Polymer 51 (2010) 5037–5043

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Reversibly thermochromic micro-fibres by coaxial electrospinning

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ARTICLE INFO

Article history:
Received 30 August 2010
Accepted 7 September 2010
Available online 16 September 2010

Keywords:
Coaxial electrospinning
Thermochromic
Core-shell fibres

ABSTRACT

A 'solvent facilitated' coaxial electrospinning process was used to produce reversible narrow temperature gap thermochromic, core-shell fibres. A thermochromic composite composed of crystal violet lactone (the leuco dye), bisphenol A (the developer) and 1-dodecanol (the phase-change solvent) was entrained as core material inside poly(methyl methacrylate) shells. A mutual core and shell solvent (chloroform) was used to obtain low interfacial tension between the core and shell spinning solutions. This enabled room temperature entrainment of the low molecular weight, low viscosity core fluid. In order to minimize the effect of light scattering and subsequently produce fibres with visible colour transitions, the fibres were produced with external diameters of 3–8 μm and core diameters of 1.7–5.7 μm. In order to produce core-shell fibres with repeated, reversibly thermochromic behaviour and a stable colour developed state, it was necessary to entrain a dye composite that contained an excess developer, essentially making this composite non-thermochromic prior to entrainment. The fibres were analyzed using SEM and DSC.

1. Introduction

Materials that can change their properties in response to external stimuli such as temperature, pH, moisture, stress, and electric and magnetic fields have important functions in application areas like sensing, actuation, logic and control. Thermochromic materials that are able to reversibly change colour in response to variations in temperature are useful in temperature sensing applications. The direct incorporation of thermochromic materials into fine electrospun fibres could allow the production of highly sensitive, temperature-responsive, fibre-based products for use in medical, safety and quality control applications. Thermochromic materials for textile applications are typically composed of a leuco dye, a developer and a phase-change medium [1–7]. Crystal violet lactone (CVL) is the most commonly used and widely studied leuco dye for thermochromic applications [7–10]. Colour developers are weak acids that act as proton donors to induce the coloured state of the leuco dye components [2]. The phase-change medium, also referred to as the 'solvent', can be a fatty alcohol or ester. The melting and crystallisation points of this 'solvent' largely control the temperatures of colour change [8,9]. The components must be entrained together within a protective shell to allow reversibility of the thermochromic effect and to prevent loss of the 'thermochromic composite' due to fluidity after melting. Thermochromic materials are typically microencapsulated prior to application to textile and other substrates [11]. A process of direct entrainment of thermochromic materials into fibres is an alternative.

Core-shell fibres, with various functionalities, have been produced using the coaxial electrospinning technique [12–17]. This modified electrospinning process allows the incorporation of low viscosity and low molecular weight fluids into fine fibres. Furthermore, electrospun fibres have greater surface area to volume ratios compared to conventional, melt-spun, synthetic fibres [18,19]. This is because the diameters of the electrospun fibres are much smaller than the diameters of conventional fibres. The diameters of electrospun fibres range from tens of nanometres to a few micrometres [20]. Coaxial electrospinning could be used to produce core-shell fibres that contain phase-change thermochromic composites if the thermochromic composite, which is typically a solid at room temperature, can be temporarily transformed into a fluid during processing.

A process that combines melt electrospinning with the use of a coaxial spinneret has been developed [21]. It has also been used to entrain a thermochromic composite into core-shell fibres [22]. The thermochromic effect of these fibres was, however, not visible. The absence of visible colour transitions was attributed to interference by light scattering, which masked the colour developed state of the thermochromic composite in the cores of the fibres. The scattering phenomenon was a result of the small core diameters (200–400 nm) and shell thicknesses (200–500 nm) of these fibres.

In this study we describe an alternative approach to coaxial electrospinning of core-shell fibres containing a thermochromic

