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Modeling of creep and creep recovery behaviors of PDLLA/PCL/bioactive glass nanocomposites as promising ACL reconstruction screws: the effects of bioglass reinforcement phase

Abstract

Background: To study the creep behavior for a series of biodegradable nanocomposites, which are used as implantable devices in the body such as bioscrews, is a crucial factor. In the current paper, we are investigating these biomaterials -short-time creep and creep recover manners- in several classic models.

Methods: The creep and creep recovery behaviors of nanocomposites composed of biodegradable polymer blends, poly (D/L) lactic acid (PDLLA) and polycaprolactone (PCL) reinforced with three different contents of 1, 3 and 6 percent weight percentage bioactive glass nanoparticles (m-BGn) were modeled. Several theoretical models including Findley power law, Burgers and Weibull models were used to establish the relations between m-BGn dispersion and final creep and creep-recovery behaviors of nanocomposites.

Results: The Findley power law model confirmed that the lowest 'A' and highest 'n' parameters (A is the amplitude of the transient creep strain and n is the time exponent) belong to the sample with the highest young modulus and the nanocomposites compared to PDLLA/PCL blends have the lower 'A' and higher 'n' which can be related to retardation effect of m-BGn on creep strains. Besides, the burgers model results illustrated that all viscoelastic and viscoplastic parameters for nanocomposites possess higher values than those of the neat PDLLA/PCL blend. It means that the addition of glass nanoparticles leads to decrease creep strain , increasing the Burgers model prediction values which have inverse trend with $\varepsilon(t)$. Moreover, the weibull distribution model results acknowledge that the introduction of m-BGn into PDLLA/PCL polymeric blends cause decrease in the viscoelastic strain recovery values. This is due to hindering effects of m-BGn on creep recovery behavior of nanocomposites.

Conclusion: The results obtained from modeling of creep-recovery manners of PDLLA/PCL blend and its nanocomposites approved that the bioactive glass reinforcement nanoparticles play impeding role on creep and creep recovery behaviors.

Level of evidence: I

Keywords: PDLLA/PCL blend; bioactive glass nanoparticles; creep and creep recovery behavior; modeling

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Introduction

The mechanical properties of polymeric based composite such as bio-screws which work within the body as implants for long periods of time are dependent on time, as well as on the characteristics of the applied stress [(1)]. Additionally, it is required that these implants do not deform significantly under constant loading, which may lead to excessive displacement into bone tunnel. For these reasons, the design of materials used in osteosynthesis (plates, screws) has to consider that these materials have to show relatively high creep resistance. Creep is a slow continuous deformational process occurring in materials under constant load conditions, lower than the yielding load of materials for prolonged period of time [(2)]. 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: (i) immediate deformation, (ii) primary and (iii) secondary stages in the creep graph [(3)]. Creep recovery is also a manner which is related to unloading section followed by the instant recovered strain, the creep recovery trend gradually decreases over time up to a constant value [(4)]. In this regard, several factors such as nature of polymers matrix, size, morphologies, volume fractions and distribution of filler phase throughout the polymeric matrix may affect the creep and creep recovery manner of polymeric based composites [(5-7)]. .

We previously studied the mechanical properties of PDLLA/PCL blends and its nanocomposites with superior promising goal for Anterior Cruciate Ligament (ACL) screws [8,9]. In addition, the creep and creep recovery behaviors of PDLLA/PCL/modified bioactive glass systems (m-BGn) are investigated in other work (10). In the current paper, the creep and creep recovery manner of nanocomposites under different stresses and temperatures are modeled by means of some typical models. The aim is to elucidate the effect of composite composition and bioactive glass on the viscoelastic deformation of the PDLLA/PCL/m-BGn systems.

The influence of filler phase on creep and creep recovery of polymeric composites and its modeling have been frequently investigated [11, 12]. As case in point, in a study the effect of wood fiber on creep behaviors of poly butylene adipateterephthalate (PBAT)/ polylactic acid (PLA) were analyzed and modeled by means of burgers model and Findley's power law [13]. The results show that wood fiber can enhance the creep performance of PBAT/PLA blends throughout the increasing in E_E, E_{VI} and η_{VI} burgers parameters and decreasing of A, power law parameter. In other work, creep trend of PLA/PCL fiber was analyzed and linearly modeled. The results show that there is a stress level threshold which below it the burgers model can be used in order to predict the creep behaviors and above it due to nonlinear viscoelastic, the burgers model cannot be used [14]. To best of our knowledge there are no analysis and data on creep behavior modeling of triple-component polymeric composites especially on PDLLA/PCL and bioactive glass systems. So, to enrich the studies about the creep behaviors more insight research is needed.

