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Some investigations on the fiber formation by utilizing a side-by-side bicomponent electrospinning approach

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Abstract

Simultaneous electrospinning of two polymer solutions in a side-by-side fashion is conducted for two bicomponent polymer systems—poly (vinyl chloride)/segmented polyurethane (PVC/Estane®) and poly(vinyl chloride)/poly(vinylidiene fluoride) (PVC/PVDF). The new experimental device is described and suitable process conditions to electrospin bicomponent fibers are described. Field emission scanning electron microscopy and energy dispersive spectroscopy were utilized to interpret the results regarding local structure and chemical composition, respectively.

Keywords: Bicomponent fiber; Electrospinning; Microfibers

1. Introduction

Electrospinning is a process to easily produce polymeric fibers in the average diameter range of 100 nm–5 μm [1–4]. The average diameter of the fibers produced this way is at least one or two orders of magnitude smaller than the conventional fiber production methods like melt or solution spinning [5]. As a result, these fibers possess a high aspect ratio that leads to a larger specific surface. These electrospun nanofibers have been suggested to find applications ranging from optical [6] and chemo sensor materials [7], nanocomposite materials [8], nanofibers with specific surface chemistry [9] to tissue scaffolds, wound dressings, drug delivery systems [10–12], filtration and protective clothing [13,14].

A typical experimental setup of the electrospinning process consists of a syringe-like apparatus that contains the polymer solution. The narrow end of the syringe is connected to a glass or Teflon capillary. A platinum electrode dipped in the polymer solution is connected to a high voltage DC supply. When the high voltage DC supply is turned on, the electrode imparts an electrical charge to the polymer solution. A jet is ejected from the suspended liquid meniscus at the capillary-end when the applied electric field strength overcomes the surface tension of the liquid [15]. Near the critical point, where the electric field strength is about to overcome the surface tension of the fluid, the free surface of the suspended drop changes to a cone, also commonly referred to as the Taylor cone. The jet is ejected from the surface of this Taylor cone as the electric field strength is increased. When this idea is extended to polymer solutions or melts, solidified polymer filaments are obtained on the grounded target as the jet dries. It has now been well established by the use of high-speed photography results that the jet undergoes a series of electrically driven bending instabilities [16–18] that gives rise to a whip-like motion beginning in the region close to the capillary tip. As the jet travels to the target, it undergoes this undulating motion and elongates at the same time to minimize the instability caused by the repulsive electrostatic charges. Suitable mathematical models describing this electrically driven instability have been proposed [16,19,20]. The series of electrically driven instabilities cause the jet to undergo large amounts of plastic stretching that results in the formation of extremely thin fibers that have a diameter in the range of several nanometers to a few micrometers. The amount of orientation induced in the fibers during this process will depend on the relaxation time of the chains and the rate of

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evaporation of the solvent. In addition, crystallinity may be induced if the polymer has molecular symmetry.

The effects of several process parameters, such as the applied electric field strength, flow rate, concentration, distance between the capillary and the target have been explored in great detail for different polymer materials [1,2,4,5,21]. Primarily, most of the systems that have been investigated to date have utilized electrospinning from a single polymer solution or melt. A few systems where blends of polymers (in the same solvent) and blends of polymer solutions (a four component system) have been electrospun have recently been investigated. Blends of polyaniline, a conducting polymer, with poly(ethylene oxide), PEO, in chloroform were electrospun to produce filaments in the range of 4–20 nm [22]. More specifically, PEO was blended with polyaniline to increase the viscosity of the solution to achieve stable electrospinning. In addition, a blend of a solution of polyamides (Nylon 6 and Nylon 66) in formic acid with a solution of poly(ethylene terephthalate) in triflouroaceticacid have also been electrospun to make fibers that will possess a combination of properties from each of the components in the blend [23]. However, a few aspects need to be considered when utilizing blends this way. For a blend of two polymers (in the same solvent), the mixture should be homogenous and the two polymers should be thermodynamically miscible. For a blend of two polymer solutions (a four component system), in addition to the factors mentioned above, the interactions between the polymer and the solvent of the opposing pair are also of critical importance. Hence, the thermodynamic and kinetic aspects of mixing need to be considered when utilizing blends for electrospinning. One way to surpass these complicated issues is to electrospin two polymers simultaneously in a side-by-side fashion. In this case, the two polymer solutions do not come in physical contact until they reach the end of the spinneret where the process of fiber formation begins.