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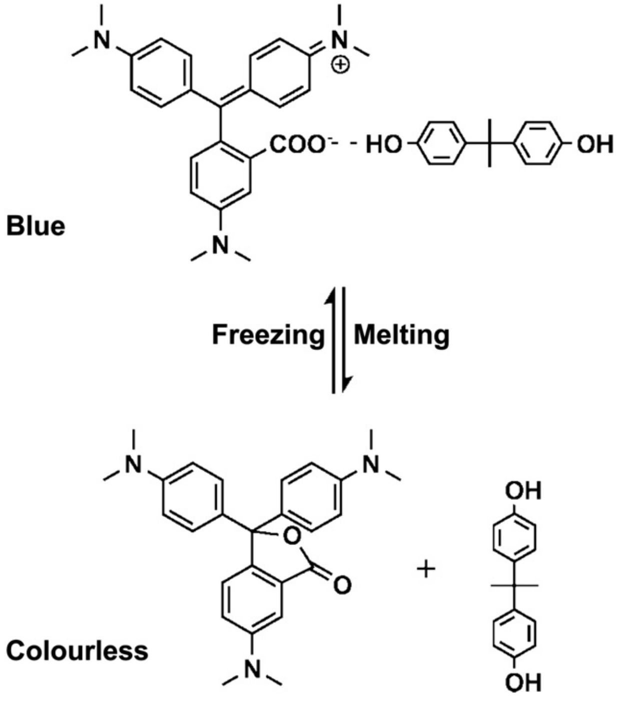
doi:10.1016/j.polymer.2010.09.018

composite. This process is carried out at room temperature. The components selected to form the thermochromic composite in this study were CVL as dye, bisphenol A (BPA) as developer and 1-dodecanol as phase-change medium. The mechanism of colour transition induced by CVL–BPA interactions is shown in Scheme 1. In the approach used here, the thermochromic composite core material is dissolved in a facilitating solvent prior to coaxial electrospinning. The facilitating solvent evaporates during the electrospinning process, leaving behind only the thermochromic dye composite in the core of the fibre. A poly(methyl methacrylate) (PMMA) shell spinning solution was used to entrain the dye composite inside PMMA fibres. Potential interference from light scattering effects was eliminated by electrospinning fibres with external diameters in the range of 3–8 μm and core diameters in the range 1.7–5.7 μm. This resulted in the formation of core-shell fibres that exhibited visibly reversible thermochromic transitions.

2. Experimental

A solvent facilitated coaxial electrospinning method was developed to allow the inclusion of a thermochromic composite into core-shell fibres without the necessity of heating the whole apparatus as in melt coaxial electrospinning. During coaxial electrospinning the charges accumulate predominantly on the surface of the shell droplet. Subsequently, the core material, especially when it is a low molecular weight and low viscosity fluid such as the current dye composite, is entrained by viscous dragging of the shell spinning liquid on the core spinning liquid. To achieve sufficient viscous drag it is important to have a low interfacial tension between core and shell spinning liquids, i.e. similar surface tensions for the core and shell spinning solutions. Other important properties to consider include the need for an electrospinnable shell solution, a higher shell than core solution viscosity, and the use of low vapour pressure solvents to dissolve the core and shell components [13]. It was also important to have compatible core and shell spinning liquids to avoid any precipitation at the spinneret exit. In order to achieve this it was beneficial to have mutual solubilities, i.e. the selected core facilitating solvent was also a solvent for the shell polymer.



Scheme 1. Schematic representation of the mechanism of the reversible thermochromic process involving structural changes of CVL, through complex formation with bisphenol A, in response to the phase (solid or liquid) of the phase-change solvent (e.g. 1-dodecanol).

Selection of the thermochromic components (CVL, BPA and 1-dodecanol) and the initial molar ratio in which the components were mixed was based on literature [5,9,10,22]. The molar ratio of the initially used thermochromic composite was 1:3:50 CVL:BPA:1-dodecanol. However, at a ratio of 1:50 CVL:1-dodecanol, the CVL was found to be insoluble in the 1-dodecanol, even at 70 °C. The relative ratio of CVL to 1-dodecanol was therefore increased to 1:100, giving an overall molar ratio in the thermochromic dye composite of 1:6:100 for CVL:BPA:1-dodecanol. When increasing the CVL:1-dodecanol ratio to achieve full solubility of CVL in molten dodecanol (at temperatures between 27 °C and 35 °C), it was found to be more important to maintain the original BPA:1-dodecanol (3:50) ratio rather than the original CVL:BPA (1:3) ratio. The 1:6:100 CVL:BPA:1-dodecanol composite gave full colour reversibility above and below the melting point of 1-dodecanol (24–27 °C). The ratio was however later changed to 1:20:100 CVL:BPA:1-dodecanol to successfully produce stable reversibly thermochromic core-shell fibres. The reason for this final change will be explained in Section 3.

