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Co-electrospun poly(ε-caprolactone)/cellulose nanofibers-fabrication and characterization

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ABSTRACT

We report fabrication of poly (ε-caprolactone) (PCL)/cellulose (CEL) nanofiber blends via co-electrospinning for the possible use as biofilters and biosensor strips. Five different ratios of PCL to CEL were fabricated to investigate the wicking behavior. The cellulose acetate (CA) was taken as precursor to make cellulose nanofibers. Double nozzles were employed for jetting constituent polymers toward collector drum independently and resultant nanofibers webs were deacetylated in aqueous alkaline solution to convert CA into CEL as confirmed by FTIR spectra. FTIR further revealed that there is no effect of deacetylation on PCL nanofiber. The morphology of each blend webs under SEM showed uniform and bead-free nanofibers. Wicking behavior for five different ratios of PCL/CEL suggested that increasing CEL ratio in the blend enhanced the wicking front height; however, X-ray diffraction patterns of PCL/CEL showed a slight decrease in crystallinity.

1. Introduction

During current era technical application of nanofibers is substantially growing, owing their ability to meet stringent specialized requirements (Khatri, Wei, Kim, & Kim, 2012). Blending different nanofibers to enhance structural, physical or chemical properties for particular application is a common practice worldwide. Many researchers exercised blending nanofibers to explore their potential in terms of tissue engineering and scaffolds as; poly(L-lactide-*co*-glycolide) PLGA (Bini, Gao, Wang, & Ramakrishna, 2006), poly(L-lactic acid)–poly(D-lactic acid) PLLA–PDLA (Zong et al., 2002), poly(DL-lactide-*co*-glycolide)–poly(ε-caprolactone) PLGA–PCL (Panseri et al., 2008), poly(ε-caprolactone)-poly(L-lactic acid) PCL–PLLA (Khatri et al., 2013a), poly(L-lactic acid-*co*-ε-caprolactone) PLCL (Tian, Prabhakaran, Ding, Kai, & Ramakrishna, 2012), poly(L-lactic acid–ε-caprolactone), P(LLA–CL) (Xu, Inai, Kotaki, & Ramakrishna, 2004), silk fibroin (Marelli et al., 2010), for filtration and capillary absorption (Ma, Kotaki, & Ramakrishna, 2005; Ma & Ramakrishna, 2008; Callegari, Tyomkin, Kornev, Neimark, & Hsieh, 2011) and fabrication of different biodegradable polymers (Braganca & Rosa 2003; Cho & Lee, 2002; Nishio, Matsuda, Miyashita, Kimura, & Suzuki, 1997; Kusumi, Inoue, Shirakawa, Miyashita, & Nishio, 2008; Chen et al., 2005; Rosa, Guedes, & Bardi, 2007; Zhou & Huang, 2004; Yang, Wu, & Zhu, 2001). Blending also aims to get control on properties of resultant web in order to serve specific purpose effectively. Many researchers carried out blending to harmonize component polymers with each other or to address their deficiencies (Shalumon et al., 2010; Gassner & Owen, 1994; Suave, Dall'Agnol, Pezzin, Meier, & Silva, 2010). For instance, PCL is characteristically recognized for better physical and mechanical constancy but lacks in water retention property which limits its application in biofilters and biosensors (Vertuccio, Gorrasi, Sorrentino, & Vittoria, 2009; Han, Branford-White, & Zhu, 2010; Xu, Wang, Stark, Cai, & Chu, 2012). On the contrary cellulose fibrous web is largely accepted for excellent wettability, which is 10 times higher than that for fabric (Khatri et al., 2012; Callegari et al., 2011; Shuiping, Lianjiang, Weili, Xiaoqiang, & Yanmo, 2010).

Many applications like water filtrations webs, biosensors strips, implants for tissue engineering; not only necessitate high degree of absorbency and wicking rate to transport liquor without any impediment but also demand some strength to stand against

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strains acting upon them. Blending of these two fibers via co-electrospinning may upshot in firm fibrous web with improved wicking rate. Since it is very difficult to electrospun cellulose directly into nanofibers, therefore, usually cellulose acetate, a distinctive organic ester is used as a precursor to fabricate cellulose nanofibers (Khatri et al., 2012; Ali, Khatri, Oh, Kim, & Kim, 2014). As a matter of fact cellulose acetate lacks wetability, owing to acetyl group in chemical structure so; these acetyl groups are removed through deaccetylation. Deacetylation is a common practice to convert cellulose acetate into regenerated cellulose by treating in aqueous solution of NaOH or EtOH to enhance wicking ability (Khatri et al., 2012; Liu & Hsieh, 2002).