In this paper, the effects of bioactive glass nanoparticles on modeling of creep and creep recovery behaviors for PDLLA/PCL blends systems throughout the application of different temperatures and stresses were investigated. Our hypothesis is that our proposed system is a good candidate for ACLR screws which work for long periods of time into human body.

Methods

PDLLA/PCL/m-BGn nanocomposites have been prepared using solvent casting evaporation technique. The procedure details have been described in previous paper[9]. Creep and creep-recovery experiments were conducted in tension mode in the linear viscoelastic region for neat PDLLA/PCL blends and its nanocomposites with 1, 3 and 6 weight percentage of m-BGn filler phase using dynamic mechanical analyzer (DMA-triton, Tritec 2000 DMA, Triton Technology Co. England). The creep and recovery strains were determined as a function of time. The tests were performed at different conditions including the temperature 25 °C, stress 3 MPa (25-3), temperature 37 °C, stress 3 MPa (37-3) and temperature 37 °C, stress 6 MPa (37-6). The duration of creep and recovery measurements was also chosen for 20 and 30 minutes, respectively. The rectangular specimens with the same dimensions of 20 mm × 5 mm × 0.5 mm (length × width × thickness) were used for each test. The creep and creep recovery modeling was performed by means of Findley's power law and Burgers models and Weibull distribution, respectively.

Results

The creep and creep recovery manners of PDLLA/PCL with different amount of m-BGn filler phase at 25 and 37 ℃ as applied temperature and stresses of 3 and 6 MPa have been studied in previous work [10]. To further investigate the effects of m-BGn addition in creep and creep recovery behaviors, several classic creep and creep recovery models were used. One of the models is power law which is developed by Findley *et al.*[15] and is determined as:

Creep strain $\varepsilon(t) = \varepsilon_0 + At^n$ Equation

Table 1						
Test condition	(a) 25 ℃ / 3 MPa		(b) 37 ℃ / 6 MPa		(c) 37 ℃ / 6 MPa	
Model parameters	A	n	A	n	A	n
PDLLA/PCL blends	12.48	0.0077	38.9	0.0085	19.15	0.0148
PDLLA/PCL/1wt% m-BGn	12.25	0.007	15.28	0.0112	17.76	0.01652
PDLLA/PCL/3wt% m-BGn	0.0396	0.4571	21.14	0.011	21.53	0.01585
PDLLA/PCL/6wt% m-BGn	3.484	0.007	7.146	0.022	13.15	0.01886

Table 2 : Burger Adjusted with PDLA/PCL and addition of nano-composite

	Condition	Sample	η_{VI} (GPa.s)	E_{VI} (GPa)	η_{VP} (GPa.s)	E_E (MPa)
a	σ (MPa) = 3 T(ºC)=25	PDLLA/20PCL	0.3615	0.355	32.9	0.752
		PDLLA/20PCL/ 1wt % m-BGn	0.8473	0.6350	54.57	1.355
		PDLLA/20PCL/ 3 wt % m-BGn	8.88	3.52	79.1	4.462
		PDLLA/20PCL/ 6 wt % m-BGn	6.294	2.536	58.55	2.264
b	σ (MPa) = 3 T(ºC)=37	PDLLA/20PCL	0.439	0.181	17.8	1.23
		PDLLA/20PCL/ 1wt % m-BGn	0.6168	0.308	21.31	0.8711
		PDLLA/20PCL/ 3 wt % m-BGn	0.8716	0.4561	30.73	1.57
		PDLLA/20PCL/ 6 wt % m-BGn	2.344	0.6617	64.3	0.965
c	σ (MPa) = 6 T(ºC)=37	PDLLA/20PCL	1.15	0.5905	28.06	1.56
		PDLLA/20PCL/ 1wt % m-BGn	1.363	0.7106	31.76	2.017
		PDLLA/20PCL/ 3 wt % m-BGn	1.128	0.6148	23.86	1.936
		PDLLA/20PCL/ 6 wt % m-BGn	3.195	0.7375	82.7	2.019

Where $\varepsilon(t)$ and ε_0 is the creep strain at time t and initial strain, respectively. . The values of ε_0 can be obtained from the first point received of the creep test, and "A" and "n" parameters can be prepared from the power law model fitted on creep raw data. The Findley's power law model has a good adaptation with the experimental creep strain data for PDLLA/PCL blend and its nanocomposites.