2.1. Preparation of solutions and electrospinning setup

CVL (Leapchem, China), BPA (>99%; Sigma–Aldrich, RSA), 1-dodecanol (≥95%; Sigma–Aldrich, RSA), PMMA (molecular weight ≈ 350 000 g/mol; Sigma–Aldrich, RSA), chloroform (KIMIX, RSA) and ethanol (Sasol, RSA) were used as received. PMMA (16 wt %) was dissolved in a combined solvent of 3:2 v/v chloroform:ethanol to form the shell spinning liquid. CVL, bisphenol A, and 1-dodecanol were mixed in 1:6:100 or 1:20:100 M ratios at 70–80 °C until homogeneous solutions were obtained. The mixture was cooled to ±40 °C and mixed 5:2 v/v with chloroform to form the core spinning liquid.

The coaxial electrospinning setup is shown in Fig. 1. The coaxial spinneret (assembled from standard stainless steel HPLC components from VICI AG International, Switzerland) was fitted with an inner needle to create two concentric stainless steel capillaries. The inner (core) capillary was a needle with a blunt tip with inner diameter of 0.3 mm and outer diameter of 1 mm. The outer (shell) capillary had an inner diameter of 2.0 mm. The solutions were pumped from syringes through plastic tubes to the coaxial spinneret. The flow rates were controlled by a 33 dual syringe pump (Harvard Apparatus, USA). The electric potential was supplied by a 30 kV high voltage supply (custom built by the Electrical Engineering Department, Stellenbosch University, RSA).

2.2. Coaxial electrospinning process

The 16 wt% PMMA solution in 3:2 v/v chloroform:ethanol and the selected thermochromic dye composite (dissolved 5:2 v/v in chloroform) were loaded into the shell and core feed syringes, respectively. The syringes were connected to the coaxial spinneret by plastic (polypropylene) tubes. The shell and core flow rates were controlled at 12 ml/h and 2 ml/h, respectively. The positive electrode was attached to the top of the spinneret and the collector plate (covered with aluminium foil) was grounded. The voltage was set at 17 kV DC. The spinning distance was set at 27 cm. The humidity was controlled at 55–60% RH and the temperature was between 21 °C and 23 °C.

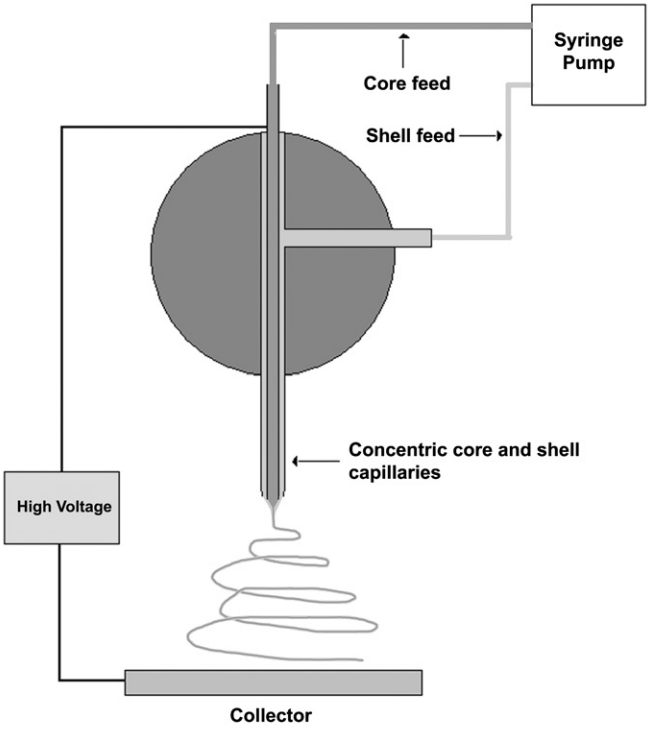


Fig. 1. Coaxial electrospinning setup used to produce thermochromic core-shell PMMA fibres.

2.3. Characterization

Scanning electron microscopy (SEM) images were obtained with a Leo® 1430VP Microscope.

The thermochromic transitions of the core-shell fibre webs were recorded as follows: To enable easy manipulation and efficient heat transfer, each electrospun fibre web was kept on the aluminium foil backing onto which it was originally spun. The web with foil backing was sealed inside a thin-walled polyethylene zip-seal bag and all residual air was rubbed out of the bag before sealing. The bag was suspended between two glass rods and placed inside a glass beaker filled with water on a hotplate stirrer. Under constant magnetic stirring, the temperature of the water surrounding the sample bag was slowly decreased and increased between 22 °C and 3 °C by addition of small amounts of cold water or application of heat from the hotplate stirrer. The water temperature was allowed to stabilise for at least 30 s after each small temperature step. The colour of the web was then recorded as a digital photograph, using a Canon HG10 camera.

Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q100 DSC, using a 1 C°/min heating rate.

