

Cross-linked poly(methyl vinyl ether-co-maleic acid)/poly(ethylene glycol)/nanocellulosics foams via directional freezing

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Abstract

Aligned micro- and nanoporous materials have gained tremendous interest since they provide great potential in organic electronics, absorbents, biomedicine and tissue engineering. Herein, cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) cross-linked with poly(methyl vinyl ether-co-maleic acid) (PMVEMA) and poly(ethylene glycol) (PEG) foams were prepared by both the directional and un-directional freezing technique. Aligned three-dimensional porous structures were observed for the directional frozen foams after lyophilization via scanning electron microscope (SEM). As a result, these highly organized structures exhibited enhanced mechanical performance properties. Particularly, for the 25% CNF foams, the compression modulus increased 60% compared with the un-directional frozen samples. These nanocellulosics-based foams could absorb up to 10-fold water of their initial weight with excellent water stability when immersed in water for more than 48 h. Overall, this study describes a novel process combining cross-linking and directional freezing which successfully fabricates naturally derived foams with anisotropic structure.

Keywords: Cellulose nanofibrils, Cellulose nanocrystals, Cross-linking, Directional freezing, Foams

1. Introduction

Highly porous biopolymer-based materials with competitive mechanical performance and physicochemical properties, such as excellent strength-to-weight ratio and good thermal properties, are of interest in both academic and industrial fields. These porous materials with aligned micro- and nanostructures have a significant effect on their applications which have shown broad prospects in tissue engineering, drug delivery, molecular filtration, building industry, green packing and so on (Herrera, Mathew, & Oksman, 2017; Lavoine & Bergström, 2017; Svagan, Samir, & Berglund, 2008; H. Zhang et al., 2005). Various methods have been investigated to fabricate aligned porous materials, including electrostatic repulsion, strain or compress-induced reorientation, and self-assembly (Kong et al., 2018). Of the many techniques, directional freezing followed by sublimation has been shown to be a versatile, promising and straightforward technique to yield engineered porous structures (Z. Xu et al., 2014).

Directional freezing is based on freezing a liquid suspension along a controlled orientation, followed by the sublimation of the solidified ice crystals (Gorauskis, Graves, Moreno, & Nieto, 2017). During the directional freezing process, ice crystals start regularly growing parallel to the freezing direction, the suspended particles are ejected from the solidification crystals front, concentrated, and finally entrapped between the growing ice crystals, which leads to an aligned and highly porous structure after sublimation under reduced pressure (Dash, Li, & Ragauskas, 2012). This process yields a replica of the solidified solvent which has been used to create a variety of porous structures.

Nanocellulosics, including cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs), can be extracted and derived from large number of sources, including higher plants, marine animals, algae and fungi (Klemm et al., 2011). Various properties such as high aspect ratio, strong mechanical properties, low density, renewability, biodegradability, and general biocompatibility of nanocellulosics render them a desirable reinforcing material, especially in biopolymer community (Feldman, 2015; X. Yang & Cranston, 2014).

However, the hydrophilic nature of nanocellulosics due to the abundant hydroxyl groups limits some of their practical applications in high humidity or aqueous environments (W. Yang et al., 2017). Therefore, covalent or non-covalent cross-linking methods are being developed as an effective method to enhance its water stability (Jiang & Hsieh, 2017; Leppiniemi et al., 2017). Jiang and Hsieh demonstrated a cross-linked water stable CNFs/methylene diphenyl diisocyanate (MDI) aerogels with the water adsorption value of 5.3 mL/g (Jiang & Hsieh, 2017). Moreover, Song et al. also reported that cross-linked polyvinyl alcohol (PVA)/CNCs composite film can maintain its original shape after soaking in water for 48 h, and its water adsorption value is 175.7% of initial weight (Song, Yu, Gu, Ye, & Zhou, 2018).

Cross-linked poly(methyl vinyl ether-co-maleic acid) (PMVEMA)/poly(ethylene glycol) (PEG) hydrogels have been used in controlled drug-delivery systems and cell culture matrix (Raj Singh, Woolfson, & Donnelly, 2010; T. Zhang, Chen, Zhang, Dou, & Gu, 2013). Recently, the combination of PMVEMA, PEG and cellulosic materials has also gained noteworthy interests. Goetz et al. reported cross-linked PMVEMA/PEG/CNCs films exhibiting high water absorbencies, which demonstrated that nanocellulosics cross-linked with a water-soluble biopolymer matrix PMVEMA/PEG led to the development of a well-dispersed nanocomposite with stability in aqueous medium (Goetz, Mathew, Oksman, Gatenholm, & Ragauskas, 2009). In the current work, CNCs and CNFs were cross-linked with the PMVEMA/PEG system. The resulting cross-linked nanocellulosics-based materials were converted into aligned porous foams via the directional freezing technique followed by sublimation. The mechanical properties, water stability, and water absorbency of achieved foams were also investigated.

