Compression Properties of Polyvinyl Alcohol – Bacterial Cellulose Nanocomposite

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Abstract: Despite the established use of total joint replacement for the treatment of advanced degeneration of articular cartilage, component loosening due to wear and osteolysis limits the lifespan of these joint prostheses. In the present study, nanocomposites consisting of poly(vinyl alcohol) (PVA) and bacterial cellulose (BC) nanofibers were investigated as possible improved cartilage replacement materials. Nanocomposites were synthesized by adding small amounts (<1%) of BC to PVA, and subjecting the mixture to thermal cycling. The mechanical properties of the resulting material were evaluated using unconfined compression testing. By the addition of BC nanofibers to the PVA matrix, a nanocomposite with a wide range of compressive mechanical properties control was obtained, with elastic modulus values similar to those reported for native articular cartilage. The nanocomposite also showed improved strain-rate dependence and adequate viscoelastic properties. The PVA–BC nanocomposite is therefore a promising biomaterial to be considered as a possible replacement material for localized articular cartilage injuries and other orthopedic applications such as intervertebral discs. © 2009 Wiley Periodicals, Inc. J Biomed Mater Res Part B: Appl Biomater 90B: 922–929, 2009

Keywords: hydrogel; polyvinyl alcohol; bacterial cellulose; nanocomposite; unconfined compressive properties; soft tissue; articular cartilage

INTRODUCTION

An aging population increasingly suffers from osteoarthritis and other bone and joint disorders. The two most common forms, osteoarthritis and rheumatoid arthritis, lead to changes in the composition and the eventual degeneration of articular cartilage, resulting in impaired joint motion, pain, and disability.[1,2] Current arthritis therapies focus on pain minimization and preservation of joint functions, with the clinical treatments being microfracture, debridement, drilling, chondrocyte, and osteochondral transplantation (autograft or allograft). Even though these treatments show reasonable short-term success, there are still issues with difference in cartilage properties, defect size limitations, donor site morbidity, and matching host site curvature.[2–4] In worst cases, total joint replacement is required. One of the issues associated with current prosthetic devices for this application is the use of ultra-high molecular weight polyethylene (UHMWPE) inserts as the articular cartilage component. Although it has high strength and a relatively low coefficient of friction, UHMWPE is a poor match for many of the mechanical properties of articular cartilage, including viscoelasticity, stiffness, anisotropy, and strain-rate dependence. Therefore, shock absorption, lubrication, and deformation are lacking in current artificial joints, resulting in increased wear of the UHMWPE.[5,6] The release of these bioactive wear particles from the UHMWPE components into the joint compartment leads to osteolysis. The resulting component loosening and failure limits the lifespan of current prostheses, which has serious impact on the patient's quality of life, and increases the economic burden of the disease.[6] An artificial material that more closely matches the mechanical and frictional properties, as well as matching the topography and curvature of articular cartilage at the implantation site is expected to improve both the function and the lifespan of the treated joint.[2]

Articular cartilage is a composite material with a unique composition and structural organization. It consists of ~75% collagen fibrils and 20–25% proteoglycans (dry weight). The solid matrix is saturated with about 65–85% water.[1,2,7] Among the functions are bearing load during joint loading, transmitting mechanical force from one bone

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TABLE I. PVA–BC Solutions Composition

Solution No.	PVA (wt %)	BC (wt %)
1	10	0
2	10	0.30
3	10	0.85

to another, and contributing to joint lubrication. Articular cartilage displays non-linear response, viscoelasticity, anisotropy, and strain-rate dependent properties.[1,2,4,7] The time-dependent viscoelastic behavior of cartilage results from interstitial fluid inflow and expulsion from the cartilage matrix. Strain-rate dependence is also an important function that enables continuous joint function throughout the wide range of loads and movements experienced during walking, running, and other strenuous physical activity. It is also one of the features that has proven most difficult to replicate in artificial cartilage materials.[1,4] Values of compressive modulus of human articular cartilage range from 2 to 10 MPa shortly after loading, with values of around 0.6 MPa at equilibrium.[1]