3. Results and discussion

The solvent facilitated coaxial electrospinning method was successfully used to produce fibres with core-shell structures and with visible and reversible, temperature dependent colour transitions. The average external diameters of these fibres, as measured from SEM images, varied between 3 and 8 μm, and the core diameters varied between 1.7 and 5.7 μm.

Thermochromic fibres with core-shell structure and bead-free morphology were first obtained by coaxial electrospinning a shell solution of 16 wt% PMMA in 3:2 v/v chloroform:ethanol and a core solution of 1:6:100 CVL:BPA:1-dodecanol (molar ratio) dissolved 5:2 v/v in chloroform. Fig. 2(a) is a SEM image showing the bead-free surface morphology of the fibres. Fig. 2(b) is a cross-section SEM image of a freeze-fractured fibre showing the core-shell structures. In Fig. 2(c), a section of Fig. 2(b) has been digitally zoomed and contrast enhanced in order to better illustrate the core-shell structure of the fibers.

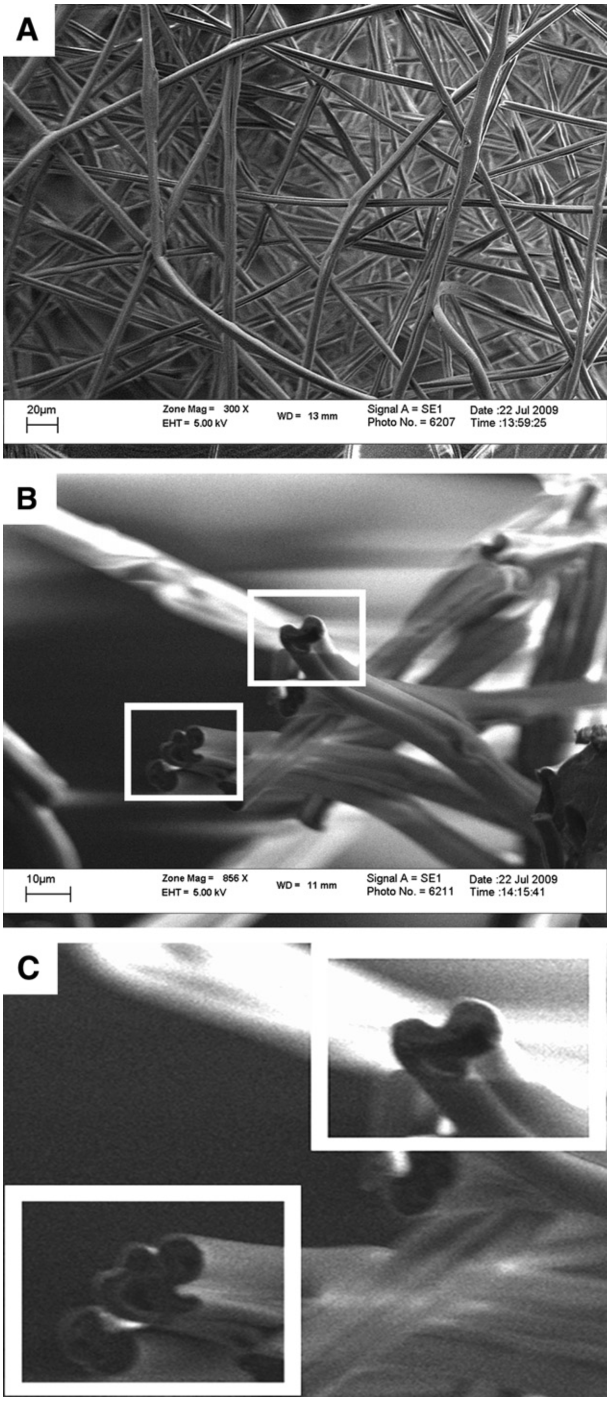


Fig. 2. SEM images showing (a) surface morphology and (b) cross-section of thermochromic core-shell fibres (shell solution: 16 wt% PMMA, 3:2 v/v chloroform:ethanol; core liquid: 1:6:100 CVL:BPA:1-dodecanol, 5:2 v/v dye composite:chloroform). (c) Digitally zoomed and contrast enhanced image showing the core-shell structures from (b).

Properties of the spinning solution are tabulated in Table 1. Although the core spinning solution was not conductive and had

Table 1
Compositions and properties of core and shell spinning solutions.