This report investigates fabrication of PCL/CEL nanofibers blend in different ratios via co-electrospinning with an aim to improve wicking rate. PCL and CA polymers were electrospun simultaneously and independently into nanofibers and collected over metallic drum. The co-electrospun PCL/CA nanofibers were deacetylated to eliminate acetyl group, as a result, CA converted into PCL/CEL nanofibers. The resultant nanofibers webs were characterized by wicking rate, FTIR and SEM analysis and compared to untreated nanofibers.

2. Experimental

2.1. Materials

PCL (poly(ε-caprolactone) having Mw = 80,000) and CA (cellulose acetate, 39.8% acetyle content having average Mw = 30 kDa). These chemicals were supplied by Aldrich chemical company and utilized without any additional purification.

2.2. Co-electrospinning

Concentration for PCL solution was 9% (wt%) and prepared with dimethylformamide: chloroform in 1:9 wt%. While CA solution was 17% (wt%) and formed with acetone/dimethyl formamide (DMF) in 2:1 by weight. In addition to neat PCL and neat CA five other blend ratios of PCL/CA were prepared as, 1:1 one syringe of each solution (w/w), 1:2 one syringe of PCL and 2 syringes of CA, 1:3 one syringe of PCL and 3 syringes of CA, 2:1 two syringes of PCL and 1 syringe of CA, and 3:1 three syringes of PCL and one syringe of CA (w/w). Each solution was supplied through plastic syringe attached to a capillary tip with an inner diameter of 0.6 mm. Copper wire inserted in polymer solution was connected to a positive electrode (anode), and negative electrode (cathode) was attached to metallic collector. Capillary tip to collector distance for PCL was set at 15 cm and 12.5 cm for CA, whereas capillary tips were placed at an angle of 10° from horizontal plane.

Electrospinning of these solutions was carried out by generating electric field with a high voltage power supply (Har-100*12, MATUSADA Co. Tokyo, Japan), which has potential of generating voltages up to 100 kV. For PCL solution voltage kept at 12 kV and CA was electrospun at 12.5 kV voltages. PCL and CA solutions were co-electrospun individually and in combination and resultant webs were collected on rotating metallic drum at room temperature. The thickness of each nanofiber webs was kept between 30 and 35 μm. These nanofibrous webs were air dried for 48 h and then subjected to deacetylation.

2.3. Deacetylation

In order to convert CA into cellulose, deacetylation of resultant webs was carried out to eliminate Acetyl group of CA nanofibers, by immersing them in an aqueous solution of 0.05 M NaOH at 30 °C for 48 h (Khatri, Mayakrishnan, Hirata, Wei, & Kim, 2013b). After conversion fibrous webs were rinsed off thoroughly until their pH values became neutral. Samples were then dried for 4 h at 50 °C.

2.4. Characterization

2.4.1. Wicking rate

Improvement in water retention potential can be observed with the aid of wicking test. Wicking rate was carried out by vertical capillary routine, which measures the increase in height of wicking front per second (Khatri et al., 2012). In order to access the wicking rate, samples of 20 mm long and 5 mm wide were secured in an upright stationary clamp, beneath a Petri dish containing reactive dye solution was placed on a movable jack. Dye solution of 1% (w/v) was prepared with CI Reactive Blue 19 (Sumfix Brilliant Blue R, Sumitomo Chemicals, Japan) dissolved in distilled water. Up to 5 mm portion of sample was dipped in reactive dye solution and remaining 15 mm hanging portion was under observation for wicking rise. A stop watch was used to record time in seconds. Provided a camera (Sony with 12.1 Mpixel) took multiple shots per second to evaluate the height of wicking front per second. The test lasted for either for 90 s or the wicking front reaches to maximum height of 15 mm.

2.4.2. Nanofibers web thickness

The average thickness of all nanofiber webs were measured by a digital micrometer MCD130-25 with measuring sensitivity of 1 μm.

2.4.3. ATR-FTIR spectroscopy

ATR-FTIR spectroscopy (IR-prestiage 21 by Shimadzu Japan) was employed to analyze modification within chemical structure of participant nanofibers, with and without blending. Moreover, FTIR spectra of before and after deacetylation of nanofibers blends were investigated to confirm conversion of CA in to CEL nanofibers.