2. Materials and methods

2.1 Materials

Poly(methyl vinyl ether-alt-maleic acid) (PMVEMA) with Mw of ~216,000 was purchased from Sigma-Aldrich (St. Louis, MO, USA). Polyethylene glycol 4000 (PEG) was obtained from Alfa Aesar (Haverhill, MA, USA). The University of Maine kindly

provided cellulose nanocrystals (CNCs), and cellulose nanofibrils (CNFs) was purchased from American Process Inc. (Atlanta, GA, USA).

2.2 Preparation of nanocomposite foams

The procedure of preparing the PMVEMA/PEG/nanocellulosics foams was accomplished with a modification to a literature procedure (Goetz et al., 2009). In brief, PMVEMA (3.35 g) and PEG (0.50 g) were dissolved in D.I. water (34.65 ml) at 68 °C for 1 h. The mixture was added to an aqueous slurry of nanocellulosics (CNCs or CNFs at 25%, 50%, and 75%, w/w) and stirred for 4 h at room temperature (RT). The final solid content of the obtained suspension was set at 10 wt%. During the solidification process, 5.00 ml of such mixture was transferred into glass vials and frozen by two methods: (1) directional freezing with only the bottom of the vial was in contact with liquid nitrogen for 5 min, and vertical heat transfer was prevented by insulation of the vial using polystyrene foam; (2) un-directional freezing by plunging the vials into liquid nitrogen for 5 min. Frozen samples were placed in a freeze-drier for 24 h under vacuum. After freeze-drying, the samples were further cured at 90 °C for 8 h and then stored in a desiccator before physical testing. The resulting samples are described according to the percent nanocellulosics in each sample (as shown in Table 1).

Table 1. Prepared material combinations

Sample coding	Ratio of nanocellulosics : PMVEMA/PEG	Preparation methods
CNC 25%	1:3	Directional freezing
CNC 50%	1:1	Directional freezing
CNC 75%	3:1	Directional freezing
CNC 25% Un-DF	1:3	Un-directional freezing
CNC 50% Un-DF	1:1	Un-directional freezing
CNC 75% Un-DF	3:1	Un-directional freezing
CNF 25%	1:3	Directional freezing
CNF 50%	1:1	Directional freezing
CNF 75%	3:1	Directional freezing

CNF 25% Un-DF	1:3	Un-directional freezing
CNF 50% Un-DF	1:1	Un-directional freezing
CNF 75% Un-DF	3:1	Un-directional freezing

2.3 Characterization

Fourier transform infrared spectroscopy (FT-IR) was used to analyze the chemical group transformation of the nanocellulosics composites by recording the spectra at a resolution of 4 cm^{-1} with a PerkinElmer Spectrum 100 FT-IR spectrometer (Waltham, MA, USA) over the range of $4000 - 800\text{ cm}^{-1}$ at the accumulation of 64 scans. Before the FT-IR measurement, one set of the samples was treated with 0.1 M NaOH in order to remove the influence of the unreacted carboxylic acid groups. A second set of the samples was not treated with 0.1 M NaOH and set as control groups.

^{13}C CP/MAS solid-state nuclear magnetic resonance (NMR) measurements were conducted at ambient air relative humidity/temperature using a Bruker Advance III 400-MHz spectroscopy (Germany) with a Bruker double-resonance MAS probe head. The samples were packed into 4-mm cylindrical Zirconia MAS rotors and operated at a frequency of 100.59 MHz at spinning speed of 10 kHz with 5000 scans. Before NMR analysis, the cross-linked PMVEMA/PEG/nanocellulosics foams were Soxhlet extracted with D.I. water for 24 h to remove unreacted cross-linkers and then air-dried.

The morphology structure of the inner surface parallel to the cylinder axis were studied by scanning electron microscope (SEM Zeiss EVO MA15, Germany) at an accelerating voltage of 20 kV with backscattered electron detector. Prior to SEM analysis, samples were cut to small piece parallel to the cylinder axis and placed on aluminum mounts, then sputter coated with gold for 20 s.