Spinning solution	Composition	Surface tension at 20 °C (mN/m)	Conductivity (μS/cm)	Viscosity at 20 °C (mPa/s)
Shell	16 wt% PMMA in 3:2 v/v chloroform:ethanol	24.3	1.67	369
Core	1:6:100 M ratio CVL:BPA:1-dodecanol dissolved 5:2 v/v in chloroform	23.1	Not conductive	6.50

a low viscosity, the low interfacial tension (i.e. similar core and shell spinning liquid surface tensions, as shown in Table 1) resulted in sufficient viscous dragging forces of the shell solution on the core solution to pull the core solution into the compound jet and form core-shell fibres. The viscosity of the shell solution could protect the core solution from breaking into droplets, due to Raleigh instability, during the whipping process.

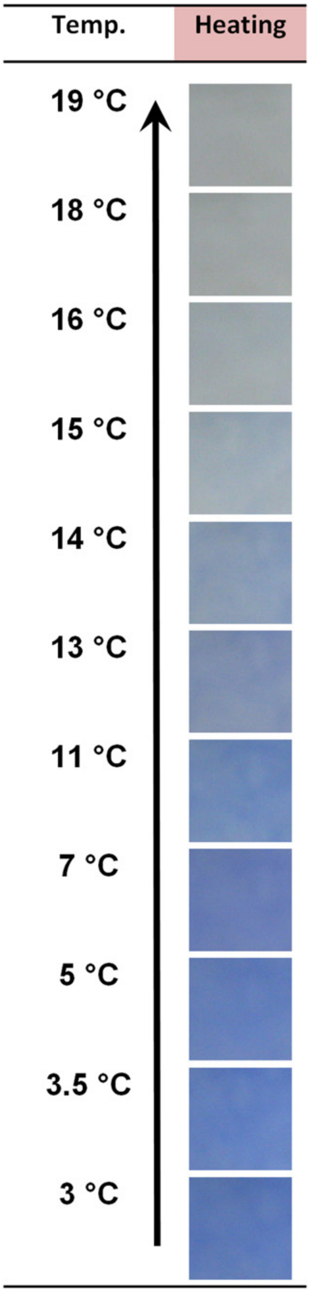


Fig. 3. Photographs depicting the colour transition of 1:6:100 (molar ratio CVL:BPA:1-dodecanol) thermochromic PMMA fibres as a function of temperature.

The temperature dependent colour of the resulting fibre mat is shown in Fig. 3. Although a reversible thermochromic transition with a transition temperature around 14–15 °C was observed, the thermochromic behaviour of the fibres was unstable. After several heating and cooling cycles, and even when new fibre mats were stored at 4 °C immediately after spinning, the fibre mats turned white within 6–12 h and the thermochromic behaviour disappeared.

An interfering interaction between the polymer shell (PMMA) and the developer component (BPA) of the thermochromic composite was the suspected cause of the disappearance of the coloured state. To test this hypothesis, the proportion of BPA in the dye composite was increased to provide the dye composite with excess developer. The molar ratio of the dye composite was changed to 1:20:100 CVL:BPA:1-dodecanol.

Fig. 4 on the left shows the temperature dependent colour of the 1:6:100 thermochromic composite in bulk. The thermochromic transition of the bulk composite could be repeated several times without similar disappearance of the coloured state as observed for the composite encapsulated inside core-shell fibers. Fig. 4 on the right shows the temperature dependent colour of the 1:20:100 composite in bulk. The excess developer caused the dye composite in bulk to stop exhibiting a thermochromic transition. The blue