Recently, we have been able to design an electrospinning device where two polymer solutions have been electrospun simultaneously in a side-by-side fashion. This allows having a bicomponent system that will have properties from each of the polymeric components e.g. one of the polymers could contribute to the mechanical strength while the other could enhance the wettability of the resulting non-woven web. This could be useful for a protective clothing application. Other applications could be based on combining the mechanical strength from one of the components and a desired chemical functionality from the other and so forth. While not critically addressed in this study, some of the important process parameters for bicomponent electrospinning are the viscosity and conductivity of each of the polymer solutions.

In the present study, we will describe our new bicomponent electrospinning device and present preliminary results on poly(vinyl chloride)/segmented polyurethane (PVC/Estane®) and poly(vinyl chloride)/poly(vinylidiene fluoride) (PVC/PVDF) bicomponent fibers. These specific systems have been chosen primarily from their being easily identified with energy dispersive spectroscopy (EDS) analysis. This allows us to better characterize the local compositional features of the electrospun bicomponent mat. Field Emission Scanning Electron Microscopy (FESEM) in conjunction with EDS was utilized to interpret the results.

2. Experimental

2.1. Electrospinning setup

The schematic of our device is shown in Fig. 1. The two syringes that contain the polymer solutions lie in a side-by-side fashion. A common syringe pump (K D Scientific, model 100) controls the flow rate of the two polymer solutions. The platinum electrodes dipped in each of these solutions are connected in parallel to the high voltage DC supply (Spellman CZE 1000R). The free ends of the Teflon needles attached to the syringes are adhered together. The internal diameter of the Teflon needle is 0.7 mm with a wall thickness of ca. 0.2 mm. The length of the Teflon capillary is ca. 6 cm. When the syringe pump is turned on, the two polymer solutions flow outwards through each of the Teflon needles until they come in contact at the tip of the needles. The grounded target used for collecting the solidified polymer filaments was a steel wire (wire diameter ~0.5 mm) mesh of count 20 × 20 (20 steel wires per 1″ each in the horizontal and vertical axes). However, it is possible to use other kinds of substrates as well, e.g. the grounded target can be in the form of a cylindrical mesh that can be rotated to obtain filaments oriented in a specific direction.

2.2. Materials

Poly (vinyl chloride) (PVC), weight average molecular weight, M_w, of 135,900 Da in the form of a fine powder, poly (vinylidiene fluoride) (PVDF), weight average molecular weight, M_w, of 250,000 Da in the form of pellets and

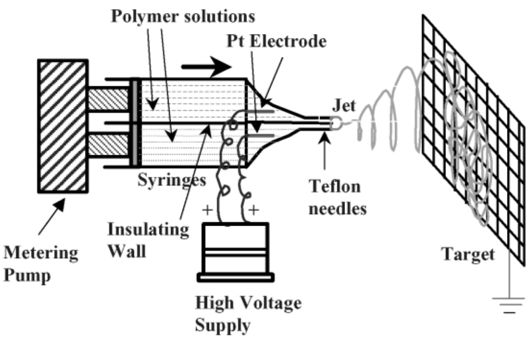

Fig. 1. Schematic representation of the bicomponent fiber electrospinning setup.

Estane® 5750, a polyether based segmented polyurethane supplied by Novion Inc., in the form of pellets was utilized for this study. Molecular weight data for Estane® 5750 could not be obtained, as the information is deemed proprietary. All the three polymers were dissolved separately in *N*,*N*-dimethyl acetamide (DMAc) at different weight concentrations ranging from 20–25 wt%.

2.3. Measurements and characterization

The viscosities of the polymer solutions were measured with an AR-1000 Rheometer, TA Instruments Inc. The measurement was done in the continuous ramp mode at room temperature (25 °C) using the cone and plate geometry. The sample was placed between the fixed Peltier plate and a rotating cone (diameter: 4 cm, vertex angle: 2°) attached to the driving motor spindle. The changes in viscosity and shear stress with change in shear rate were measured. A computer interfaced to the machine recorded the resulting shear stress vs. shear rate data. The viscosities of the polymer solutions are reported in Pa s.