2.4 Water adsorption

The foam samples were first stored in a $90\text{ }^{\circ}\text{C}$ oven for 24 h to remove trace moisture and then weighed (noted as initial weight, M_i). After this, the samples were immersed in deionized water at room temperature for 24 h, then gently blotted with tissue paper to remove excess water on the surface of the foams and weighed again (noted as saturated weight, M_f). The following equation calculated the water adsorption:

$$\text{Water adsorption (\%)} = \frac{M_f - M_i}{M_i} * 100\%.$$

2.5 Mechanical properties

Compression properties were determined by an INSTRON 5567 universal test machine (Canton, MA, USA) with a load cell of 500 kN. The compression rate of cross-head was set to 0.10 mm/s. Before the measurement, the cylindrical samples were cut to ca. 18 mm in height and ca. 18 mm in diameter and stored at RT in a desiccator at 2% relative humidity (RH) for 48 h before testing. The compression modulus was calculated from the slope of the initial linear region (strain <10%) of the stress-strain curves.

3. Results and discussion

3.1 Cross-linking

The cross-linking of CNCs and CNFs with PMVEMA and PEG was previously reported to occur through an esterification reaction, as summarized in Fig. 1 (Goetz et al., 2009). The available carboxylic acid groups on the PMVEMA were cross-linked with the hydroxyl group on the nanocellulosics surface or the terminal hydroxyl groups of PEG to establish the ester linkages. The formation of ester cross-linkages was confirmed by FT-IR and NMR characterizations. The peaks observed at 1720 cm^{-1} in FT-IR spectrum and the peaks observed at 176.32 ppm in NMR spectrum of PMVEMA/PEG/nanocellulosics samples both confirmed the establishment of ester cross-linkages between PMVEMA and nanocellulosics/PEG (Fig. S1 and S2), which were previously reported by Goetz et al. (Goetz, Foston, Mathew, Oksman, & Ragauskas, 2010; Goetz et al., 2009).

