RESEARCH ARTICLE

Creep behavior of Biodegradable Triple-component Nanocomposites Based on PLA/PCL/bioactive Glass for ACL Interference Screws

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Abstract

Background: Short-time creep behaviorfor aseries of biodegradable nanocomposites, which areused as implantable devices inthe body, is a crucial factor.The present study aimed to investigate the effect of bioactive glass nanoparticles (BGn) on creep and creep-recovery behaviors of polylactic acid/polycaprolactone (PLA/PCL) blends at different given loads and different applied temperatures.

Methods: A series of biodegradable nanocomposites consisted of PLA/PCL blends (comprising 80 parts PLA and 20 parts PCL) with different amounts of modified-BGn (m-BGn) fillers were prepared using the evaporated solvent casting technique. Creep and creep-recovery behaviors of all specimens were studied at different valuable stressesof 3 and 6 MPa and different given temperatures of 25 and 37°C.

Results: In all cases, m-BGn improved the creep resistance of the nanocomposites due to the retardation effect during the creep behaviors of the nanocomposite systems. The obtained results in terms of creep and creep-recovery properties determined that the nanocomposites of PLA/PCL/m-BGn can satisfy the required conditions of an appropriate anterior cruciate ligament reconstruction (ACL-R) screw.

Conclusion: The obtained results confirmed that the BGn plays an impeding role in the movement of PLA/PCL chains leading to in increase the creep resistance. According to the results, it was determined that the nanocomposites of PLA/PCL and m-BGn can satisfy the required circumstances of a proper ACL-R screw.

Level of evidence: I

Keywords: ACL screws, Bioactive glass nanoparticles, Creep, Creep recovery, PLA/PCL blend

Introduction

The anterior cruciate ligament (ACL) is one of the four extremely strong ligaments providing knee stability. It retains tibia from slipping anteriorly in regards to femur (1). The ACL tear mostly occurs in athletes or patients with high level of activity (2).Success of ACL reconstruction (ACL-R) surgery relies on different criteria, including patient selection, graft selection, surgical technique, graft fixation, and postoperative rehabilitation program. The ACL graft fixation is a major factor affecting the mechanical properties of the graft in the immediate postoperative period (3).

There are two major categories of interference screws used for ACL-R, including permanent metal screws, such as stainless steel and titanium, and biodegradable

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screws, which are recently developed. Biodegradable ACL-R screws are among a variety of biomedical devices that the creep resistance is of importance. Mechanical properties of fixation of agraft to the bone tunnel are primary factors in the limitation of rehabilitation.

An ideal ACL graft fixation screw requires not only sufficient initial strength and stiffness to be fixed into the bone tunnel, as well as knee stability, but also it should possess a suitable ductility to avoid brittle fracture during application. Moreover, the biodegradable ACL-R screws need to have sufficient dimensional stability under cyclic loading conditions to avoid creep rupture. Furthermore, creep behavior is a very important feature for functional materials where it has to suffer the load for a long time (i.e., ACL-R screws) (4).

Creep is a slow continuous deformational process occurring in materials under constant load conditions lower than the yielding load of materials for a prolonged period of time (5). On the other hand, creep is a typical viscoelastic-viscoplastic manner in which the strain increases with time. Three typical stages are observed in the loading part, including (i) immediate deformation, as well as (ii) primary and (iii) secondary stages in the creep graph (6). On the other hand, with the unloading section followed by the instantly recovered strain, the creep-recovery trend gradually decreases over time up to a constant value.

As above-mentioned, interference screws should provide optimal graft fixation during ligament rehabilitation that highlights the importance of screw material. In a previous effort by the authors of the present study, biodegradable bipolymeric blends comprising of polylactic acid (PLA) and polycaprolactone (PCL) phase were developed that showed optimum initial mechanical properties, as well as good dimensional stability, in favor of ACL fixation (7).

The drawback of biodegradable ACL screws is the inability to bond with surrounding area of the bone resulting in the lack of bone ingrowth. Moreover, acidic products due to screw degradation may lead to tissue inflammation resulting in foreign body responses. To solve the aforementioned problems, the use of ACL-R screws comprised of bioactive inorganic phases and biodegradable polymers may be an appropriate strategy. A previous study also investigated the mechanical properties of sol-gel derived bioactive glass nanoparticles (BGn)/PLA/PCL systems, including tensile strength, flexural strength, and biological behaviors (8).