The conductivity of the polymer solutions was measured using a Oakton® conductivity tester, model TDStestr 20. Prior to its use, the conductivity tester was calibrated by standard solutions procured from VWR Scientific®. The conductivities are reported in μS/cm.

A Leo® 1550 FESEM was utilized to visualize the morphology of the bicomponent polymer filaments. All the images were taken in the back-scattered mode, as the back-scattered detector is more sensitive to the electron density differences arising due to the presence of different chemical species. The samples were sputter-coated with a 5 nm Pt/Au layer to reduce the electron charging effects. This was done using a Cressington® 208HR sputter-coater. EDS was conducted on the bicomponent fibers to identify the chemical species present. The EDS detector was a part of the Leo® 1550 FESEM.

3. Results and discussion

Single component electrospinning of varying % weight concentrations of PVC, PVDF and Estane® in DMAc was conducted to optimize the process conditions. The results are shown in Fig. 2. The suitable process parameters at which uniform non-beaded fibers were obtained are listed in Table 1. At these conditions, stable jets were formed and the fiber diameter of these filaments was in the range of 285 nm–2 μm. The concentrations for PVC, PVDF and Estane® in DMAc were 25, 20 and 20 wt%, respectively. These concentrations were utilized for electrospinning bicomponent systems as well. Table 2 provides the zero shear rate viscosity and the conductivity of these polymer solutions.

As can be seen in Fig. 1, in the bicomponent setup, the two polymer solutions come in contact only at the tip of the Teflon needles therefore some amount of mixing of the two components is expected to take place. A fluctuating jet was observed for PVC/Estane® and PVC/PVDF at 14 and 15 kV, respectively at a distance of 20 cm. The corresponding electric fields (0.7 and 0.75 kV/cm, respectively) are relatively high when compared to those required for the stable jet formation from the single component systems

