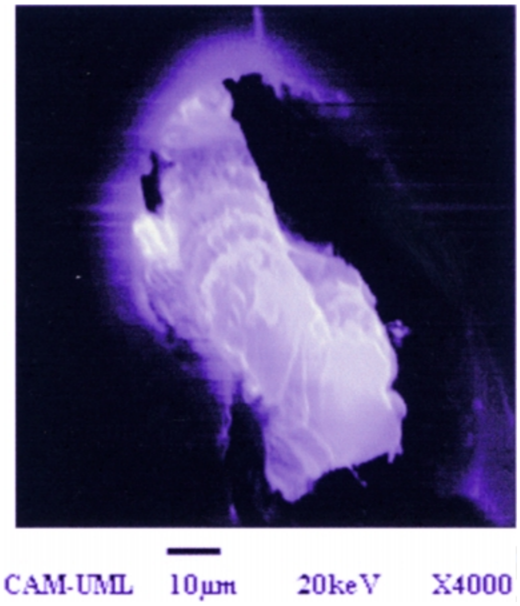

Figure 10 SEM image showing a cleanly cut cross section of a large PC-CH electrospun fiber.

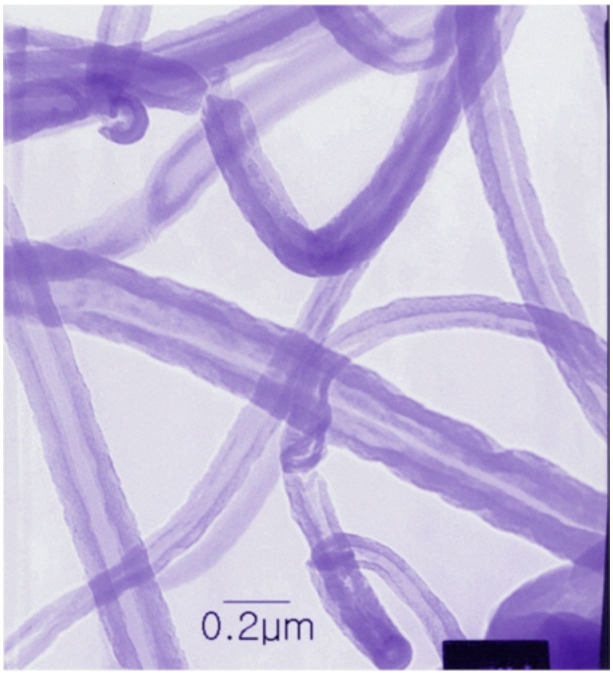

Figure 11 TEM image of PC-MIX electrospun fibers showing an internal rarified core.

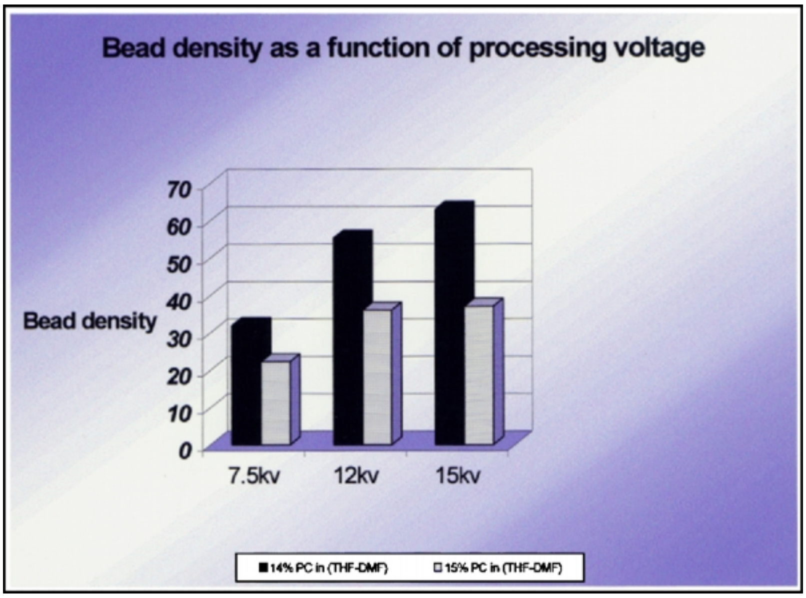

Figure 12 Bar graph showing bead density as a function of process voltage for a PC-MIX electrospun fiber-mat.