The tests performed at 25-3, the values of 'A' parameters decreased and 'n' parameters increased as function of m-BGn content. The creep results for PDLLA/PCL blend and its nanocomposites reveal that the nanocomposites contains of 3 Wt% m-BGn possess the best creep behaviors compared to other specimens [10]. Therefore, these nanocomposites have the minimum 'A' and maximum 'n' parameter values. These trends are clearly observed for other condition tests, where the specimens with the lower creep strain level have the maximum 'A' and minimum 'n'.

Another significant well-known model which is used for studying the viscoelastic-viscoplastic behavior of nanocomposites with different glass content and neat polymeric blend is the Burgers model. This model is combined from two Maxwell and Kelvin-Voigt elements which is known as four-element model. Total strain in burger model consist of elastic strain, ε_E, viscoelastic strain, ε_{VI} and viscoelastic strain, ε_{VP} and is defined as [16]:

$$\varepsilon(t) = \frac{\sigma}{E_E} + \frac{\sigma}{E_{VI}}\left(1 - \exp\left(\frac{-tE_{VI}}{\eta_{VI}}\right)\right) + \frac{\sigma}{\eta_{VP}}t$$

Equation. 2

Where E_E is elastic modulus and E_{VI} is viscoelastic modulus, η_{VI} and η_{VP} are also viscoelastic and viscoelastic viscosities, σ is the applied stress and t is the creep time. The Burger model showed good consistency for PDLLA/PCL blend and its nanocomposites.

All viscoelastic and viscoplastic parameters for nanocomposites possess higher values than those of the neat PDLLA/PCL blend.

The instantaneous creep strain, E_E which is identified as Maxwell spring modulus recovered after stress omitting, has a direct relationship with PDLLA/PCL matrix modulus [8]. Therefore, nanocomposites with highest modulus possess the highest value of E_E [9]. In following, the E_E, Burger parameters values of specimens tested in 25-3 similar to young modulus variation trends are ranked.

The viscoelastic viscosity η_{VI} comes from dashpot viscosity in Kelvin-Voigt model. The highest η_{VI} belonged to nanocomposites with 3 Wt% m-BGn and lowest values of η_{VI} related to PDLLA/PCL neat blends. Similar trend for η_{VP} can be also observed where the highest and lowest values belonged to 3 Wt% m-BGn nanocomposites and neat blends, respectively. Also, the obtained results for tests performed at 37-3 illustrated the maximum to minimum values of η_{VI} and η_{VP} obtained for 6 Wt%, 3 Wt%, 1 Wt% m-BGn and neat specimens, respectively. Besides, the results of Burger model for creep tests applied at 37-6 determine that maximum η_{VI} and η_{VP} are attributed to nanocomposites with 6 Wt% m-BGn and order of other specimens rank as: 3 Wt% m-BGn, neat blend and 1 Wt% m- BGn. The variation trend of viscoelastic modulus, E_{VI} by incorporation of m-BGn show that E_{VI} has an inverse relationship with creep strain level. In other word, the specimens with highest young modulus owing to homogenous distribution of glass content throughout the polymeric matrix possess the maximum viscoelastic modulus [9,10]. This is obvious for specimens which have the minimum creep strain level [10].

In order to predict the effect of m-BGn on unrecoverable creep part of creep-recovery results, the Weibull distribution equation could be a good choice. After unloading, the instantaneous recovered strain, $\varepsilon_r(t)$ is defined as [17]:

$$\varepsilon_r(t) = \varepsilon_{VI}\left[\exp\left(-\left(\frac{t-t_0}{\eta_r}\right)^{\beta_r}\right)\right] + \varepsilon_{VP}$$

Equation. 3

Table 3: Weibull models					
	Condition	Sample	η_r (s)	β_r	ε_{VP}(%)
a	σ (MPa) = 3 T(ºC)=25	PDLLA/20PCL	4.43	0.394	0.247
		PDLLA/20PCL/ 1wt % m-BGn	1.588	0.453	0.242
		PDLLA/20PCL/ 3 wt % m-BGn	0.326	1.018	0.0215
		PDLLA/20PCL/ 6 wt % m-BGn	0.646	0.876	0.062
b	σ (MPa) = 3 T(ºC)=37	PDLLA/20PCL	3.668	0.385	1.232
		PDLLA/20PCL/ 1wt % m-BGn	2.339	0.767	0.759
		PDLLA/20PCL/ 3 wt % m-BGn	0.866	0.768	0.622
		PDLLA/20PCL/ 6 wt % m-BGn	0.099	1.168	0.429
c	σ (MPa) = 6 T(ºC)=37	PDLLA/20PCL	4.371	0.578	1.067
		PDLLA/20PCL/ 1wt % m-BGn	1.6	0.905	0.925
		PDLLA/20PCL/ 3 wt % m-BGn	2.84	0.586	1.09
		PDLLA/20PCL/ 6 wt % m-BGn	1.366	1.017	0.595