Poly(vinyl alcohol) (PVA) is a biocompatible hydrogel with many biomedical applications. PVA can be physically crosslinked by a low temperature thermal cycling process.[8,9] PVA has been shown to display non-linear mechanical properties, both in tension and compression, as well as viscoelastic behavior, which are important design factors for cartilage applications.[4–6,10,11] PVA has been shown to have limited strain-rate dependence under unconfined compression.[4] Some studies have also found that PVA has better wear resistance, and friction coefficient than UHMWPE.[6,12] It has also been shown that PVA can be processed to possess anisotropic mechanical properties, matching the mechanical response of selective cardiovascular tissues.[13]

Bacterial cellulose (BC) fibers with an average diameter of 50 nm and high mechanical strength are produced by the bacterium *Acetobacter xylinum* using a fermentation process. BC is a nanomaterial, which has many characteristics that make it valuable for biomedical applications.[14–16] A PVA–BC nanocomposite was previously developed and found to have tensile mechanical properties similar to those of other composite soft tissues, including aorta and heart valve.[17]

Composite materials have recently been considered to better replicate the structure-function of the natural tissues, given the fact that natural tissues such as cartilage are also composite in nature.[18] We hypothesize that a composite biomaterial, using PVA hydrogel as the matrix and BC as the reinforcing nanofiber will simulate the proteoglycan and collagen structure of natural cartilage. For this purpose, the mechanical behavior of PVA–BC nanocomposite was investigated under unconfined compression for possible development of a synthetic biomaterial for cartilage replacement and other orthopedic applications.

MATERIALS AND METHODS

PVA–BC Solution Preparation

PVA (Sigma-Aldrich Canada) with a molecular weight (M_w) of 146,000–186,000, 99+% hydrolyzed, was used in all solution preparations. A suspension of 0.97 wt % BC in distilled water was produced in shake flasks in our laboratory by fermentation using the bacteria *Acetobacter xylinum*, as described by Guhados et al.[15] PVA was added to distilled water or to the homogenized BC suspension with additional distilled water to obtain the solutions shown in Table I. These mixtures were prepared using a procedure similar to that previously reported.[17,19]

Samples Preparation

Both the PVA control and PVA–BC solutions were transferred into three aluminum molds (for each composition), with a 6 mm gasket. The molds were placed in the heated/refrigerated circulator where they were cycled between 20°C and −20°C at a rate of 0.1°C/min, holding the samples for 1 h at −20°C. At the end of thermal cycles 1, 3, and 6, a sample mold was removed.[17,19] All samples were cut cylindrically using an 11 mm diameter custom designed punch for compression testing ($n = 5$). Figure 1 shows the cross-sectional structure of PVA and PVA–BC nanocomposites by scanning electron microscopy (SEM).

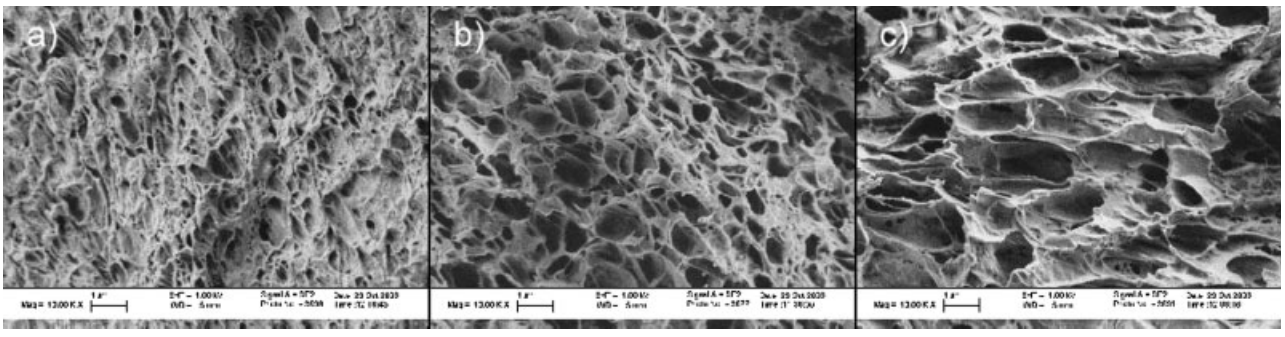

Figure 1. SEM of critical point dried (a) 10% PVA, (b) 10% PVA with 0.3% BC, and (c) 10% PVA with 0.85% BC. 1 μm scale bar.

Unconfined Compression Testing

Although natural articular cartilage experiences loading in compression, tension, and shear, the present study is limited to the most important of these, compression. All experiments were carried out within the elastic region of the PVA–BC nanocomposites.