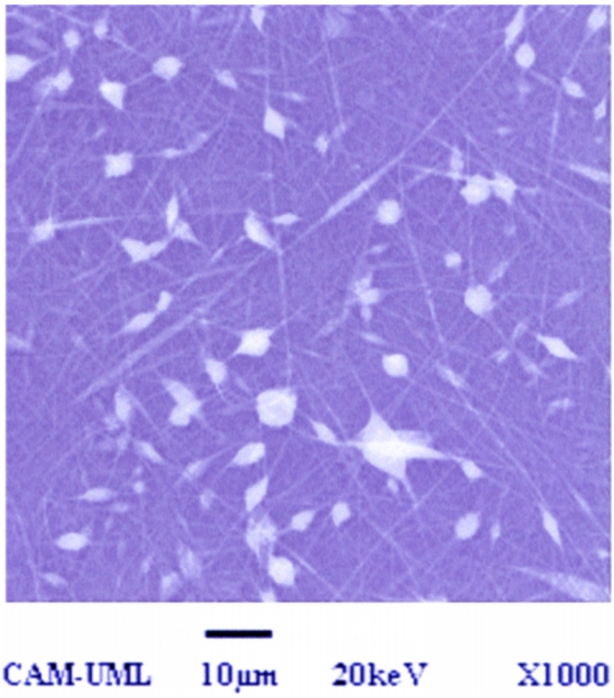

Figure 13 SEM image showing bead formation at 6 kV in a PC-MIX electrospun fiber-mat.

fiber. But if the solvent is very volatile, then a rapid evaporation of the solvent on the outer surface of the polymer solution jet would occur resulting in formation of a thin, dry polymer layer on the outside while within the solution jet, evaporation is incomplete. Thus the polymer jet possesses a fixed surface on the outside even before it has completely lost its solvent content. Further loss of the solvent from the inside of the sphere by diffusion into the ambience through the outer dry skin causes the polymer jet or fiber to warp, thus forming the raisin like structure. A dry skin model has been proposed, as shown in Fig. 8, to explain the formation of such a structure. The same effect is also believed to cause the cylindrical fibers to warp or collapse into flat bands.

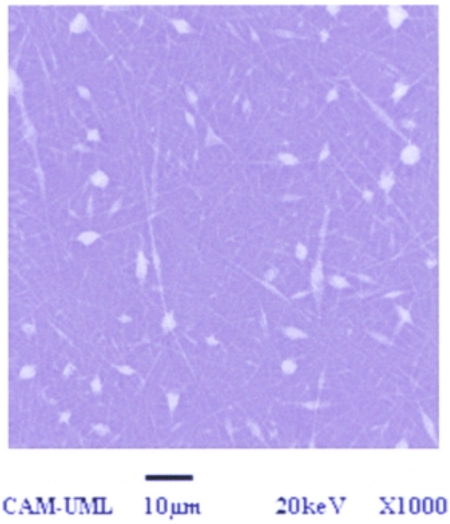

Figure 14 SEM image showing bead formation at 7.5 kV in a PC-MIX electrospun fiber-mat.

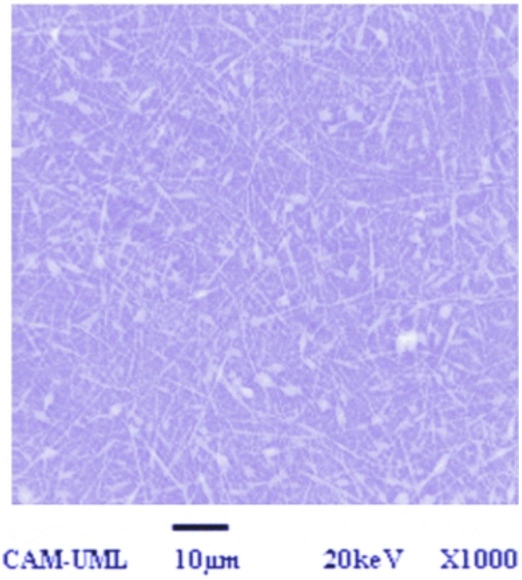

Figure 15 SEM image showing bead formation at 9 kV in a PC-MIX electrospun fiber-mat.