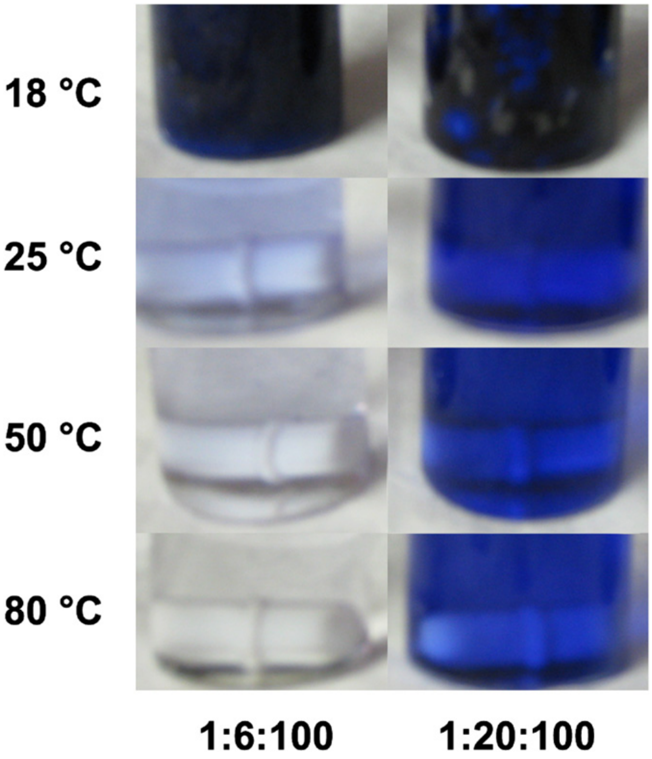


Fig. 4. Photographs indicating the colour of the different dye compositions (CVL:BPA:1-dodecanol molar ratio), in bulk, over a range of temperatures.

Table 2
Composition and solution properties of thermochromic dye composite.

Molar ratio (Dodecanol:BPA:CVL)	Spinning solution (5:2 v/v dye:chloroform)		
	Surface tension at 20 °C (mN/m)	Conductivity (μS/cm)	Viscosity at 20 °C (mPa/s)
1:20:100	24.2	Not conductive	10

colour remained at temperatures up to 80 °C. The excess BPA in the 1:20:100 composite in bulk caused permanent ring-opening and colour development of CVL regardless of the temperature.

Core-shell fibres were then produced using the core spinning liquid formed by dissolving the 1:20:100 dye composite 5:2 v/v in chloroform (solution properties are given in Table 2) and the same shell solution as before. The SEM images (surface morphology and cross-section view) of the resultant fibres are shown in Fig. 5. These fibres had an average diameter of 5.9 ± 1 μm and a core diameter of ±3 μm.

The temperature dependent colour of the core-shell fibre webs containing the 1:20:100 composite cores are shown in Fig. 6. The figure clearly illustrates the reversibility of the thermochromic transition by demonstrating the changing colour of the web in a sequence of cooling, heating and re-cooling. The return of thermochromic behaviour once the non-thermochromic 1:20:100 bulk composite is entrained inside core-shell fibres supports the hypothesis of an interfering interaction between PMMA and BPA. It is possible that the PMMA attracts some of the BPA and reduces its availability for causing CVL ring-opening (i.e. colour development). After the PMMA–BPA interaction has reached a saturation point, the remaining BPA in the dye composite is available to act as the

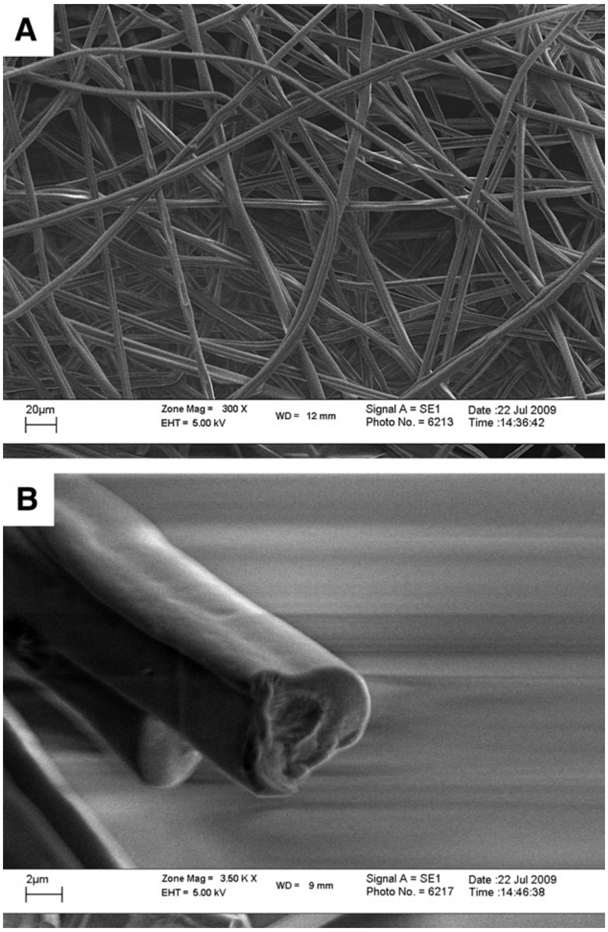


Fig. 5. SEM images showing (a) surface morphology and (b) cross-section of thermochromic core-shell fibres (shell solution: 16 wt% PMMA, 3:2 v/v chloroform:ethanol; core liquid: 1:20:100 dodecanol:BPA:CVL, 5:2 v/v dye composite:chloroform).