The testing equipment consists of a servo-hydraulic material testing system (MTS Bionix 858) equipped with a 5 Kg load cell. Sample thickness was measured using a Mitutoyo thickness tester, and testing was carried out inside a Plexiglas tank filled with distilled water at 37°C. All the specimens were placed within two non porous stainless steel plates (~6 mm grip-to-grip distance). Unconfined compression tests were performed at 1%/s, 10%/s, and 100%/s strain rates, which has been reported to cover the range of physiological strain rates for cartilage.[20] The samples were strained up to a maximum of 45% strain, reported to be within the elastic region for PVA samples.[4] All strains were referenced to the initial sample thickness. A 30 min sample recovery time between consecutive strain-rate measurements was also implemented. Before the compression tests, all specimens were preconditioned with 10 loading and unloading cycles, from 0 to 25% strain, and allowed to fully recover (30 min).

Stress Relaxation Testing

After preconditioning and compression testing, some samples ($n = 3$) were strained to the same 45% strain used for compression testing and held at constant strain for 1 h, while monitoring the load.

DATA ANALYSIS

Compression Tests

The data obtained was in the form of load-extension, which was then converted into engineering stress-engineering strain, using the sample cross-sectional area and the initial gauge length after preconditioning. The stress–strain data for both PVA and PVA–BC nanocomposites displays an exponential non-linear shape. The stress–strain of the PVA control samples was fitted by Eq. (1)[17]:

$$\sigma = y_o + A\exp(B\varepsilon) \quad (1)$$

where σ is stress, ε is strain, and y_o, A, and B are curve fitting parameters. For the PVA–BC nanocomposites, the stress–strain data has a higher gradient, and was fitted better by Eq. (2)[17]:

$$\sigma = y_o + A\exp(B\varepsilon) + C\exp(D\varepsilon) \quad (2)$$

where y_o, A, B, C, and D are curve fitting parameters. The elastic modulus as a function of strain was calculated as the first derivative with respect to strain of either Eq. (1) or (2).

Stress Relaxation

The time dependent properties of all samples were assessed by stress relaxation testing. Load-time data was converted to relative stress remaining-time, relative to the initial stress after compressing the sample ($t = 0$). The stress relaxation data was fitted to Eq. (3), as described previously[13,17,19]:

$$\sigma(t)/\sigma_o = \sigma_R/\sigma_o + A\exp(-Bt) + C\exp(-Dt) \quad (3)$$

where $\sigma(t)$ is the stress at time t, σ_o is the initial stress, σ_R is the final stress ($t = 3600$ s), t is time, and A, B, C, and D are curve fitting parameters.

Statistical Analysis

For statistical comparisons, a one-way Analysis of Variance (ANOVA) was performed, which is consistent with the statistical analysis performed previously.[13,17,19,21]

RESULTS

To facilitate the presentation of the data in all the Figures, the following convention is adopted. PVA is denoted as (P) and bacterial cellulose as (BC) when describing the concentration of the nanocomposites. The actual concentration of every component is given after the letter representing that component on a weight percentage basis.

PVA and PVA–BC Nanocomposites Compression

Figure 2 shows the stress–strain curves for the 10% PVA with 0.3% BC nanocomposites, respectively. The curves shown were tested at the highest strain rate (100%/sec). The expected stiffening effect as the number of cycles increases (1 through 6) is observed, as well as the typical non-linear stress–strain response previously observed under tensile testing.[17] A statistically significant difference of stress at a strain of 45% ($p < 0.05$) was observed among

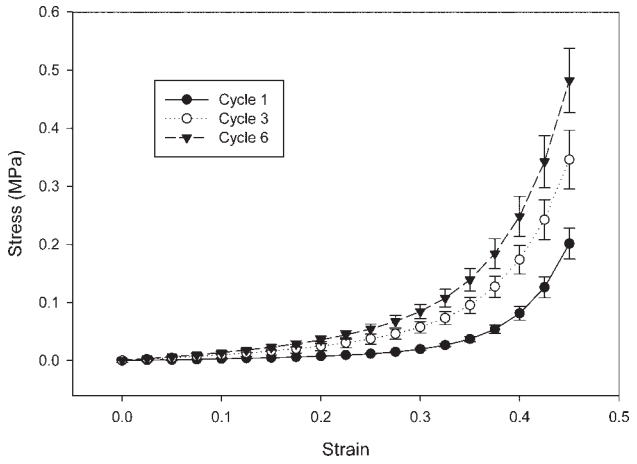

Figure 2. Stress–strain curves for 10% PVA with 0.3% BC for cycles 1, 3, and 6. Strain rate of 100%/s.