Furthermore, the composite materials used in the osteosynthesis process, such as plates and screws, which work within the human body for long enough periods of time, should provide a relatively high creep resistance. In addition, the nature of polymeric materials makes their mechanical properties dependenton time, as well as on the characteristics of the applied load. Influence of filler features, such as size, morphology, volume fraction, and distribution throughout the polymeric matrix, on the creep property improvement of polymeric nanocomposites was frequently investigated according to the literature (9).

Introduction of nanoparticles into polyethylene terephthalate improved the creep resistance of the neat polymeric matrix (10). Perez et al. studied the creep behavior of starch/PCL biodegradable composites reinforced with modified nanoclay (11). In the aforementioned study, it was confirmed that the addition of nanoclay evidently decreases the creep resistance of nanocomposites owing to polymer-clay interaction higher in the case of higher compatibility Presence of compatibilities between ceramic and polymer components resultedin homogeneous distributions that improvethe mechanical properties. In this regard, the systems in the present study, which are PLA/PCL and bioactive glass fillers, have a superior potential for biomedical application.

Since biomedical implants, such as screws, require working within the body for a sufficiently long time, the creep assessment of implants should be performed at circumstances close to the body environment. The present paperaimed to study the effect of modified bioactive glass nanoparticles (m-BGn) as fillers on creep and creep-recovery behaviors of PLA/PCL blends at various given loadsof 3 and 6 MPa, as well as different applied temperaturesof 25 and 37°C (i.e., body temperature). To the best of our knowledge, there has been no report on creep studies for the PLA/PCL and bioglass systems.

Materials and Methods

Composite preparation

Details of PLA/PCL/m-BGn nanocomposites preparation have been described in the present paper (8). Briefly, three different concentrations of 1, 3, and 6 weight percentage (wt%) m-BGn were added to the prepared PLA/PCL bipolymeric solution and stirred up to obtaina homogenized mixture. After homogenization, the mixture was poured into a flat glass plate to obtain a flake dried at 50°C and then in a vacuum oven at 80°C to remove the chloroform medium.

The dried composites were poured into molds with proper dimensions for mechanical analysis, compressed under 30 MPa at 180°C followed by water-cooling to room temperature. It should be noted that the degradation temperature of PLA, PCL, and their blends varies between 300 and 400°C. Therefore, no degradation events occurred during composite manufacturing. Meanwhile, all nanocomposites were pressed under heating for lower than 3 min (12, 13).

Creep and creep-recovery measurements

Creep and creep-recovery experiments were conducted in tension mode in the linear viscoelastic region of neat PLA/PCL blends and its nanocomposites with 1, 3, and 6wt% m-BGn filler phase under ambient conditions. The tests were applied using a dynamic mechanical analyzer (DMA-triton, Tritec 2000 DMA, Triton Technology Co., England). The creep and recovery strainswere determined as a function of time. The applied creep stresses were selected at3 and 6MPa according to the linear region of the stress-strain curves. The applied temperatures were also set at 25 and 37°C. Duration of creep and recovery measurements was also chosen for 20 and 30 min, respectively. The rectangular specimens with the same dimensions of 20 mm × 5 mm × 0.5 mm (i.e., length × width × thickness) were used for each test.

Results

Figure 1 illustrates creep and creep-recovery curves (under loading and unloading conditions) for neat PLA/PCL blends and its nanocomposites with different amounts of BGn at 25°C. For loading mode, the applied stress was determined to be 3 MPa in order to evaluate the creep behavior of all specimens over time from the viscoelastic linear region with respect to the static stress-strain curve (8). Creep behavior of all materials was a typical viscoelastic-viscoplastic manner in which the creep increases with time.

As it can be observed, after applying the load, an instantaneous strain value appeared in all specimens, and the strain rate in all the samples gradually increased over time. It was clear that the creep strain level of nanocomposites was lower than that of the neat bipolymeric blend. However, the creep strain level of nanocomposites did not pursue the reducing monotonous trend as a function of BGn filler content, and more increment at the filler phase up to 6 % wt made the elevation of the creep strain level inversely. A similar manner was also demonstrated at the un-loading part in which the unrecoverable strain of nanocomposites followed the falling trend with the addition of m-BGn phase up to 3% wt. Moreover, further addition of filler content led to an increase in the unrecoverable strain value rather than those containing lower filler contents.