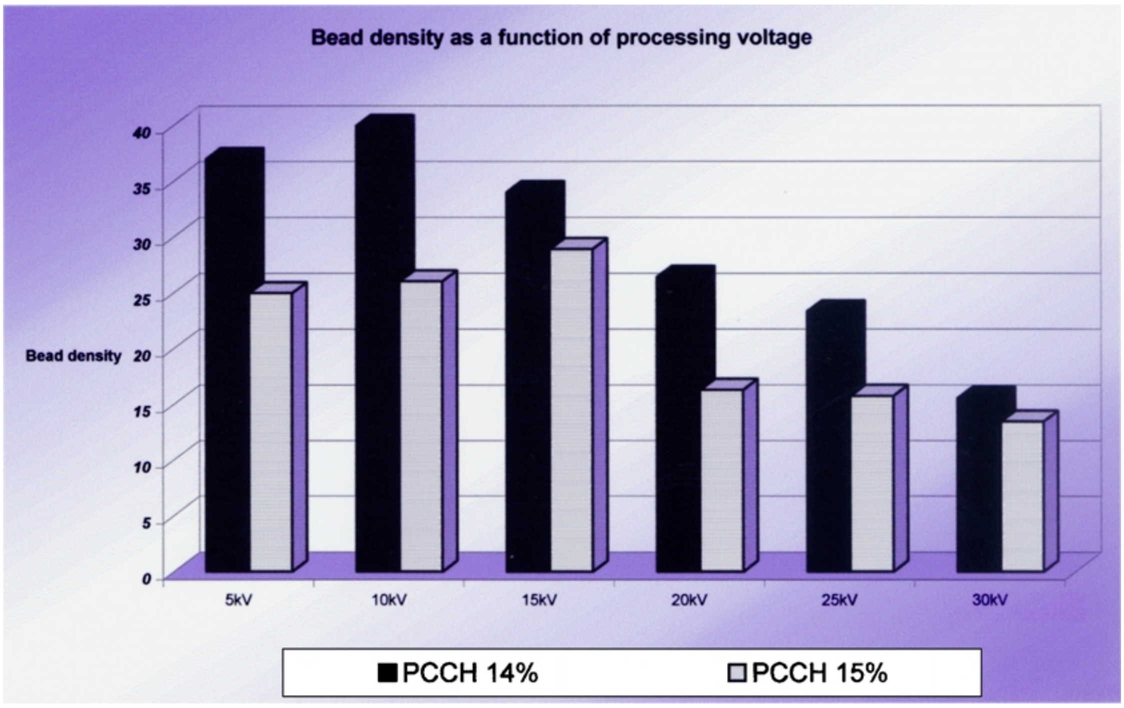

Figure 16 Bar graph showing bead density as a function of process voltage for a PC-CH electrospun fiber-mat.

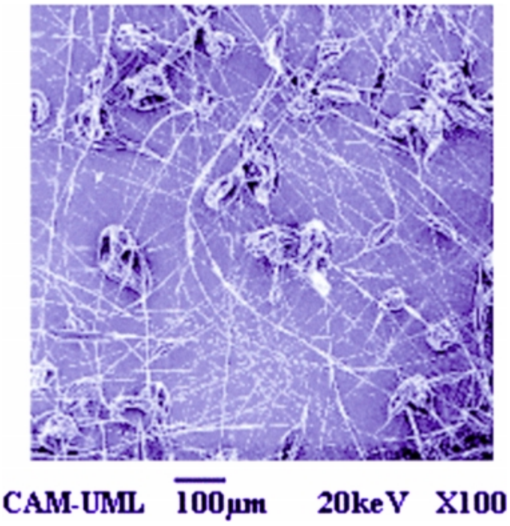

Figure 17 SEM image showing bead formation at 6 kV in a PC-CH electrospun fiber-mat.