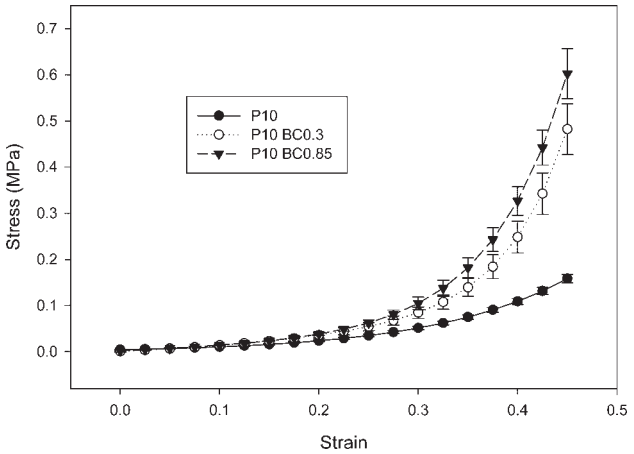

Figure 3. Comparison of compressive properties for all PVA–BC nanocomposites (cycle 6). Strain rate of 100%/s.

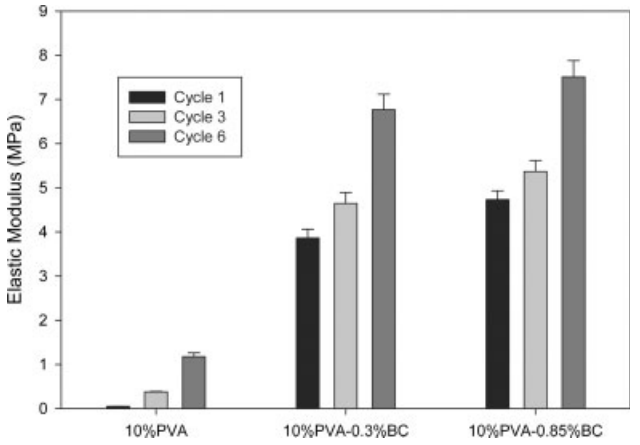

Figure 4. Effect of BC on elastic modulus of the PVA–BC nanocomposite for all compositions and number of thermal cycles (45% strain and 100%/s strain rate).

the three cycles. A similar trend was also observed for the 10% PVA reference and the nanocomposite with a higher BC concentration (0.85%). As expected, the stiffness of the BC containing nanocomposite is higher than PVA and increases with increasing BC concentration.[17]

The effect of BC concentration (0, 0.3, and 0.85%) on 10% PVA (cycle 6) can be seen in Figure 3. A similar effect is seen for all the other cycles. As expected, increasing the concentration of BC by small amounts (<1%) results in a significant increase in the compressive properties of the nanocomposite, although the increase in stiffness from 0.3 to 0.85% BC is not as large as compared with that going from 0 to 0.3% BC. In Figure 3, a statistically significant difference ($p < 0.05$) of stress at 45% strain among all three samples was observed.

The effect of BC on compression properties of PVA is demonstrated by a plot of the elastic modulus for all compositions and number of thermal cycles (45% strain and 100%/s strain rate), as seen in Figure 4. A statistically significant difference ($p < 0.05$) of elastic moduli at 45% strain among all thermal cycles within a given composition and among the different PVA–BC concentrations within a given thermal cycle was observed.

Effect of Strain Rate on PVA and PVA–BC Nanocomposites

Figure 5(a,b) show the stress–strain curves of 10% PVA at 1, 10, and 100%/s strain rates for both the cycle 1 and cycle 6, respectively. The cycle 1 sample did not show a significant difference ($p > 0.05$) among the three strain rates. This was the same case for the cycle 3 samples (not shown). On the other hand, cycle 6 samples (at 45% strain) show a significant difference ($p < 0.05$) among all the strain rates.