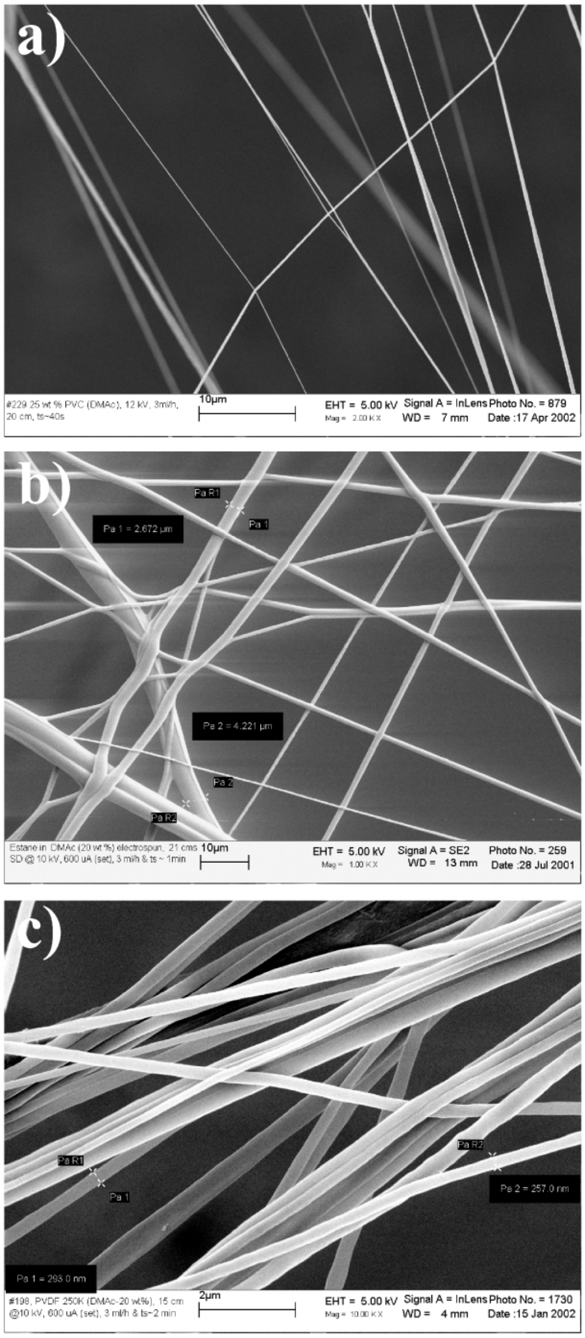

Fig. 2. (a) FESEM micrograph of PVC electrospun at 25 wt% (DMAc), 12 kV, 3 ml/h and 20 cm. Fiber diameter ~170–400 nm (b) FESEM micrograph of Estane® electrospun at 20 wt% (DMAc), 10 kV, 3 ml/h and 21 cm. Fiber diameter ~320 nm–4 μm (c) FESEM micrograph of PVDF electrospun at 20 wt% (DMAc), 10 kV, 3 ml/h and 15 cm. Fiber diameter ~230–625 nm.

Table 1
Optimized process parameters to electrospin single component PVC, Estane® and PVDF polymer systems and the resulting average fiber diameter

Polymer system	Conc. in DMAc to form non-beaded uniform fibers (wt%)	Electric potential for stable jet formation (KV)	Distance between the spinneret and target (cm)	Flow rate (ml/h)	Average fiber diameter (nm)
PVC	25	12	20	3	285
Estane®	20	10	21	3	2160
PVDF	20	10	15	3	428

Table 2
Conductivity and zero shear rate viscosities of the three polymer solutions. All measurements were done at 25 °C

Polymer system	Conductivity (μS/cm)	Zero shear rate viscosity (Pa s)
PVC (25 wt% in DMAc)	7	8.7
Estane® (20 wt% in DMAc)	38	4.9
PVDF (20 wt% in DMAc)	2	5.6

(Table 1). In fact, when the distance between the Teflon needle-tips and the target is 9 cm or larger, a single common Taylor cone was observed. From the surface of this Taylor cone, a fluctuating jet was ejected. The position of ejection of the jet on the surface of the Taylor cone changed very rapidly and led to a somewhat non-steady flow of the polymer solution. These fluctuations likely influence the extent of mixing of the two components when they come in contact at the tip of the Teflon needles. At distances larger than 25 cm the jet was not continuous and the Taylor cone dripped i.e. the field strength was not strong enough to convey the ejected jet to the grounded target. At distances less than 9 cm, two Taylor cones (with highly pulsating jets ejected from their surfaces) were observed, each emanating from one of the two Teflon needles. The conductivities of the polymer solutions are relatively different (see Table 2). For each of the pairs—PVC/Estane® and PVC/PVDF, the conductivity of the PVC solution (38 μS/cm) is distinctly higher than Estane® (7 μS/cm) and PVDF (2 μS/cm) solutions. At such low distances (<9 cm), the field strength is relatively strong and it induces a strong electrostatic repulsion force that leads to the formation of two Taylor cones and subsequently two separate jets - one from each polymer solution. This results in the formation of two zones of fiber collection on the target, each corresponding to only one of the two respective polymer components. It is expected that this phenomenon would also be an important consideration if several spinnerets were placed in a multi-channel configuration/array for mass production of electrospun fibers, but we will not address this issue further in this report. For the systems investigated in this study, bicomponent electrospinning was only conducted in the range of 10–25 cm (distance between the Teflon needle tips and the grounded substrate), where only one Taylor cone was observed.

The electrospinning conditions utilized for the PVC/Estane® system were: 14 kV, 3 ml/h, 15 cm and 25 wt% PVC with 20 wt% Estane. For the PVDF/PVC system the conditions were: 15 kV, 3 ml/h, 20 cm and 25 wt% PVC with 20 wt% PVDF. The back-scattered FESEM electron image of the PVC/Estane® electrospun web can be seen in Fig. 3(a). When EDS analysis was conducted on the regions marked as 'A' and 'B', it was found that the region 'A' is rich in chlorine indicating that it is principally PVC (Fig. 3(b)), whereas, region 'B' is rich in oxygen indicating that it is dominated by Estane® (Fig. 3(c)). Note the smaller peaks