In order to assess the creep behaviors of biodegradable nanocomposites in human body circumstances, the creep and creep-recovery tests were performed at 37°C under 3MPa stress [Figure 2]. As expected, by increasing the applied temperature, all three creep stages, including the immediate deformation, as well as primary and secondary strains, increased for all specimens in comparison to the results obtained at the temperature of 25°C. The results indicated that all nanocomposites possessed the low creep strain level in comparison with neat blends. In addition, the creep strain level (at loading part) as well as unrecoverable strain level (at unloading part), for all specimens decreased based on the amount of m-BGn content.

Figure 3 depicts the creep and creep-recovery manners of neat bipolymeric blends and their reinforced nanocomposites with m-BGn at elevated applied stress (i.e., 6 MPa) and human body temperature (i.e., 37°C). It is obvious thatthe creep strain and unrecoverable strain levels increased in comparison to the results obtained at 3 MPa [Figure 2]. However, in this field, the addition of m-BGnto neat blends helped promote the creep resistance, while the remained strain simultaneously decreased.

For the sake of comparison, the individual manner of each component at different given loads and different applied temperatures is depicted in Figure 4. As pointed out, the values of creep strains and remained strains for each component have a rising trend with increasing the given stress and temperature.

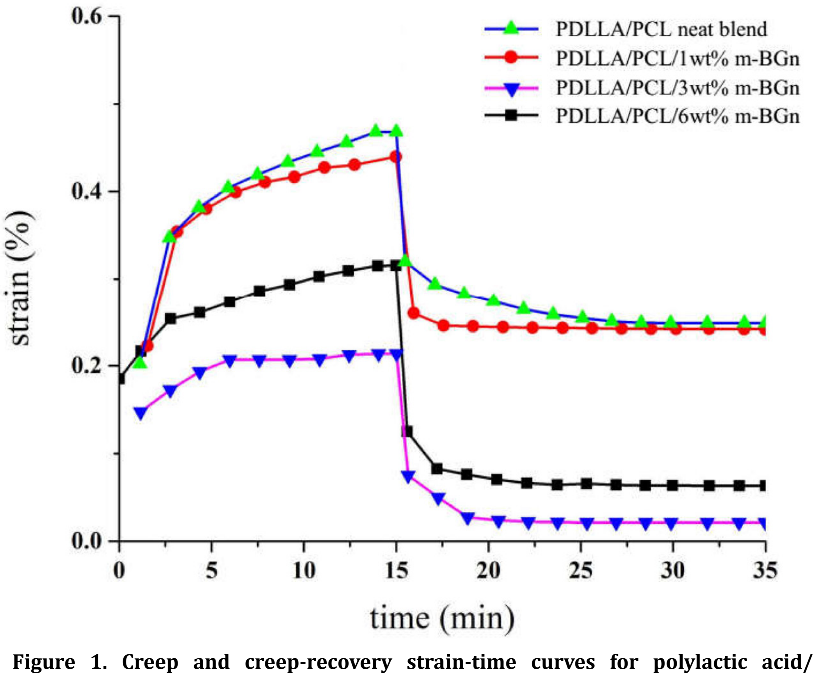

Figure 1. Creep and creep-recovery strain-time curves for polylactic acid/ polycaprolactone blend and its nanocomposites under ambient conditions and 3 MPa stress.