Figure 6(a,b) shows the stress–strain curves of 10% PVA with 0.3% BC at 1, 10, and 100%/s strain rates for both the cycle 1 and cycle 6, respectively. In this case,

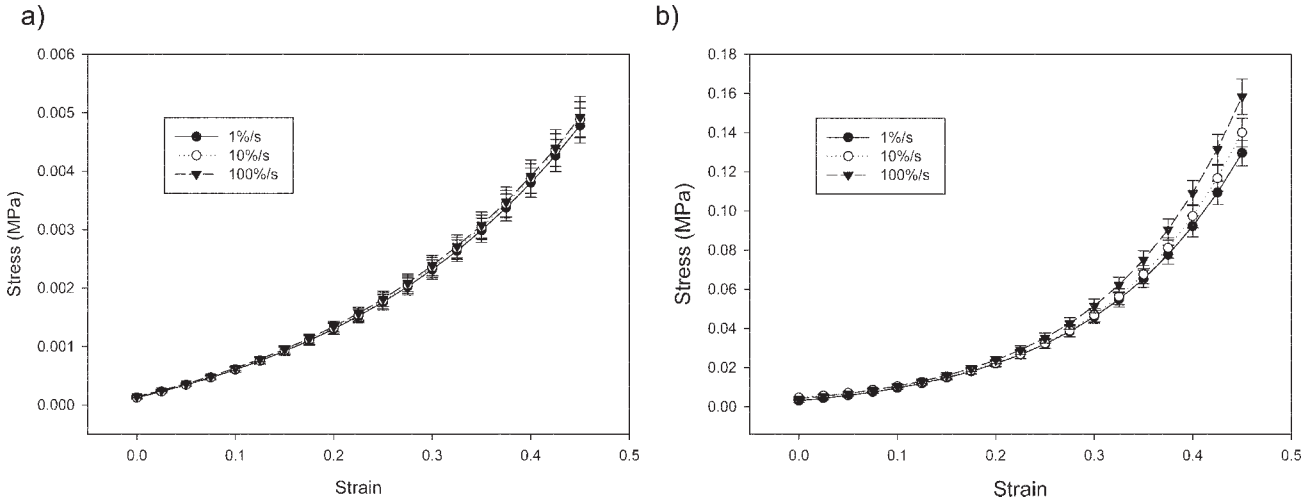

Figure 5. Effect of strain rate on the stress–strain of 10% PVA reference for (a) cycle 1 and (b) cycle 6.

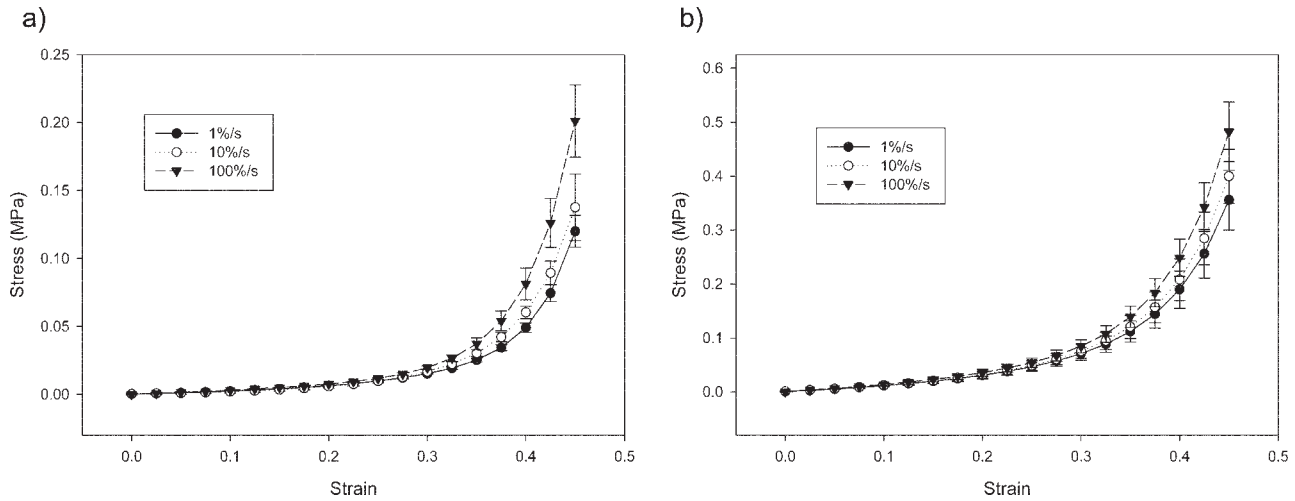

Figure 6. Effect of strain rate on the stress–strain of 10% PVA with 0.3% BC for (a) cycle 1 and (b) cycle 6.