2.4.4. Scanning electron microscopic analysis

Morphology of nanofibers was examined under scanning electron microscope (SEM, JEOL-6380 LV). All samples were sputtered with Carbon before assessment.

2.4.5. WAXD analysis

The crystallinity of electrospun webs were measured using WAXD (Bruker AXS D8 Germany), with Cu $K\alpha$ radiation (λ = 1.5402 Å) at a scanning speed of 2θ = 5°/min. The data were taken in the range of 10° to 50° in steps of 0.02° at 40 kV and 60 mA.

3. Results and discussion

3.1. Effect of deacetylation on wicking behavior of nanofiber webs

Comparison of wicking behavior before and after deacetylated co-electrospun webs are presented in Fig. 1a and b. Fig. 1a shows wicking behavior of all samples before deaccetylation and evidently points toward neat PCL and neat CA at two opposite border lines i.e. minimum and maximum wicking rate respectively which substantiate their hydrophobic and hydrophilic nature (Van der Schueren et al., 2013). Samples with higher PCL quotient i.e. 3:1 and 2:1 exhibit low wicking front heights of 2 and 3 mm at 60 and 80 s, respectively which can be attributed to dominant effect of crystallinity that resist absorption of liquid. Sample owns equal proportion of both fibers i.e. 1:1 reached a moderate wicking front height of 8 mm in 60 s and hangs around same front height up to 90 s which refers the active contribution of cellulose acetate fibers regarding wicking and by further increasing CA content perceptible improvement in wicking rate was experienced. This gradual enhancement can be credited to the reduction of crystallinity of co-electrospun webs as bulkier CA molecules disrupts the alignment of

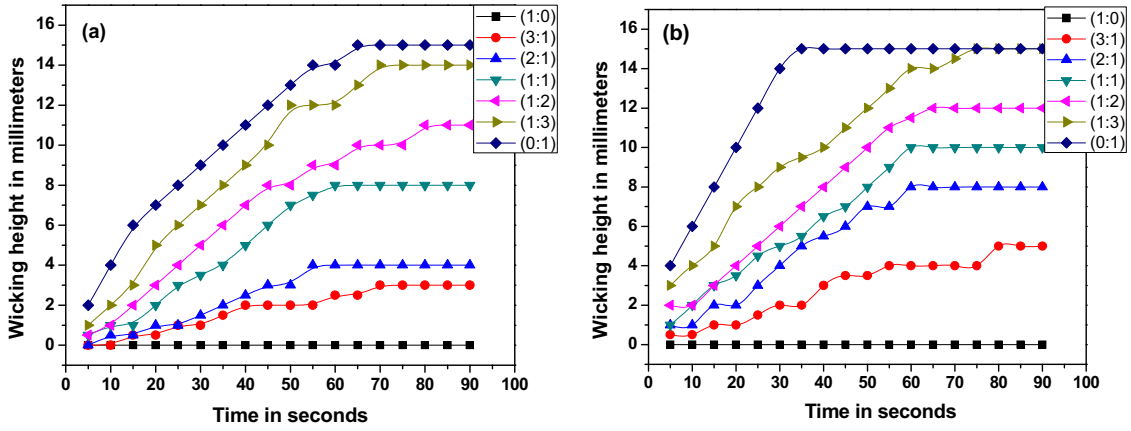

Fig. 1. Effect of deacetylation on wicking behavior of nanofiber webs.

PCL chains producing free volume within the fiber blend (Ali et al., 2014; Rosa, Guedes, Casarin, & Bragança, 2005).

Furthermore, neat cellulose acetate attained highest front height of 15 mm in 85 s. Fig. 1b depicts the wicking pattern of all samples subsequent to deacetylation. According to results neat PCL and neat CA still found at minimum and maximum wicking borderlines. Neat CA yet again reached the maximum front height of 15 mm, but after deacetylation CA attained it in 35 s which is almost half of time took before accetylation. Except neat PCL perceptible enhancement in wicking potential of all samples in relatively less time frames, is evident. This may be attributed to the replacement of acetyl groups of CA with hydrophilic OH groups (Liu & Hsieh, 2002; Son, Youk, Lee, & Park, 2004; Vallejos, Peresin, & Rojas, 2012). Provided increasing proportion of CA in nanofibers co-electrospun webs improved the wicking potential at higher rate due to supplementary OH groups available to absorb liquid and increased porosity attained after deacetylation (Callegari et al., 2011). Fig. 1a demonstrates that increasing CA nanofibers in blends increased the wicking height. Except neat PCL nanofibers, all blends showed enhanced wicking rate after deacetylation, the contributing factor is mainly due to the cellulose content in the blends PCL/CEL (Fig. 1b). The PCL/CEL (1:3) showed highest and relatively faster among the blends. However, the neat PCL showed no change after being deacetylation, as the given concentration of NaOH has no effect on PCL.