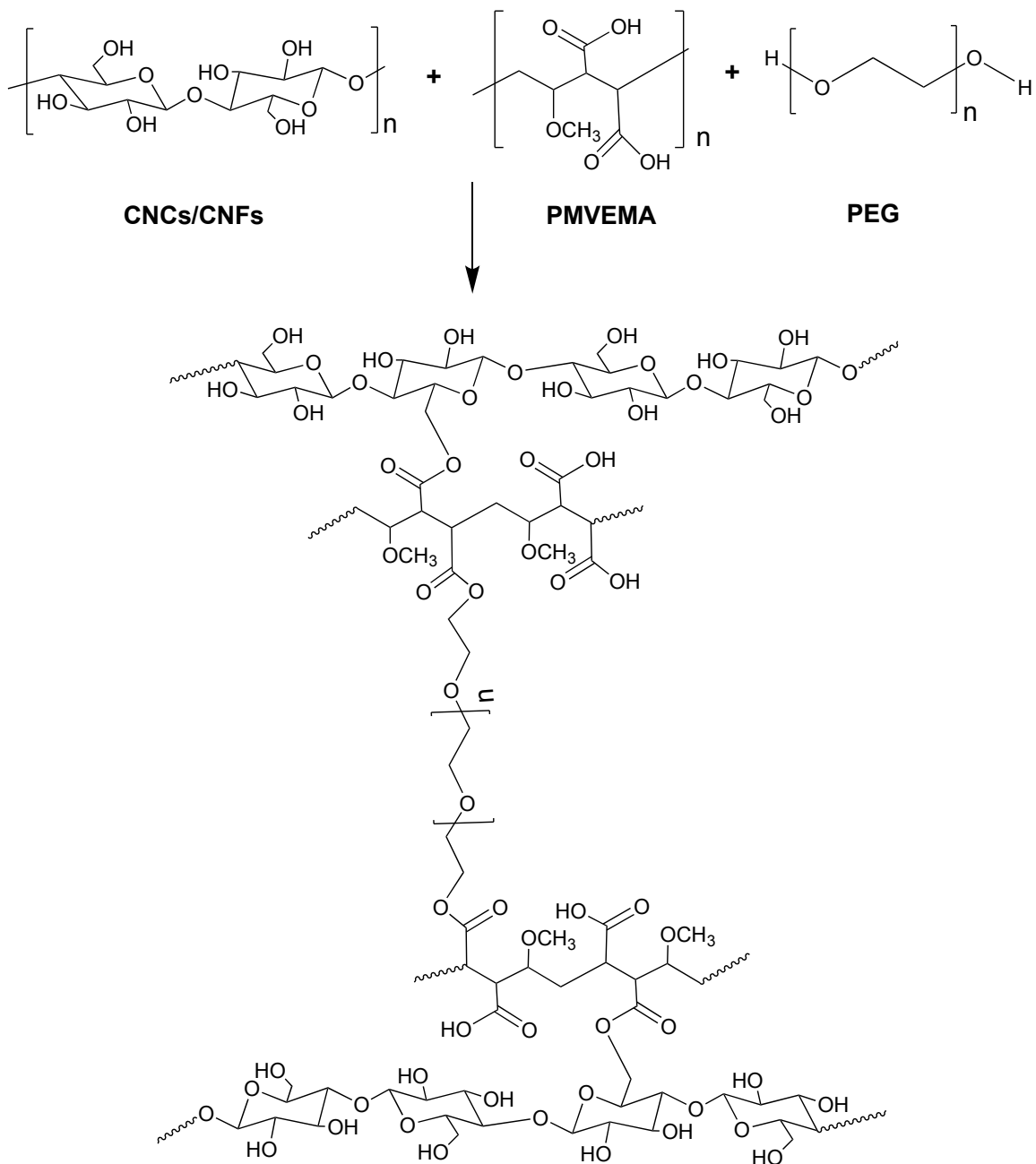


Fig. 1. Nanocellulosics, PMVEMA, and PEG cross-linking mechanism.

3.2 Surface morphology

In this study, we employed two different solidification methods, directional freezing and un-directional freezing, to fabricate the cross-linked porous foams. Surface morphologies of directional and un-directional freezing samples are shown in Fig. 2.

During the directional freezing process, the samples were accomplished by only having the bottom of the aqueous suspension vials in contact with the liquid nitrogen and resulted the imposed thermal gradient along the freezing direction (Zhou et al., 2013). Therefore, the achieved directional freezing samples have a visible, organized lamellar structure (Fig. 2a and 2b). As for the un-directional freezing process, the samples were plunged into the liquid nitrogen. There was no temperature gradient during the solution freezing and ice-crystals nucleated in any direction, resulting in a random structure after ice sublimation (Fig. 2c and 2d).

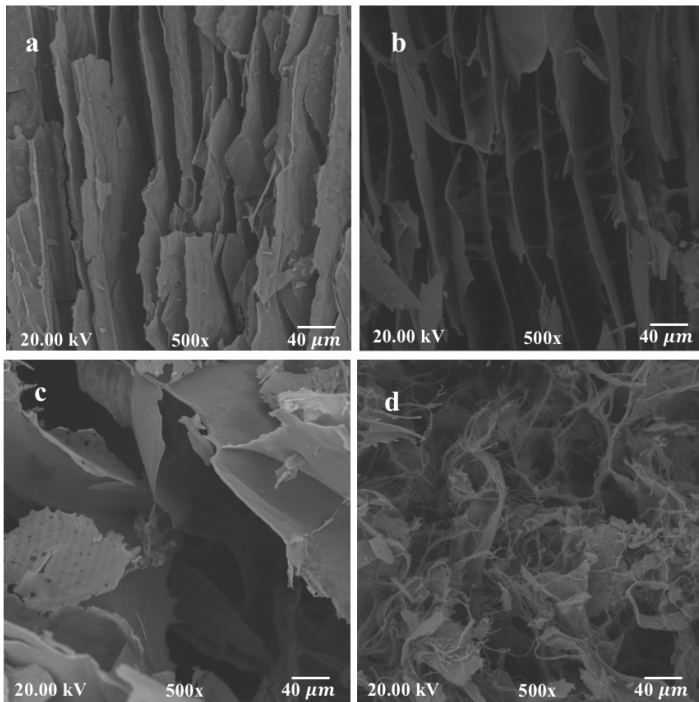


Fig. 2. SEM images of cross-linked PMVEMA/PEG/nanocellulosics foams side view of: (a) CNC 25% foam, (b) CNF 25% foam, (c) CNC 25% Un-DF foam, (d) CNF 25% Un-DF foam.