even the cycle 1 sample show strain rate dependence between the strain rates tested. Cycle 3 sample (not shown) also showed this same effect, as opposed to the 10% PVA reference, where no strain rate dependence was observed in either cycle 1 and 3. When ANOVA was applied to the stress at 45% strain for cycle 1 [Figure 6(a)], a statistically significant difference ($p < 0.05$) between the 1%/s and the 100%/s strain rates was observed. Similarly, significant differences ($p < 0.05$) were found between the 10%/s and 100%/s responses. However, no statistically significant differences were observed between the 1%/s and 10%/s strain rates, although a similar trend was observed. Statistical analysis of the results for cycle 6 yielded the same statistical differences [Figure 6(b)]. Similar results were observed for the stress–strain curves of 10% PVA with 0.85% BC at 1, 10, and 100%/s strain rates (for all cycles), which was the stiffest composition tested (data not shown). As before, all cycles clearly showed strain rate dependence, as opposed to the 10% PVA reference.

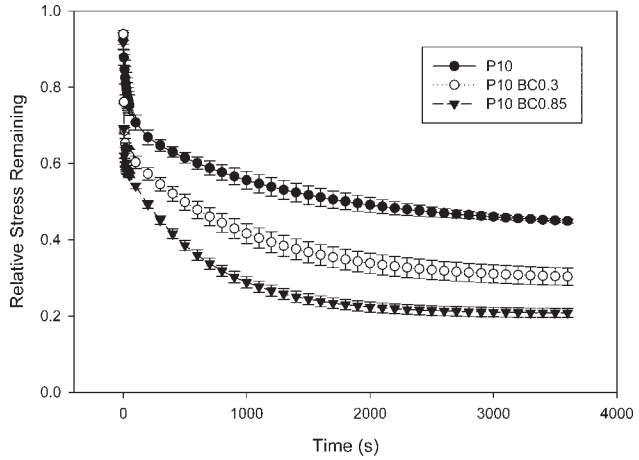

Figure 7. Stress relaxation response for the 10% PVA with BC concentrations ranging from 0 to 0.85% (cycle 6).

Stress Relaxation Properties of PVA and PVA–BC Nanocomposites

The time-dependent stress relaxation response for all PVA–BC nanocomposites was measured and compared to the PVA reference. Figure 7 shows the stress relaxation response for the 10% PVA with BC concentrations ranging from 0 to 0.85% (cycle 6). Similar results were obtained for cycles 1 and 3 as well. As seen, the relative stress remaining after 1 h holding time did not completely level off, a trend also reported for a PVA hydrogel, where the sample was held for 24 h.[4] Also, the relative stress remaining decreases as the concentration of BC is increased from 0 to 0.85%. A similar trend was observed for samples tested under tensile conditions.[17] After applying ANOVA to the relative stress remaining after 1 h for all compositions (Figure 7), a statistically significant difference ($p < 0.05$) among all samples was observed.

DISCUSSION

A clear trend seen in medical device research is the importance of having a good match of the mechanical properties between the implanted device material and the tissue being replaced.[2,6,18,22] In orthopedic applications, where prosthetic joint replacement is required, the current standard cartilage replacement material is UHMWPE. The problems with UHMWPE are its high stiffness, lack of viscoelasticity, absence of strain rate dependence, and hydrophobicity, as opposed to natural articular cartilage. Thus the lack of appropriate shock absorption and lubrication in UHMWPE inserts result in wear particles that lead to osteolysis and eventually failure of the implants.[2,5,6]

We have previously shown the application of the PVA–BC nanocomposites for other soft tissue replacement devices. Initially, we were able to closely match the mechanical behavior of selective cardiovascular tissues.[17] In another

study, a PVA hydrogel not only displays the exponential response of cardiovascular tissue, but also displays anisotropic behavior of aorta up to 65% strain was reported.[13,21] Our latest work shows that by adding a small amount of BC to the PVA matrix, an anisotropic PVA–BC nanocomposite of increased stiffness and degree of anisotropy can be prepared.[19] These studies characterize the PVA and PVA–BC nanocomposites under tension, at a constant strain rate. The work presented here describes the mechanical properties of the PVA–BC nanocomposite system under unconfined compression.