3.2. Effect of deacetylation on chemical structure of nanofibers

The ATR-FTIR spectra of electrospun webs in the range of 4000–800 cm^{-1} are demonstrated in Fig. 2a and b. The neat PCL in Fig. 2a showed the characteristic peaks at 1726 cm^{-1} (carbonyl stretching), 1240 cm^{-1} (asymmetric COC stretching), 1190 cm^{-1} (OC—O stretching), 1170 cm^{-1} (symmetric COC stretching), 1294 cm^{-1} (C—O and C—C stretching in crystalline phase) and 1157 cm^{-1} (C—O and C—C stretching in amorphous phase). The two peaks appeared at 2945 and 2866 cm^{-1} correspond to asymmetric CH_2 stretching and symmetric CH_2 stretching, respectively. The characteristic peaks of CA attributed to the acetate group at 1744 cm^{-1} (CO), 1375 cm^{-1} (C—CH3), 1236 cm^{-1} (C—O—C) and 1047 cm^{-1} disappeared and on the contrary, a peak at around 3385 cm^{-1} (O—H) increased significantly after deacetylation (Fig. 2b); this shows a complete conversion of CA into cellulose nanofibers.

The PCL/CEL nanofibers showed characteristic absorption peaks of cellulose structure at around 1000–1200 cm^{-1} (Fig. 2b). Other characteristic bands related to the chemical structure of cellulose were the hydrogen bonded OH stretching at 3550–3100 cm^{-1}, the

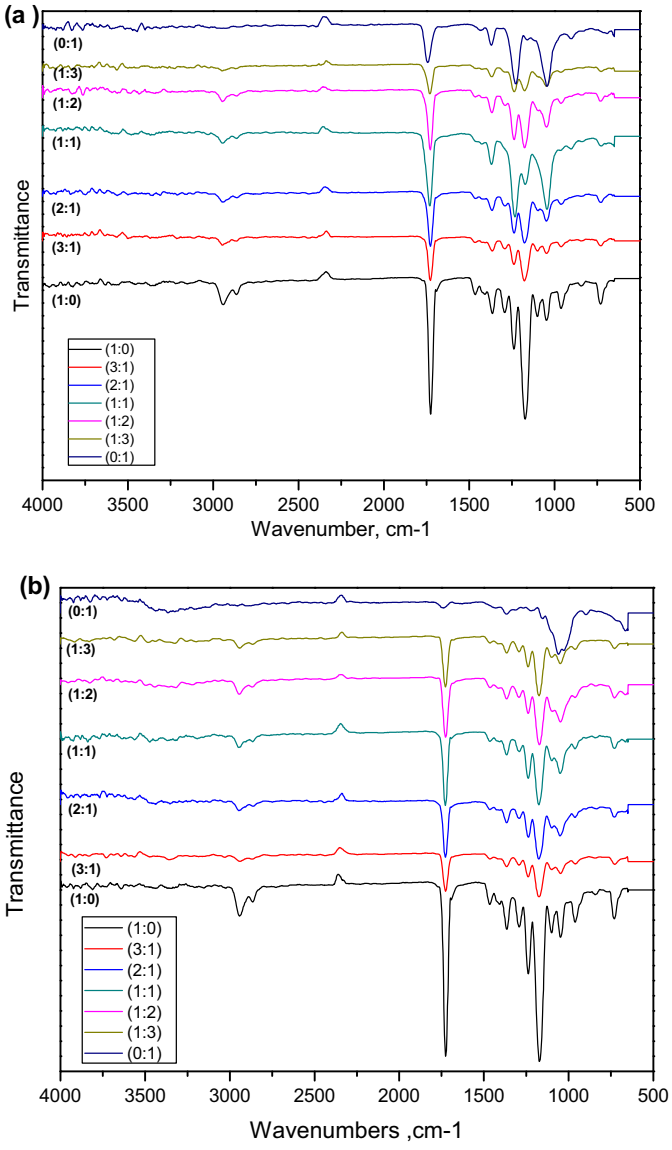

Fig. 2. Effect of deacetylation on chemical structure nanofibers.