3.3 Water adsorption

It is well known that pure nanocellulosics foams are not stable in water and show strong swelling behavior (Shimizu, Saito, & Isogai, 2016). The covalent ester linkages between carboxyl groups on PMEVEMA and hydroxyl groups on nanocellulosics or PEG can overcome this instability in water or moist environments. The cross-linking reaction

yields a networked gel and allows the cross-linked foams to retain their original shape (Fig. 3) (Goetz et al., 2009; W. Yang et al., 2017). The water adsorption values of these foams after 24 h immersion were around 8-10 folds of initial weight (Fig. 3a). Compared with previous studies reported by Jiang and Hsieh and Song et al., these cross-linked foams exhibited better water adsorption capacity (Jiang & Hsieh, 2017; Song et al., 2018). The cross-linked foams were saturated with water and reached the equilibrium state after being immersed in water for 2 h (Fig. S5). After 24 h immersion in water, cross-linked foams did not show any noticeable changes in volume or shape (Fig. 4). The original aligned structure of directional frozen foams still can be observed through SEM (Fig S4). After 24 h adsorption, the water adsorption values were almost same for directional freezing and unidirectional freezing samples (Fig. 3b). For example, the water adsorption of CNC 50% and CNC 50% Un-DF is 9.94 and 9.91 folds of initial weight, respectively, which indicated that the aligned structure did not influence the water uptake ability. However, the CNC 75% foams absorbed a higher amount of water (10.05 fold of initial weight) compared to both CNC 25% foams (8.64 fold of initial weight) and CNC 50% foams (9.64 fold of initial weight). Similarly, more water was absorbed by CNF 75% foams (9.50 fold of initial weight) compared to both CNF 25% (8.52 fold of initial weight) and CNF 50% (9.21 fold of initial weight). The water uptake amount increased with increasing nanocellulosics content which could be attributed to the decrease in cross-linkages between PMVEMA and nanocellulosics/PEG (Nair, Zhu, Deng, & Ragauskas, 2014). This result indicated that the cross-linkages within the PMVEMA/PEG/nanocellulosics foams protected the pre-existing interfibrillar hydrogen bonding from the disrupting and dissolving action, which limited the water uptake ability (Caulfield, 1994; Yang et al., 2017). Additionally, the relevant mean aspect ratios were approximately 17.2 for CNCs and 43.2 for CNFs based on measurements from TEM and SEM images (Fig. S3). The larger aspect ratio of CNFs might result in more cross-linkages and limit water adsorption value. Therefore, the water adsorption ability of CNCs samples were slightly higher than CNFs samples (e.g., 9.94 folds of CNC 50% foam compared with 9.21 folds of CNF 50% foam).

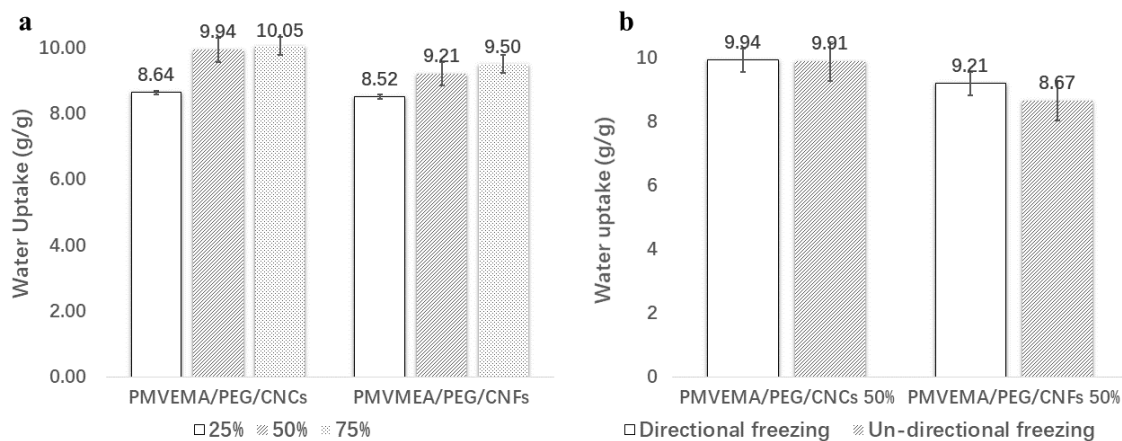


Fig. 3. Water adsorption ability after 24 h (a) nanocelluloses composites with different nanocelluloses concentration made by directional freezing, (b) nanocelluloses composites made by different methods