Figure 2 shows the compressive properties of the 10% PVA with 0.3% BC (3 cycles) nanocomposite. As seen, the PVA and the PVA–BC nanocomposites display the typical non-linear stress–strain response, with an increase in stiffness as the number of cycles increased from 1 to 6. Several studies have reported this exponential response but for higher PVA concentrations without BC.[4,5,23] Figure 3 is a comparison of the effect of adding small amounts of BC to PVA. The mechanical strength in compression is clearly increased in the PVA–BC nanocomposites as well as showing a more exponential stress–strain response than for PVA alone. This trend is comparable with that reported for articular cartilage.[24] Figure 4 demonstrates the effect of BC on the elastic modulus of the nanocomposite at 45% strain and a strain rate of 100%/s. By adding 0.85% BC, the elastic modulus increases from 1.18 ± 0.08 MPa to 7.51 ± 0.37 MPa (cycle 6). Also, the stiffness of the PVA–BC nanocomposites is higher when tested under compression than values previously reported under tension.[17,19] The increase in stiffness for PVA–BC samples by increasing BC content from 0.3 to 0.85% is not as large relative to that of the addition of 0.3% BC to the PVA reference. In our previous study under tension, a similar effect was observed.[17]

Figure 5(a,b) shows the effect of strain rate (1, 10, and 100%/s) on compressive properties of 10% PVA reference as a function of thermal cycles. As shown, only the cycle 6 sample showed a statistical difference among the strain rates. A previous study using high concentration PVA hydrogels also showed weak strain-rate dependence.[4] These results indicate that although PVA does have some of the desired characteristics of an articular cartilage replacement material, it lacks sufficient strain-rate sensitivity. The effect of the addition of BC to PVA on the resulting nanocomposites is shown in Figure 6(a,b) for 0.3% BC (cycles 1 and 6, respectively). A larger strain-rate dependence as compared to PVA can be clearly seen, at all thermal cycles. A similar trend was also seen at a higher BC concentration of 0.85%. Thus the PVA–BC possesses both improved mechanical strength and increased strain-rate dependence.

The mechanical behavior observed can be understood in terms of the nanocomposite structure. The structure of the matrix biomaterial (PVA) has been investigated by several groups. In thermal crosslinking, when the liquid PVA gel freezes, ice crystals grow and push the polymer chains towards high concentration regions, where crystallites are formed by hydrogen bonding and van der Waals forces. When the material is thawed, ice crystals melt in the polymer-poor regions while the crystallites are concentrated within a polymer-rich mesh. Subsequent thermal cycles will increase the size of the initial crystallites while forming new secondary ones as well.[8,21,25–27] Ricciardi et al.[25] has clearly shown an increase in the degree of crystallinity of the PVA as a function of thermal cycling, but this increase reaches a plateau beyond seven thermal cycles. The polymer-rich regions contain crystallites of around 3 nm with spacing in between crystallites of 17–19 nm. The polymer-poor regions, where the ice crystals are mainly formed, are >100 nm with dimensions that might reach the μm range.[21,25–27] The reinforcing biomaterial (BC) is a highly crystalline, hydrophilic nanofiber with high mechanical strength and it is expected to have a strong interfacial interaction with the PVA matrix, due to the large number of hydrogen bonding sites.[14,15,17,19,28] Moreover, the crystalline regions of the BC fiber can serve as nucleation sites for the PVA chains. Further cycling increases the degree of crystallinity around the BC fibers, as well as other newly formed crystallites elsewhere in the matrix, leading to a significant increase in stiffness as observed.[17,19]