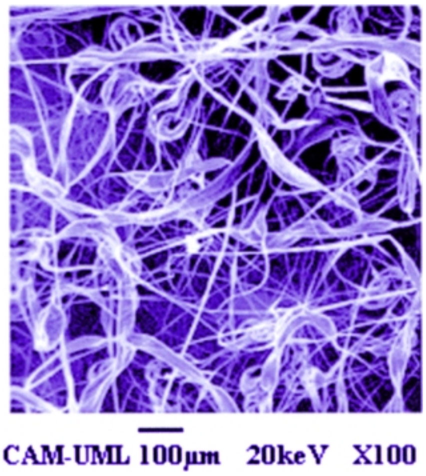

Figure 18 SEM image showing bead formation at 10 kV in a PC-CH electrospun fiber-mat.

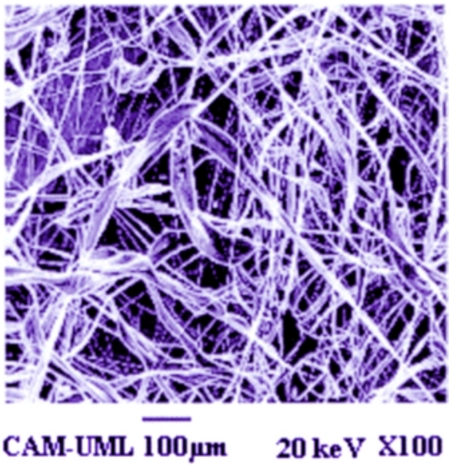

Figure 19 SEM image showing bead formation at 15 kV in a PC-CH electrospun fiber-mat.

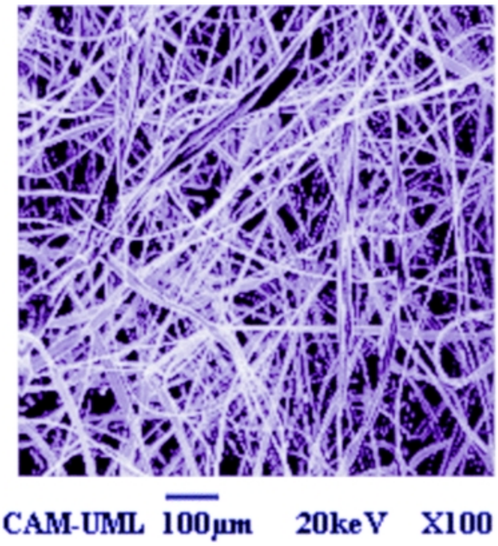

Figure 20 SEM image showing bead formation at 30 kV in a PC-CH electrospun fiber-mat.

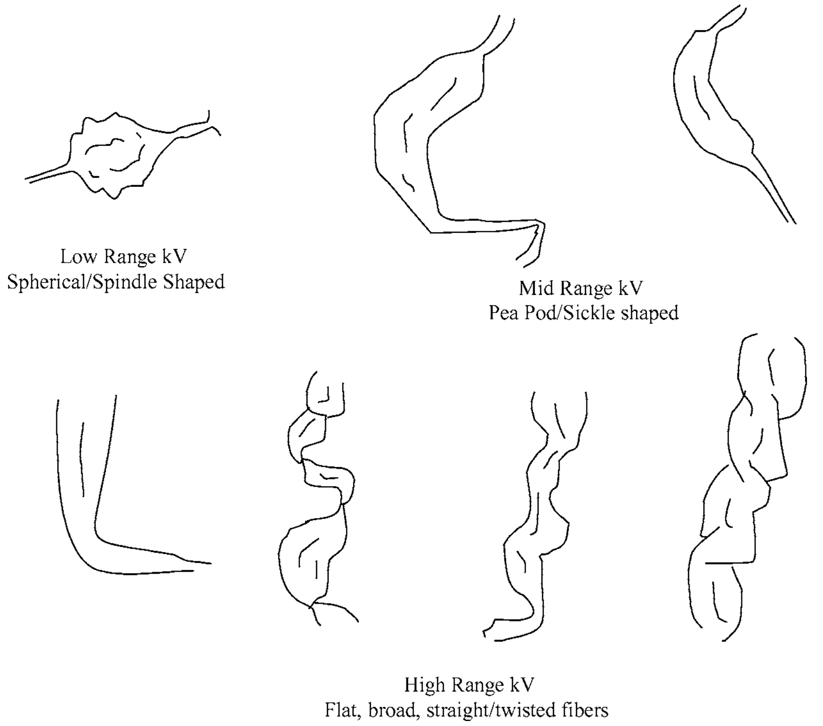

Figure 21 Illustration of bead shape variation with process voltage in PC-CH electrospinning.