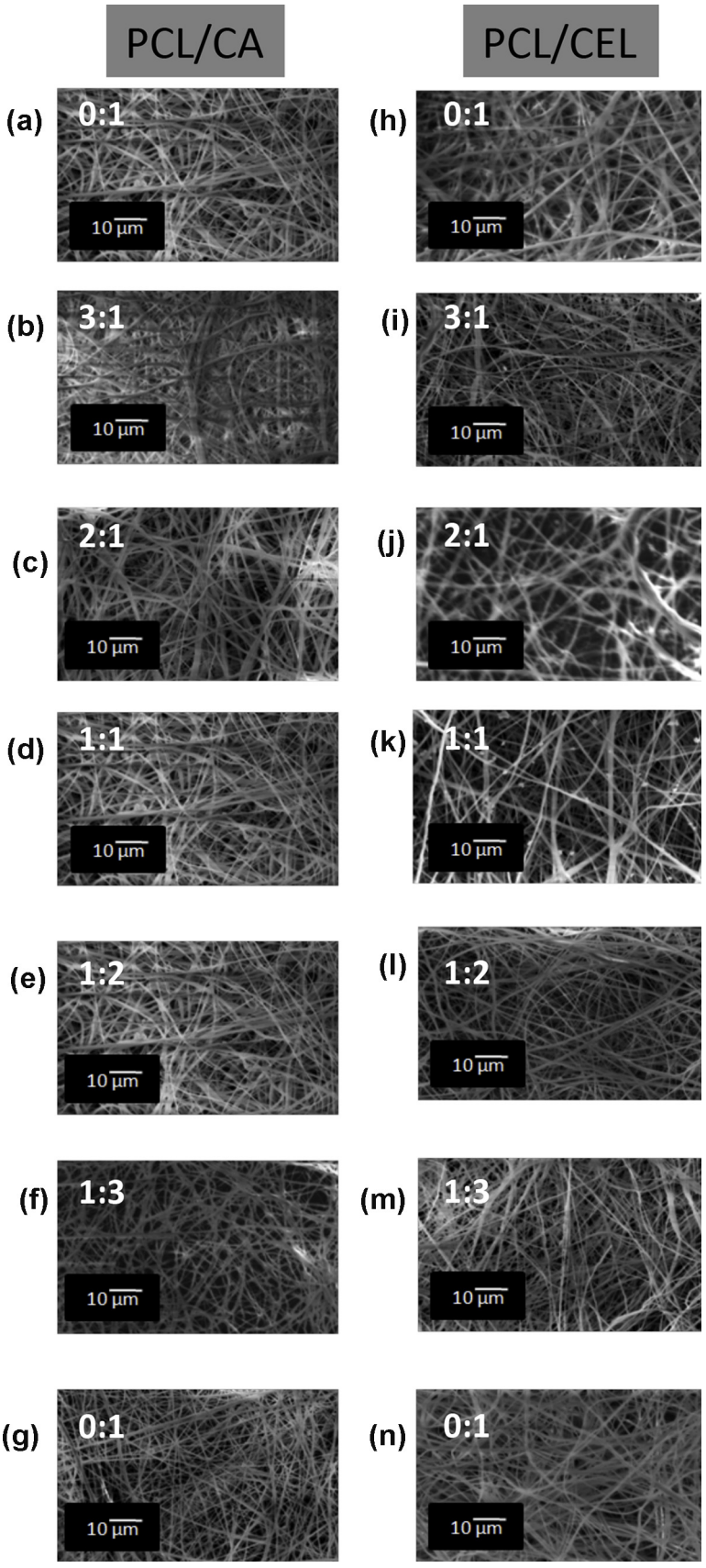

Fig. 3. SEM images of ((a)–(g)) PCL/CA before deacetylation and ((h)–(n)) PCL/CEL after deacetylation.