Other PVA based hybrids or composites for orthopedic applications have been reported in the literature. PVA/Hydroxyapatite (HA) composites have been investigated towards forming a bioactive artificial cartilage, with good thermal stability and homogeneity, and proposed that the HA crystallites also served as nucleating agents to improve PVA crystallization.[22,29] Joshi et al.[30] studied the compressive properties of a PVA-polyvinyl pyrrolidone (PVP) composite for intervertebral disc (IVD) applications. They reported improved mechanical properties, with no change in either stiffness or polymer content after fatigue testing (10 million cycles). Grant et al.[31] recently reported a PVA hydrogel with an adsorbed layer of hyaluronic acid and fibronectin towards the adhesion of chondrocytes on the hydrogel surface, for a tissue engineered cartilage replacement. El Fray et al.[32] also reported the effect of several crosslinking agents, namely succinic and gluconic acids, on the compressive properties and microstructure of PVA. Finally, the use of polyethylene glycol (PEG) to induce physical crosslinking of PVA was investigated, as well as giving stability to the pores after annealing, reporting an increase in both creep resistance and equilibrium water content of the PEG-treated PVA hydrogels versus the PVA hydrogels annealed without PEG.[33,34] All these composite systems did not report strain-rate dependent properties as part of their investigations.

Since most soft tissues are viscoelastic in nature, the time dependent properties of the materials in question are very important design parameters. Stress relaxation provides information on the ability of the material to relax under an applied stress. The stress relaxation of a high concentration PVA (20–25%) under compression has been reported.[4] Our group has reported stress relaxation of PVA

TABLE II. Important Properties and Parameters of Articular Cartilage and Related Materials

	Articular Cartilage	PVA (10%)	PVA (20–25%)	PVA–BC	UHMWPE
Elastic modulus (MPa)	0.4–10[1]	0.004–1.17	1.1–18.4[4]	0.024–7.51	1400[5]
Water content (%)	65–85[1]	90	75–80[4]	89.15–89.7	0
Wear resistance	Little wear[1]	Little wear[6]		N/A	Wear debris[12]
Friction coefficient	0.001–0.04[35]	0.028–0.055[12]		N/A	0.08–0.11[36]
Strain rate dependence	Yes[20]	Limited		Yes	No

N/A is not available.

and PVA–BC nanocomposites under tension.[13,17,19] Figure 7 shows the time-dependent characteristics of the PVA and PVA–BC nanocomposite under compression (cycle 6 samples). As noticed, the relative stress remaining after 1 h holding time has not fully levelled off, a trend previously reported by Stammen et al. for PVA,[4] which might require further investigation. On the other hand, the PVA–BC nanocomposites relax at a fast rate and, as the concentration of BC is increased from 0 to 0.85%, to a lower final stress. Thus the degree of viscoelasticity is increased by adding small amounts of BC, which helps to explain the increase in strain-rate dependence of the PVA–BC nanocomposite compared to the PVA reference. As the degree of viscoelasticity of a material increases, it will have more viscous flow as stress is applied, and thus, the strain-rate dependence is incremented. Given the greater time-dependent response of the PVA–BC nanocomposite versus the PVA reference, this novel nanocomposite material should more closely mimic the behavior of natural articular cartilage than PVA alone.

Material properties that are important for articular cartilage replacement applications are detailed in Table II and compared with that of the articular cartilage. The PVA–BC modulus range (0.03–7.51 MPa) is close to that reported by Stammen et al.[4] (1.1–18.4 MPa), but using a much higher PVA concentration (20–25%), which is known to be difficult to handle because of its high viscosity.[11,17] Although the stiffest PVA–BC composite investigated has elastic modulus that was slightly lower than that of articular cartilage, by altering the number of thermal cycles or concentration of either PVA or BC, the range of the modulus could be further increased. Both cartilage and PVA based biomaterials contain a large proportion of fluid, which plays a major role in the tissue mechanics as well as promoting fluid film lubrication and lower wear, which is completely lacking from the UHMWPE material.[6,12] While the PVA–BC nanocomposite exhibited strain-rate dependence, viscoelasticity, and a modulus of elasticity close to that of articular cartilage, there are some features including friction and wear properties, which have not yet been determined. Several reports in the literature have studied the wear resistance of PVA, with mixed results.[6,10,12,23,35,37,38]

In summary, PVA–BC nanocomposites were prepared and tested in unconfined compression. The nanocomposite demonstrated improved mechanical strength, viscoelasticity, and strain-rate dependence as compared to PVA alone. The PVA–BC had an apparent elastic modulus within the range reported for articular cartilage, and showed a broader range of mechanical properties control and improved strain-rate dependence. These are important features in the design of artificial replacement materials for orthopedic applications including articular cartilage and IVDs. However, friction and wear as well as durability tests of the PVA–BC nanocomposite have to be investigated to further assess its capability as a cartilage replacement biomaterial.

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