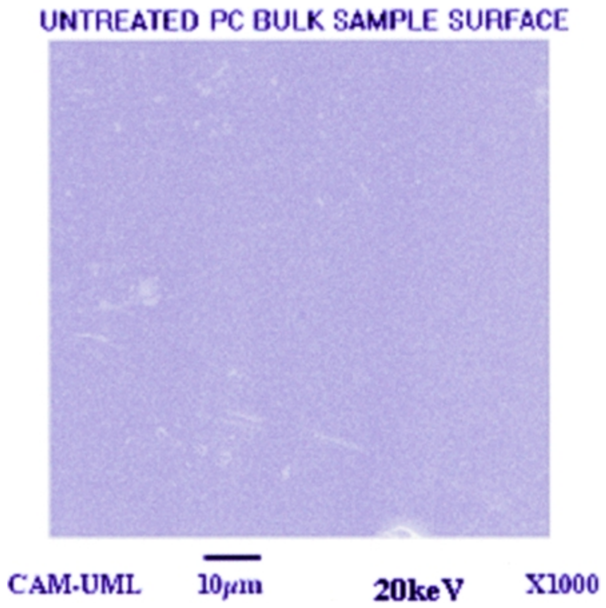

Figure 22 SEM image of the surface of a neat, untreated bulk Polycarbonate.

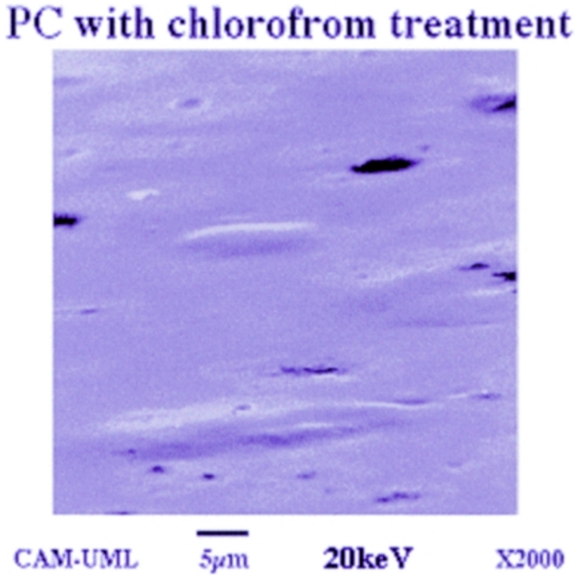

Figure 23 SEM image of the surface of a bulk Polycarbonate after treatment with Chloroform.

3.3. Internal structure of the fiber

TEM image of fine PC-CH electrospun fibers shown in Fig. 9 reveals that the fiber is largely solid with air pockets that are randomly distributed along the length of the fiber. Microtomed fiber cross-section examination has supported this observation. The cross-section images are shown in Fig. 10. TEM images of PC-MIX electrospun fiber-mat show a hollow core in the fibers. The dimensions of the hollow core are fairly uniform along the length of the fiber. This uniformity is clearly seen in the TEM image, shown in Fig. 11.

3.4. Bead density as function of the processing voltage

"Beads" can be defined as any irregularity in PC-MIX electrospun fiber-mat, as the processing voltage is increased from a low value of about 6 kV to a high value of about 30 kV, the bead density correspondingly increases from a low value to a high value. Fig. 12 is a bar graph showing the variation of bead density with voltage for both 14% PC-MIX and 15% PC-MIX electrospun fiber-mats. Figs 13, 14 and 15 show the increasing bead density with voltage in 15% PC-MIX electrospun fiber-mats. Deitzel *et al.* state that the instability of the originating surface with increasing voltage contributes to the increasing bead density.