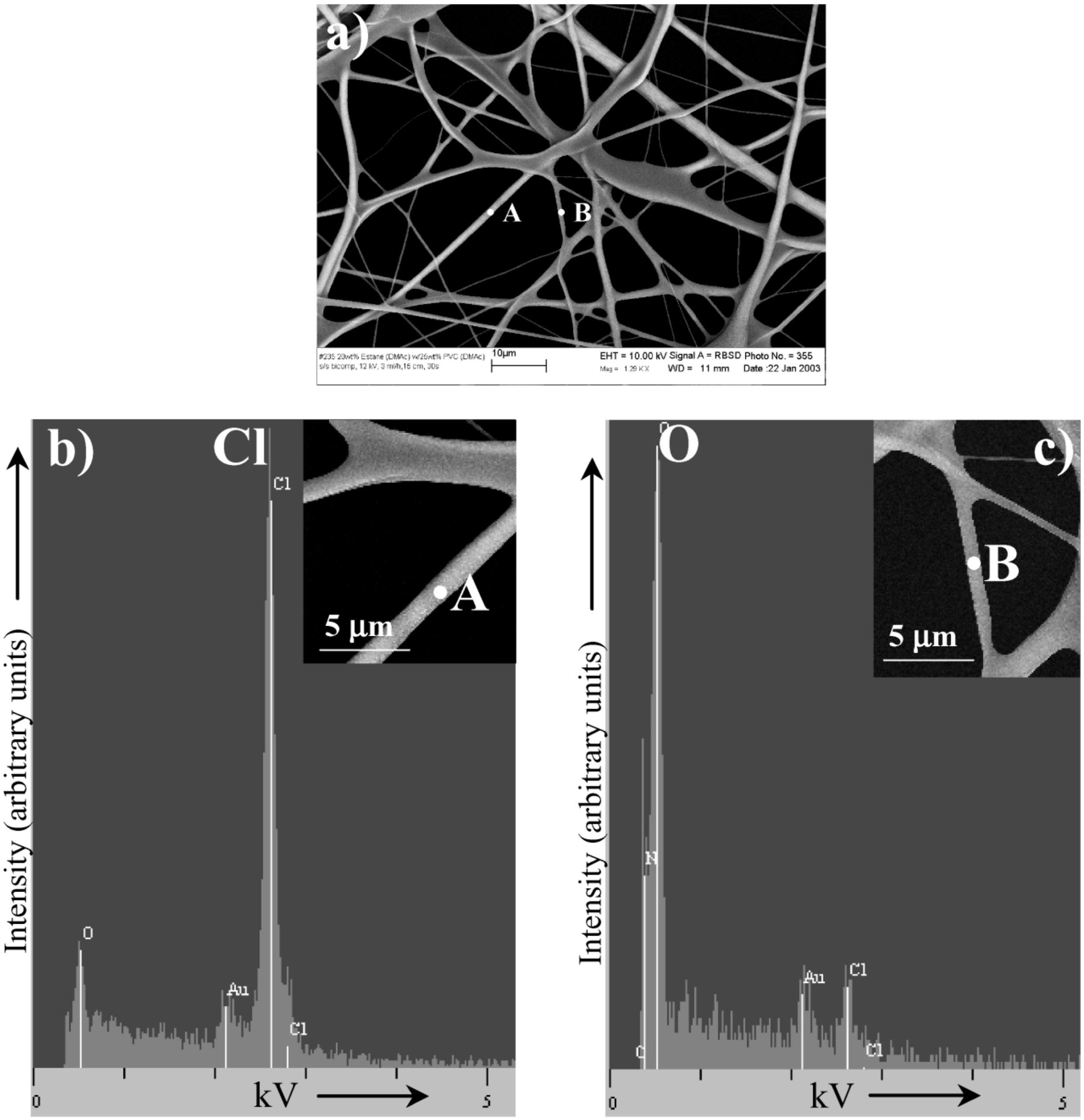

Fig. 3. (a) Scanning electron micrograph of side/side bicomponent electrospun PVC and Estane polymeric web. EDS results conducted on points ‘A’ and ‘B’ are shown in figures (b) and (c), respectively. The region ‘A’ is rich in chlorine indicating the PVC phase and the region ‘B’ is rich in oxygen indicating the Estane® phase.