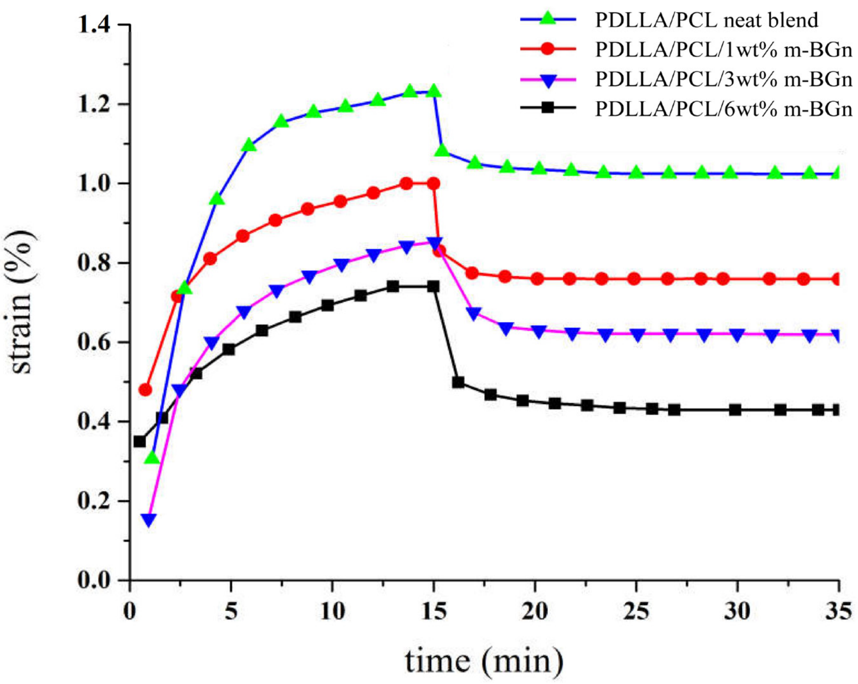

Figure 2. Creep and creep-recovery strain-time curves for polylactic acid/ polycaprolactone blend and its nanocomposites at 37°C and 3 MPa stress.

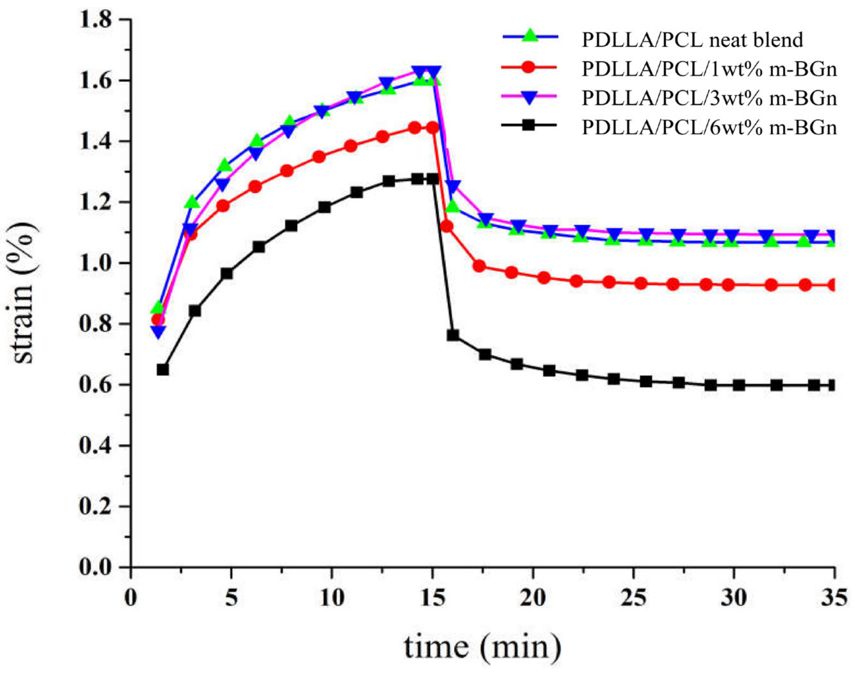

Figure 3. Creep and creep-recovery strain-time curves for polylactic acid/ polycaprolactone blend and its nanocomposites at 37°C and 6 MPa stress.