The results showed that the nanocomposites with 3 Wt% m-BGn for 25-3 and 6 Wt% m-BGn for 37-3 and 37-6 have the minimum ε_{VP}. Considering the creep recovery behaviors of all specimens tested in different conditions, it may be concluded that each specimen with lower unrecoverable creep strain has lower ε_{VP}.
The η_r parameter results confirmed that the maximum values belong to 3 Wt% m-BGn nanocomposites for test condition of 25-3, and 6 Wt% m-BGn nanocomposites for both tests performed at 37-3 and 37-6.

Discussion

A previous study investigated the creep and creep recovery behaviors of neat PDLLA/PCL blends and their nanocomposites contain of 1, 3, and 6 Wt% m-BGn [8]. The results confirmed that the addition of m-BGn into PDLLA/PCL polymeric matrix lead to improvement in the creep and creep recovery behaviors (10). The best creep performances were obtained for the nanocomposites with 3 Wt% m-BGn in test conditions of 25-3 and 6 Wt% m-BGn for 37-3 and 37-6. These are due to good dispersion and good binding of m-BGn as reinforcement throughout the PDLLA/PCL matrix in these nanocomposites [9]. Overall, the obtained results determined that the nanocomposites have better creep and creep recovery behaviors than the neat polymeric blends [10]. The Findley's power law model results fitted on creep behaviors of PDLLA/PCL blend and its nanocomposites for different test conditions showed that the model parameters, i.e. 'n' and 'A' of neat blends have been varied by introductions of m-BGn. The values of 'A' parameters decreased and 'n' parameters inversely increased as function of m-BGn content depending on the creep behaviors of specimens. So that, the specimens with lowest creep strain level have the minimum values of 'A' and maximum values of 'n'. According to table 1a (25-3) data, the highest "n" and lowest "A" belong to PDLLA/PCL with 3% wt m-BGn and further increase in reinforcement content lead to increase in "A" and decrease in "n". This is due to poor distribution and dispersion of glass reinforcement contents at higher content level, resulting in weakening their effective filling volume [9].
It was also found similar trends for other condition tests, i.e. 37-3 and 37-6 which on them the 6 Wt% m-BGn nanocomposites possessed the minimum

'A' and maximum 'n' owing to lowest creep strain level.

On the other hand, in comparison with PDLLA/PCL blends which have higher creep strain than its nanocomposites, the nanocomposites with highest young modulus which is leaded to lowest creep strain, the 'A' parameter has lowest values while the values of 'n' parameter is highest. Similar results have also been observed in PU/ CNT [11] and PCL/ SiO_2 (12) systems.

Generally, considering the creep manner of PDLLA/PCL blend and its nanocomposites [10], it could be found that there is a direct relation between creep strain level and "A" and "n" power law model parameters.

Since, the addition of glass nanoparticles into–polymeric matrix lead to decrease creep strain levels, it may cause an increasing on the Burger model prediction values which have inverse trend with ε(t) (refer to equation 2).

The η_{VP} represents the unrecoverable creep strain of all specimens. Based on the creep recovery behaviors of all specimens [10] it be found that the viscoplastic viscosity values have the inverse trends with unrecoverable creep strain. For all material types, incorporation of m-BGn into polymeric matrix causes η_{VP} increase. On the other hand, the rising trend of η_{VP} illustrated a decreased levels of permanent deformation. Similar results have also been reported on the polyurethane/carbon nano tube nanocomposites [11]. Generally, according to creep behaviors of all specimens ~~(10)~~, the specimen with the lower creep strain has a higher η_{VP} than other samples. These parameters as a retardant modulus are related to amorphous region of polymeric chains and show the similar behaviors as well as E_E which reflect the reinforcement role of m-BGn in Kelvin-Voigt model.

Conclusion

From the results of this study, the following conclusions can be pointed out:

- The creep and creep recovery behaviors of PDLLA/PCL blend and its nanocomposites were nicely fitted with some mathematical models such as Findley power law, Burgers and Weibull models.
- The Findley power law model results show that the lowest 'A' and higher 'n' parameters belong to nanocomposites with higher young modulus.
- According to burgers model, the specimens with highest young modulus have the highest E_E and E_{VI} and specimens with lowest creep strain level and lowest creep recovery strain level possess the highest η_{VI} and η_{VP}, respectively.
- Based on Weibull distribution model, the compounds with lowest creep strain have highest η_r and β_r parameters confirm an inverse trend with creep recovery strain.

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