corresponding to oxygen and chlorine, respectively in Fig. 3(b) and (c). These peaks are relatively weak but they do indicate the presence of the other component. Another example where the two polymer components have been electrospun in a side–side bicomponent fashion is shown in Fig. 4(a). Here, a back-scattered FESEM image of the PVC/PVDF electrospun web is shown. An EDS analysis was done similarly on the regions marked as ‘A’ and ‘B’ to identify the respective polymer components. The region ‘A’ (Fig. 4(b)) is rich in chlorine indicating that this region is primarily PVC, whereas region ‘B’ (Fig. 4(c)) is rich in fluorine, indicating that this region is ‘rich in’ PVDF. Again, in Fig. 4(b) and (c), smaller peaks corresponding to trace amounts of fluorine and chlorine respectively can be observed as well. Note that the filaments chosen for the EDS analysis are larger than a micron as the minimum resolution of the EDS detector is an area of 1 μm × 1 μm with a penetration depth of 1 μm. Typical diameter ranges observed were 100 nm to a few micrometers for each of these components in the two examples discussed above. The fibers are relatively polydisperse in terms of the diameter. It is difficult to control the fiber diameter dispersity in the electrospinning process as the fluctuations in the jet cause the polymer solution to undergo a somewhat non-steady

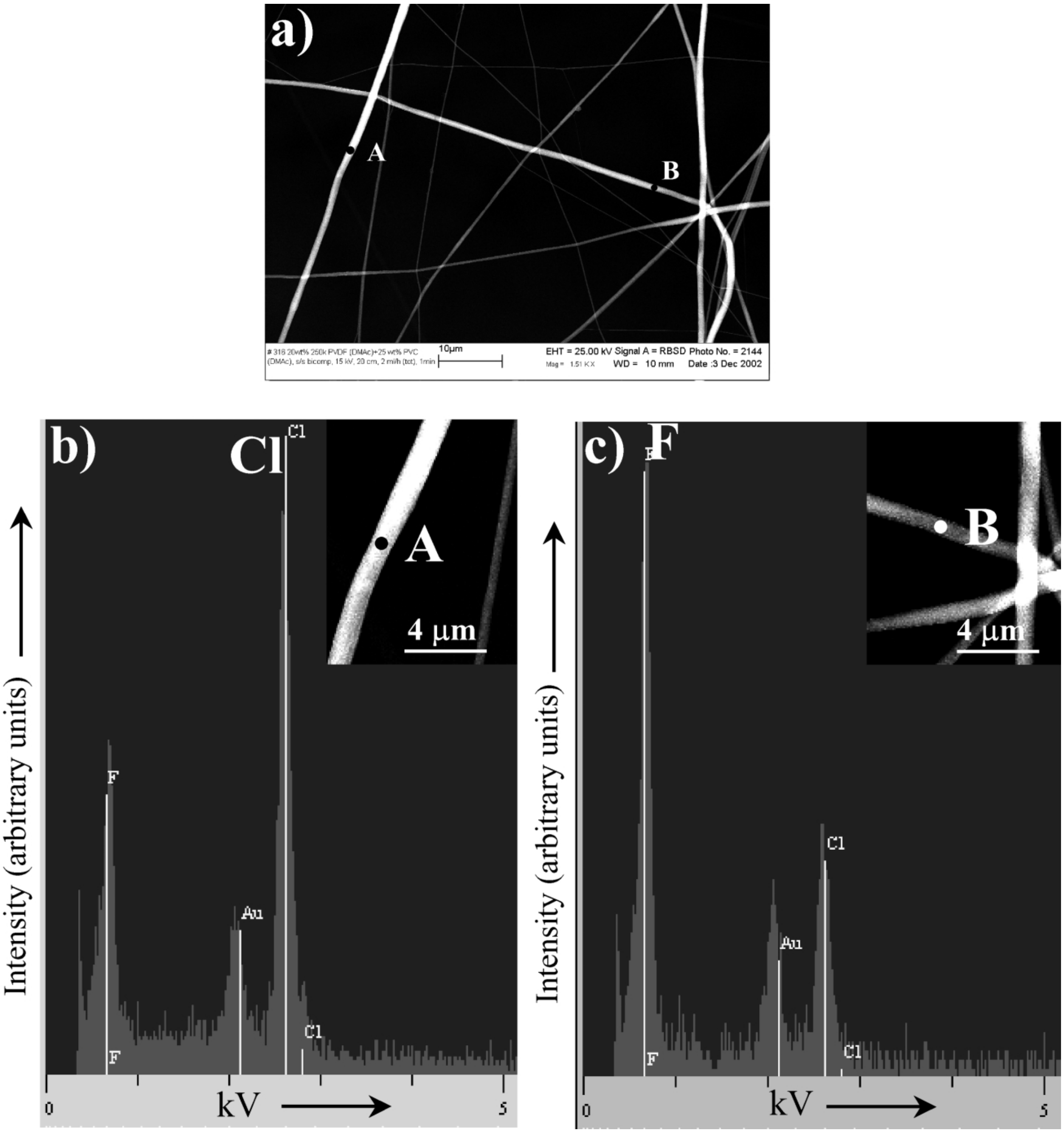

Fig. 4. (a) Scanning electron micrograph of side/side bicomponent electrospun PVDF and PVC polymeric web. EDS results conducted on points 'A' and 'B' are shown in figures (b) and (c), respectively. The region 'A' is rich in chlorine indicating the PVC phase and the region 'B' is rich in fluorine indicating the PVDF phase.

flow. This leads to the formation of fibers that have a range of fiber diameter. For the single component electrospinning, a stable Taylor cone and jet were observed, whereas, for the bicomponent electrospinning (at process conditions of 14–15 kV, 3 ml/h of total flow rate and the capillary-tip to target distance between 9 and 25 cm), a steady but pulsating jet was observed from the surface of a stable Taylor cone. A nanofiber garland-like formation, as reported by Reneker et. al. [24] was not observed in either of the single or bicomponent electrospun systems described in this study.

EDS analysis was conducted at different regions along the fiber length to ascertain the change in the chemical composition of the fibers. When EDS was conducted on different regions along the length of a 'chlorine-rich' fiber in the case of the PVC/Estane® system, it was found that the ratio of the peak intensity corresponding to chlorine with that of oxygen varied from 3 to 7. Similar experiments performed on a 'fluorine-rich' fiber