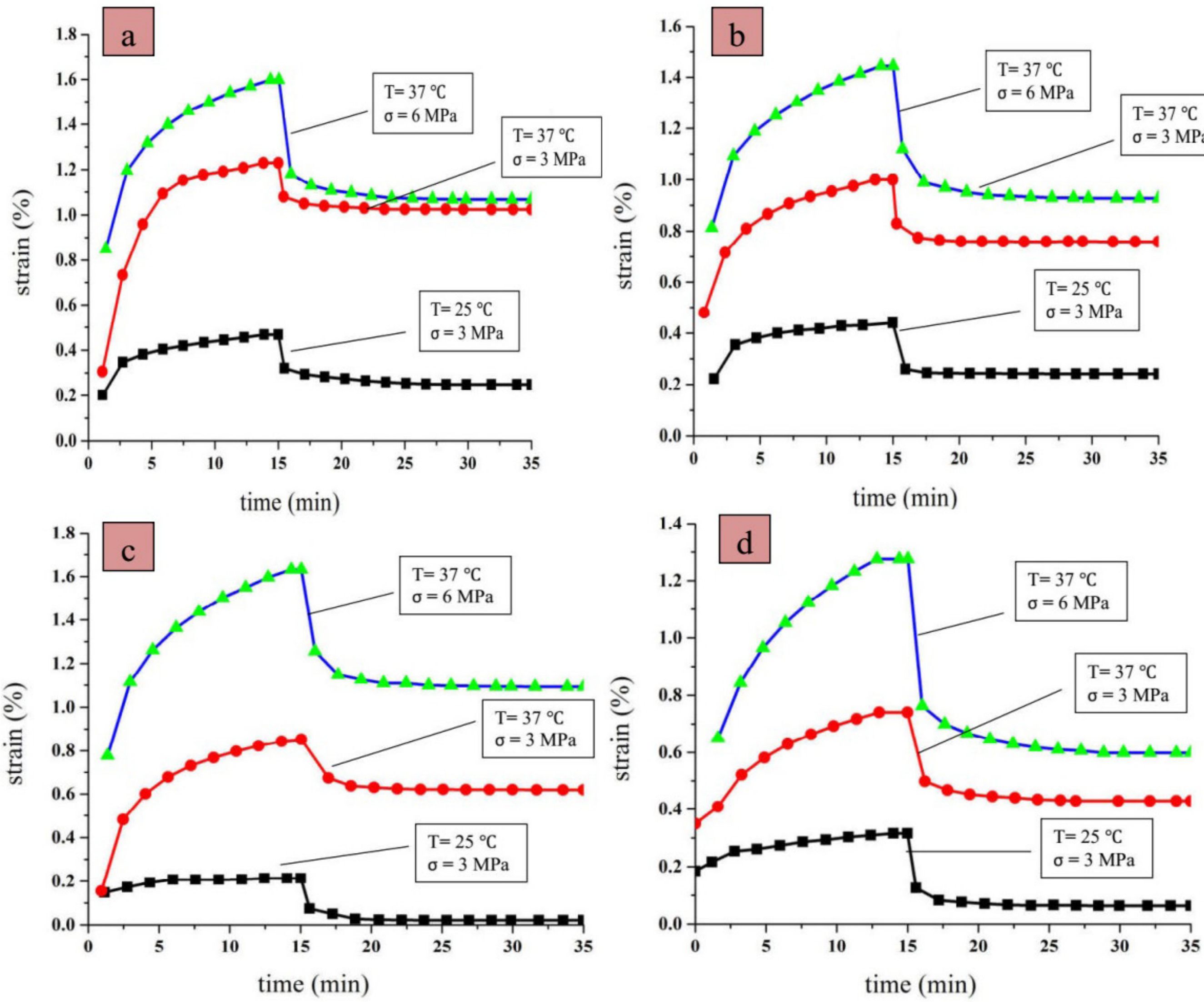

Figure 4. Creep and creep-recovery behaviors of different samples at different given loads and different temperatures; (a) polylactic acid/polycaprolactone neat blend; (b-d) polylactic acid/polycaprolactone nanocomposites with different modified-bioactive glass nanoparticles contents.

Discussion

Aprevious study investigated the morphologies of neat PLA/PCL blends and their nanocomposites contained of 1, 3, and 6 wt% BGn (8). In addition, the effects of m-BGn function on their dispersion qualities were also investigated. It was demonstrated that the functionalizing of BGn could eliminates the contradistinction between hydrophilic BGn and hydrophobic PLA/PCL and induce a good matching with polymeric matrix. However, m-BGn has a good distribution throughout the matrix, but some agglomerates appeared by increasing the amount of them to 6 wt%.

Figure 1 displays that the creep resistance of all blends improves and the unrecoverable strain similarly decreases by the addition of inorganic filler phase. Lower creep strain level of nanocomposites than that of the neat blends indicatesd that the creep of PLA/PCL blend matrix was restrained by the presence of m-BGn. As it was expected, the presence of BGn throughout the matrix polymeric phase improved the dimensional stability due to the higher rigidity of the filler/reinforcement. Creep resistance of nanocomposites can be related to the young modulus of nanocomposites.

As described in a previous study, the introduction of m-BGn into neat polymeric blends can improve the elastic modulus of nanocomposites (8). The functionalizing of the BGn surface can help to homogeneously disperse throughout the matrix, resulting in an increase in the young modulus of the nanocomposites (8). Moreover, the well-dispersed BGn are able to restrain polymer chain segments and hinder the movement of the chain during the creep as a result (14-16). Therefore, the creep of PLA/PCL matrix, especially viscoelastic-viscoplastic manner enhances at the presence of rigid phase.However, the reduced trend of creep strain level is not monotonic with the increase of m-BGn contents.