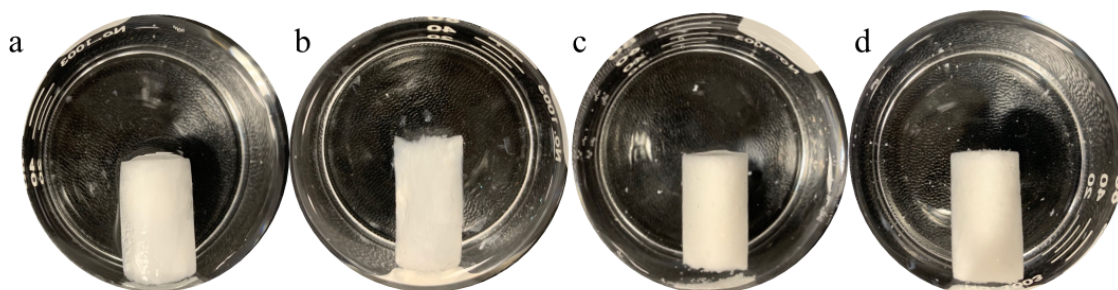


Fig. 4. Water stability of (a) CNC 75% foam, (b) CNC 75% Un-DF foam, (c) CNF 75% foam, (d) CNF 75% Un-DF after 24 h.

3.4 Compression properties

The mechanical properties were studied in order to evaluate the effect of morphological structures on the mechanical performance of the foams (Table 2). It was found that all directional freezing samples showed improved compression performance compared to un-directional freezing samples. The directional freezing of CNF 25%, CNF

50%, and CNF 75% foams exhibited higher compression modulus of 2.76, 2.14, and 1.55 MPa, respectively, that of the un-directional freezing CNF 25%, CNF 50%, and CNF 75% foams (1.73, 1.65, and 1.00 MPa, respectively). The compression stress (at 50% strain) of directional freezing CNFs samples was also slightly increased compared with un-directional freezing ones. Similar results were also observed on the CNCs foams. The better compression performance of directional freezing samples can be attributed to the strong anisotropy porous structure along the compression loading direction (Koehnke, Lin, Elder, Theliander, & Ragauskas, 2012). Also, comparing with the CNCs foams, the CNFs foams at the same preparation condition showed even better mechanical performance presumably due to the different aspect ratio of CNCs and CNFs. Because of the larger aspect ratio and entanglement of CNFs, more hydrogen bonds can be formed during the water removal process and larger friction forces appeared between the entangled network, which assisted in load transfers of fiber-matrix and fiber-fiber (Sun et al., 2018; Xu et al., 2013).

Moreover, it was found that the mechanical performance increased with decreasing nanocellulosics content which could be seen in Table 2. For example, take the CNCs samples, the maximum modulus, and stress of CNC 25% were 0.47 and 0.15 MPa compared to 0.37 MPa modulus and 0.12 MPa stress of CNC 75%. This effect could be explained by that more cross-linkages formed as cross-linking agent content increased which also was verified in water uptake results, and yielded a foam with enhanced mechanical properties. The results are consistent with previous literature reported by Jiang and Hsieh that methylene diphenyl diisocyanate (MDI) cross-linked CNFs aerogels are strengthened by increasing MDI cross-linking (Jiang & Hsieh, 2017).

Table 2 Compressive test data of different PMVEMA/PEG/nanocellulosics data at 2% RH.

Samples	Modulus (MPa)	Stress at 50% Strain (MPa)
CNC 25%	0.47 ± 0.08	0.15 ± 0.02
CNC 50%	0.43 ± 0.02	0.13 ± 0.03
CNC 75%	0.37 ± 0.02	0.12 ± 0.01
CNC 25% Un-DF	0.44 ± 0.01	0.13 ± 0.06
CNC 50% Un-DF	0.36 ± 0.04	0.11 ± 0.02

CNC 75% Un-DF	0.34 ± 0.03	0.10 ± 0.01
CNF 25%	2.76 ± 0.13	0.86 ± 0.09
CNF 50%	2.14 ± 0.32	0.76 ± 0.08
CNF 75%	1.55 ± 0.11	0.69 ± 0.02
CNF 25% Un-DF	1.73 ± 0.05	0.82 ± 0.02
CNF 50% Un-DF	1.65 ± 0.09	0.74 ± 0.07
CNF 75% Un-DF	1.00 ± 0.05	0.71 ± 0.01

4. Conclusion

In conclusion, our results demonstrated a simple approach to fabricate highly aligned lamellar porous nanocellulosics-based foams by cross-linking nanocellulosics with PMVEMA/PEG matrix via directional freezing technique. Water adsorption studies verified these cross-linked foams were water stable and had high water adsorption capacity. In addition, reinforced mechanical performance was also achieved on highly ordered nanocellulosics-based foams. As a result, these nanocellulosics-based foams have shown the possibility to be used in medical or packaging applications.

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