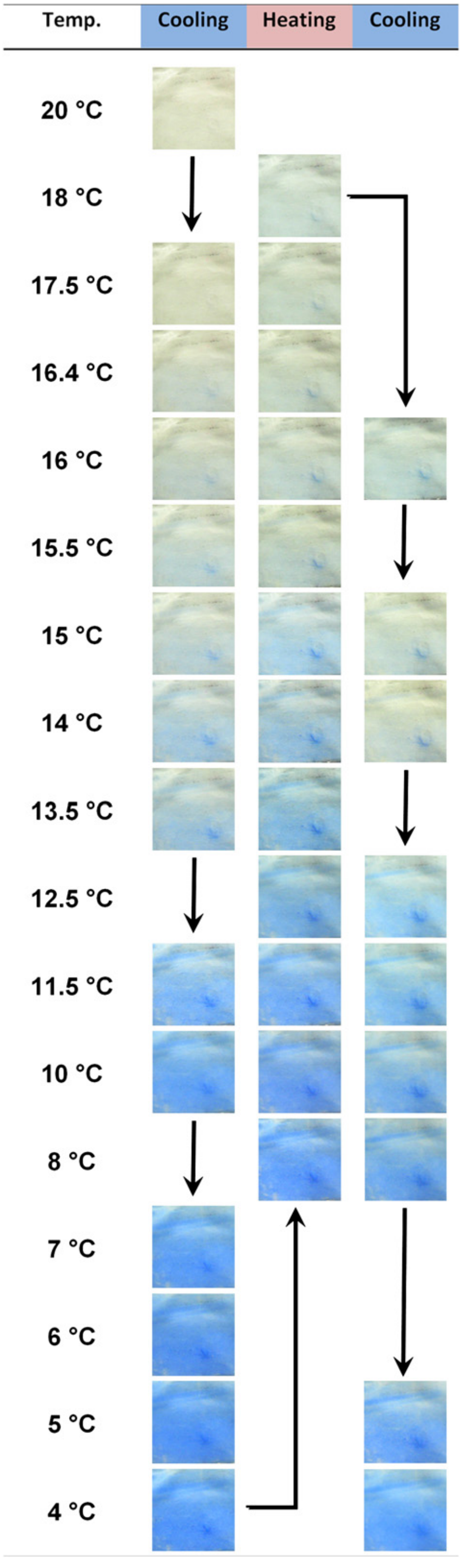


Fig. 6. Photographs depicting the reversible colour transition of the PMMA fibre web containing 1:20:100 (molar ratio CVL:BPA:1-dodecanol) thermochromic composite cores as the temperature is cycled between higher and lower temperatures.

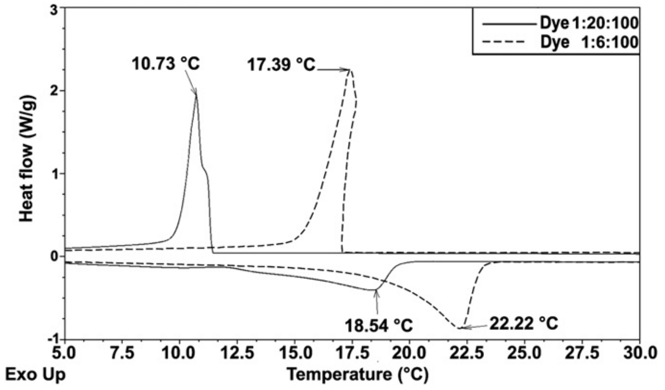


Fig. 7. DSC analysis showing melting and solidification peaks of the bulk thermochromic dye composite with molar ratio of 1:6:100 and 1:20:100 CVL:BPA:1-dodecanol respectively.

developer in the dye composite and enable reversible, thermochromic behaviour.

The 1:20:100 core-shell fibres exhibited repeated loss of and re-development of the coloured state when the temperature of the fibre mats was cycled repeatedly between 22 and 3 °C. The thermochromic behaviour of these fibres can therefore be considered fully reversible. The colour developed state and thermochromic behaviour remained stable. Samples retained their blue colour even after 6 months of storage at 4 °C and when these samples were exposed again to higher temperatures, the thermochromic behaviour could still be observed and the effect was shown to be as fully reversible as with newly spun fibres.

The DSC thermograms of the bulk 1:6:100 and 1:20:100 thermochromic dye composites and of the core-shell fibres containing the 1:20:100 composite are given in Fig. 7 and Fig. 8, respectively. Comparison of the thermograms of the two dye composites in bulk (Fig. 7) clearly illustrates the colligative property of freezing point depression, where the higher fraction of dissolved substances, i.e. BPA and CVL, in the 1:20:100 composite leads to lowering of the freezing point to 10.73 °C, compared to the 17.39 °C observed for the 1:6:100 bulk composite.