As the m-BGn contents reached above 3 wt%, the nanocomposites showed a higher creep level and higher unrecoverable strain than those containing lower contents of m-BGn. As above-mentioned, the presence of agglomerates at the further content of m-BGn causes the stress concentration and consequently declines the mechanical properties, such as creep. Similar results have also been reported on the other polymer based nanocomposites. For example, it is reported for the polyurethane (PU)/carbon nanotube (CNT) nanocomposites prepared by in situ polymerization that shows enhanced creep resistance behavior highly depends on the CNT content and dispersion quality (17).

Figure 2 presents the creep and creep recovery of all specimens at the simulated body temperature of 37 °C. At elevated temperature close to glass transition of major part of matrix (i.e., PLA), the movements of polymeric chain segments are superior, especially in the presentcase in which the blends contained PCL component with glass transition temperature about -60°C. In this regard, the creep resistance possesses a linear trend with filler content, as the nanocomposites containing the higher filler content have the desired creep properties.

Figure 3 illustrates the creep and creep-recovery manners of pure bipolymeric blend and its reinforced nanocomposites at elevated applied stress (i.e., 6 MPa) and human body temperature (i.e., 37°C). It is obvious that the creep strain and unrecoverable strain levels increased in comparison to the results obtained at 3 MPa [Figure 2]. However, in this field, the addition of m-BGn to neat blends helped promote the creep resistance, while the remained strain simultaneously decreased.

It is apparent that with increasing the applied stress due to good adhesion between filler content and polymeric matrix at high applied load and temperature, the rigid filler createdmore strain; therefore, the creep resistance decreased in comparison to a lower applied load and temperature, while it is yet suitable for fixation in ACL treatment. This claim is due to the fact that no significant deformity occurred under constant loading for 15 min that may lead to losing the fixation screw into bone.

The obtained results at 3 and 6 MPa applied stresses, as well as 25 and 37°C as given temperatures showed that the increase in creep strain and residual strain levels for PLA/PCL blends containing 3wt% m-BGn with the elevation of the temperature and given load is acceptable; nevertheless, the desired creep behavior was obtained at 3 MPa and 25°C. Similar results were reported in a study that investigated the creep behaviors of composite bioscrews containing polysulfone reinforced by continuous carbon fibers (PUS/CF 1D) and short fibers (PUS/CF MD) [18].

In the above-mentioned study, it was proposed that the PUS/CF 1D system in dry conditions and body temperature for 300 N applied load have 0.367 initial strain, and its strain was 0.04 mm after 15 min. Moreover, these values for PUS/CF MD were 0.8319 and 0.83 mm, respectively. However, the creep results of the present study were reasonably comparative where the initial strain and strain percentage of the present system were 0.35 and 0.7 after 15 min at 3 MPa and body temperature, respectively. It was convinced that the PUS/CF is a promising material as either short-term bioimplants subjected to relatively high stress or long-term bioimplants, which bear relatively low stresses.

This concept is in accordance with Figure 4 where the creep and creep recovery of each component is individually represented. However, by increasing the applied stress and temperature, the creep resistance decreased.As the highest creep resistance belonged to the lowest levels of stress and temperatures, the creep performance of nanocomposites containing BGn as an osteoinductive phase was acceptable for ACL screws.

Overall, the materials with implant capability in the human body shouldbe biocompatible and biodegradable. Biodegradability of PLA and PCL polymers and bioactivity of glass nanoparticles make the studied nanocomposites categorized among these materials. One of the most crucial requirements for the fixation of a soft tissue or bone block graft to the bone tunnel, which is an essential factor for the ligament repairing, is mechanical stability during the rehabilitation.

The obtained results in the terms of creep and creep-recovery properties determined that the nanocomposites of PLA/PCL and BGn can satisfy the required circumstances in terms of dimensional stability forproper ACL-R screws. Although the obtained findings promise the prosperity of these materials, further *in vivo* biomechanical tests and clinical trials are required to present a more precise statement.

The PLA/PCL/BGn triple-component nanocomposites showed an enhanced creep resistance behavior with a decreased creep strain level in comparison to the neat PLA/PCL blends. However, the creep strain level in some condition tests does not reduce monotonously with the increase of BGn contents, which also highly depends on the dispersion quality of BGn. The obtained results confirmed that the BGn plays an impeding role in the movement of PLA/PCL chains in increasing the creep resistance. The findings determined that the nanocomposites of PLA/PCL and BGn can satisfy the required circumstances of proper ACL reconstruction screws.

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