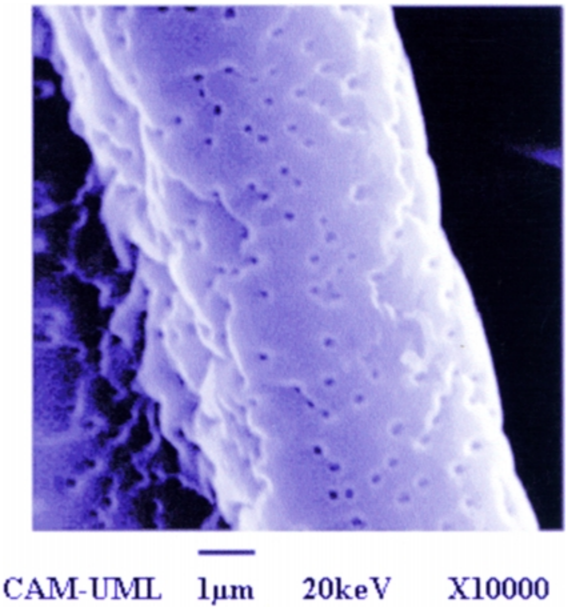

Figure 24 SEM image of the surface of a 15% PC-CH electrospun fiber with features similar to those caused by crazing.

Fig. 16 is a bar graph showing the variation of bead density with voltage for both 14% PC-CH and 15% PC-CH electrospun fiber-mats. Figs 17, 18, 19 and 20 show the variation in bead density with voltage in 14% PC-CH electrospun fiber-mats. This trend in the bead density can be explained by the variation in the shape of the beads with voltage, as shown in Fig. 21. On increasing the voltage the beads begin to occupy larger area resulting in increased bead density. At still higher voltages the beads merge into the fiber to form larger diameter fibers, resulting in a decrease in bead density.

3.5. Crazing of electrospun fibers

The evaporation of the solvent from the surface of a bulk PC is very similar to the evaporation of the solvent from the surface of an "almost-dry" fiber as it is nearing the target during electrospinning. Since solvents can craze polycarbonate, we can expect to see a similarity in the surface features of a crazed bulk PC and the surface of an electrospun PC fiber. Fig. 22 shows the surface of an untreated bulk PC. Fig. 23 shows the bulk PC after being subjected to a solvent wipe on its surface. Fig. 24 shows a high magnification SEM image of the surface of a PC-CH electrospun fiber. These figures clearly show the similarity between a crazed bulk PC surface and an electrospun PC fiber surface, indicating that electrospun PC fibers undergo crazing while losing its final solvent content. Such modified surface features could enhance specific surface area. However the decrease in the mechanical properties of the fiber due to such surface degradation needs to be studied closely.

4. Conclusions

There exists a natural conflict between the electrostatic forces and the forces of surface tension to affect the surface area of a polymer solution droplet. While surface tension tends to limit the surface area by forming spheres, electrostatic tension tends to achieve least charge density (charge per unit area), by increasing surface area. As this conflict occurs during electrospinning, the polymer solvent from the polymer solution begins to evaporate causing the viscosity of the polymer droplet to increase drastically. This increased viscosity prevents rapid changes in the shape of the polymer solution droplet. So, surface tension, electrostatics and viscosity, which are a function of the concentration of the polymer in the solution, play a major role in determining the morphology of the spun material. In the case of PC-MIX electrospinning, viscosity is low relative to PC-CH solution and the forces of surface tension dominate over viscous forces. Hence, spinning PC-MIX solutions at varying voltages yields beads which are spindle shaped, and whose area in the fiber-mat depends on the applied voltage. In the case of PC-CH electrospinning, viscosity is much higher relative to PC-MIX solution and viscous forces dominate over of surface tension. Hence, spinning PC-CH solutions yields beads which are not spindle shaped, and whose shape or area in the fiber-mat depends on the applied voltage.

The appearance of the raisin like structure is related to the relative rates of evaporation of the solvent from the surface of the polymer solution jet and the rate of evaporation at the core of the fiber, during electrospinning. A "Dry Skin" model has been proposed, to explain the formation of such a structure. This study has also shown a relation between a crazed PC surface and electrospun PC fiber surface.

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