in the case of the PVDF/PVC system indicated that the ratio of the peak intensity corresponding to fluorine with that of chlorine varied from 2 to 5. These results indicate that even though fibers rich in either component were observed, the relative amount of a given component can vary significantly. In other words, some amount of mixing of the two solutions takes place when they are electrospun together. This mixing changes with time within the time frame of electrospinning process and is believed to be primarily due to the fluctuations of the jet on the surface of the Taylor cone.

The zero shear rate viscosity of 20 wt% Estane® (8.7 Pa s) is relatively larger than that of 25 wt% PVC (4.9 Pa s) and 20 wt% PVDF (5.6 Pa s). Bicomponent electrospinning was also performed where lower concentrations (and consequently relatively lower viscosities) of PVDF and PVC were utilized. When EDS was conducted on any one of these filaments, peaks corresponding to both the components were observed with no relative dominance of either component. This is tentatively conjectured to be due to the fact that at lower viscosities, a larger amount of mixing of the polymer solutions takes place. Hence, it can be said that larger viscosities are helpful in the formation of fibers that are rich in either of the polymer components.

It may be useful to point out that both the jets emanating from the Teflon needle tips carry the same electrostatic charge. The mutual electrostatic repulsion of the jets helps prevents the mixing of the two solutions to some degree. In addition, PVC can develop a low degree of crystallinity while PVDF is quite highly crystalline when solidified from solution. Hence, the amount of crystallinity induced in these fibers when the solvent evaporates and the fibers are pulled towards the grounded target will also govern the extent of mixing of the two components.

The role of viscosity and critical chain overlap concentration on fiber formation by electrospinning will be considered in future investigations.

4. Conclusions

The potential of bicomponent fiber electrospinning, where two polymer solutions have been electrospun simultaneously in a side-by-side fashion, has been demonstrated. PVC/Estane® and PVC/PVDF were electrospun in this fashion. EDS was utilized to determine the composition of the resulting bicomponent electrospun web. For each bicomponent combination (PVC/Estane® and PVC/PVDF), fibers rich in each of the two components were identified. However, the ratio of the dominant component to the trace component varied along the length of the fibers. Fibers from each of the two components were obtained in a diameter range of 100 nm to a few micrometers.

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