The DSC thermogram of the core-shell fibers containing the 1:20:100 dye composite (Fig. 8) is markedly different from that observed for the bulk 1:20:100 dye composite. Both the melting and freezing points of the entrained dye composite occur at higher temperatures than for the bulk dye composite. In addition, the entrained dye exhibits multiple solidification peaks, while bulk dye exhibits a sharp solidification peak, with a single shoulder on the high temperature side. The observed thermal behaviour of the entrained dye further supports the hypothesis of an interfering interaction between PMMA and BPA. While the freezing point depression of the 1-dodecanol is quite pronounced in the bulk 1:20:100 dye composite, an interfering interaction between the PMMA fibre shell and the BPA in the fibre core is believed to limit the amount of freely available BPA, thereby limiting the amount of BPA that can dissolve in the 1-dodecanol and cause freezing point depression.

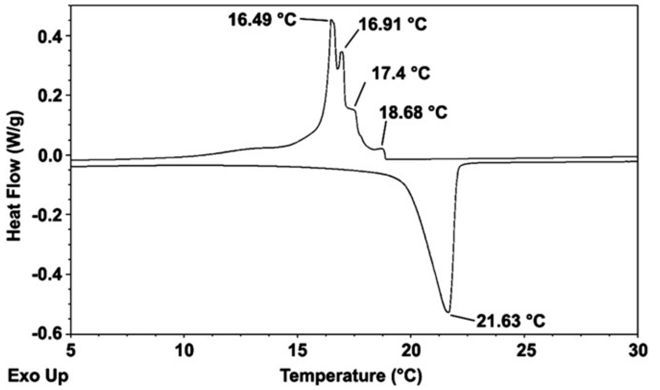


Fig. 8. DSC analysis showing melting and solidification peaks of the thermochromic core-shell fibres with a dye composite of 1:20:100 M ratio CVL:BPA:1-dodecanol.

The ratio of the internal surface area of the PMMA fibre shell, to the volume of entrained dye composite in the fibre core will depend on the diameters of the fibre cores, with smaller core diameters leading to higher surface-to-volume ratios. Assuming that there is some interfering interaction between the PMMA shell and the BPA in the core, this variation in PMMA shell surface to dye core volume can be expected to affect the amount of free BPA that can dissolve in the 1-dodecanol in the core, thereby affecting the degree of freezing point depression. It is proposed here that the multiple solidification peaks observed in the thermogram of the core-shell fibers containing the 1:20:100 dye composite can be attributed to a distribution of fibre core diameters, i.e. a distribution in core diameters that arose from instabilities in the electrospinning process.

A comparison of the melting and solidification temperatures of the 1:20:100 composite (Fig. 8) with the actual colour transition temperatures (Fig. 6) reveals that the melting point is not the only parameter governing the colour transition temperature of the dye composite, especially not when the dye composite is entrained in the fibres.

4. Conclusions

A solvent facilitated coaxial electrospinning process was developed and used to fabricate reversibly thermochromic core-shell fibres with a PMMA shell and a CVL:BPA:1-dodecanol dye composite core. A solvent, chloroform, was used to facilitate the room temperature entrainment of the non-electrospinnable thermochromic dye composite into the cores of the fibres. The use of this facilitating solvent allowed the manipulation of the surface tension of the core liquid and, consequently, the interfacial tension between core and shell spinning solutions. The use of miscible solutions to obtain low interfacial tensions was effectively used to entrain the low molecular weight core liquid and produce core-shell fibres. This method effectively prevented needle blockage and allowed processing of the dye composite without the need for high processing temperatures. The facilitating solvent evaporated during electrospinning and the phase-change and thermochromic properties of the dye composite entrained in the fibres was restored. A stable coloured state of the core-shell fibres could only be achieved by entraining a 1:20:100 (molar ratio) CVL:BPA:1-dodecanol dye composite, which contained an excess amount of developer (BPA) that rendered the bulk dye composite permanently blue. Core-shell fibres containing this non-thermochromic dye composite had a reversible thermochromic effect. These results indicated possible interfering interactions between the PMMA shell material and the BPA in dye composite.

Acknowledgements

The authors would like to acknowledge the financial assistance of the National Research Foundation (NRF) towards this research. Opinions expressed and conclusions arrived at, are those of the authors and are not necessarily to be attributed to the National Research Foundation.

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