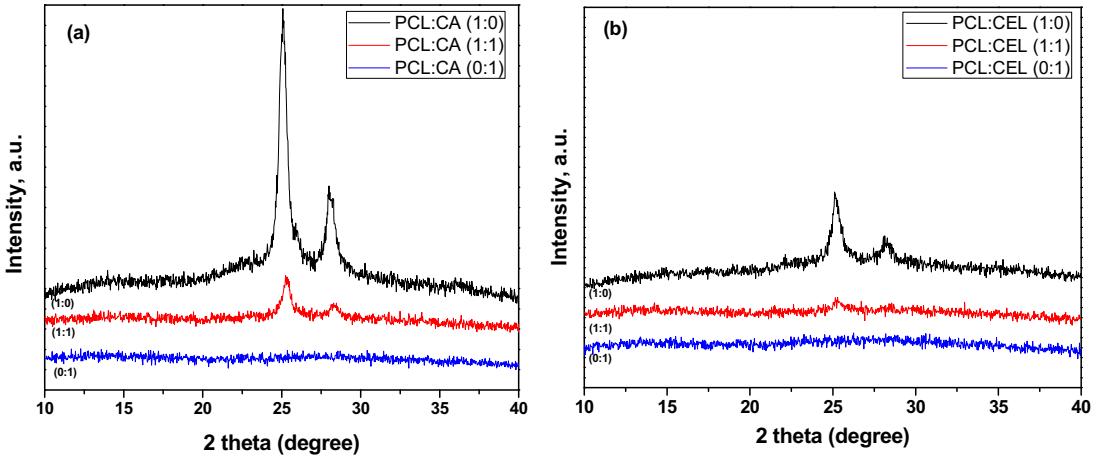

Fig. 4. XRD patterns of (a) PCL/CA before deacetylation and (b) PCL/CEL after deacetylation.

CH stretching at 2917 cm^{-1}, and the CH wagging at 1316 cm^{-1} (Khatri et al., 2013c). It is worth noting that the characteristic peak of PCL at 1726 cm^{-1} (carbonyl group) remained unaffected after deacetylation that shows deacetylation has no negative effect on PCL chemical structure.

3.3. Morphology of PCL/CEL nanofibers

The SEM images in Fig. 3a–g for PCL/CA and Fig. 3h–m for PCL/CEL were studied in terms of the effect of deacetylation on the nanofibers morphologies. The diameter for PCL nanofiber obtained in the range 700–850 nm, whereas for CA obtained in the range 300–550 nm (Fig. 3a and g). It was observed that increasing PCL ratio in the PCL/CA showed a dominancy of coarse nanofibers; this was mainly due to the larger diameter of PCL the CA (Fig. 3b–f). Irrespective to the blend ratio, the morphology of nanofibers was uniform and bead free. It was observed that the surface morphology after deacetylation changed slightly particularly for neat CA and blends of dominant CA in the blend shown in Fig. 3l and m. Moreover, the CA nanofibers after being converted into cellulose Fig. 3n demonstrated random orientation of nanofibers. SEM study revealed that the PCL nanofibers add mechanical stability to the nanofiber blend webs. The nanofibers thickness for pure PCL and overall, the thickness of nanofibers webs was reduced around 15% after deacetylation due to shrinkage.

3.4. Crystallinity of nanofibers

X-ray diffraction patterns of PCL/CA and PCL/CELL nanofibers blends have been shown in Fig. 4a and b. The neat PCL nanofibers showed two main peaks at Bragg angles $2\theta = 25.1^\circ$ and 28.2°, which were attributed to the diffraction of the (1 1 0) lattice plane and the (2 0 0) lattice plane of semi-crystalline PCL, respectively. On the contrary, XRD pattern of neat CA nanofibers did not exhibit a crystalline nature. Besides, substantial peaks at $2\theta = 25.1^\circ$ and 28.2° were observed in the PCL/CEL nanofibers blends by increasing PCL ratio in the blends. These peaks corresponded to the diffraction of PCL crystals. Comparing to the treated PCL, the peak intensities were significantly reduced for PCL/CEL, (1:1) blend suggesting a possible decrease in the crystallinity of the blend. (Ali et al., 2014).

4. Conclusion

PCL/CEL nanofiber blends were successfully co-electrospun. The morphology of each blend webs under SEM showed uniform and bead free nanofibers. FTIR confirmed that the precursor CA was completely converted into CEL nanofibers. Wicking behavior for five different ratios of PCL/CEL suggested that increasing CEL ratio in the blend enhance the wicking front height, PCL/CEL 1:3 blend ratio shows better wicking behavior than other blends. However, XRD patterns revealed that the crystallinity of the resultant nanofibers decreased with increasing CEL ratio. The resultant nanofibers may be used, where higher wicking with necessary strength is required such as biofilters and biosensor strips.

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