

# Creep of glutaraldehyde-crosslinked gelatin films

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## Abstract

Creep behavior of glutaraldehyde-crosslinked gelatin films was evaluated by short-time flexural tests at 30 °C. Samples were characterized by the number-average molecular weight between two crosslinking points, determined by using the Flory–Renher equation. Creep response decreased with increasing degree of crosslinking, which is an indication that crosslinking improves the film stiffness. Experimental creep data were compared with calculated ones by using two different approaches, the creep power-law and the four-parameters model. Good fitting of the experimental results with both models was found, leading to a relationship between the observed creep behavior and the structure of the crosslinked gelatin films. Chemical crosslinkages seemed to induce a decrease of the viscous creep and an enhancement of the elastic contribution.

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## 1. Introduction

Environmental concerns associated with the handling of plastic waste have encouraged the development of new packaging materials to alleviate the plastic waste disposal problems. In this sense, natural biopolymers offer a possible alternative to the traditional non-biodegradable polymers, especially in short life-time application. In addition, degradable materials promote resource conservation as well as a more sustainable way of life. Polysaccharides such as starch and derivatives [1,2], cellulose and derivatives [3] and proteins [4–8] have suitable overall mechanical, barrier and optical properties to be effectively used to produce biodegradable coatings and films to replace short-shelf life plastics.

Gelatin is a denatured form of collagen, a connective tissue protein, present in most of the vertebrates and represents a typical renewable material from natural resources of animal origin. Gelatin can be obtained from inexpensive sources derived from wastes and by-products generated in different manufacturing processes comprising tannery, pharmaceutical and food segments [9,10]. The poor water resistance and low mechanical strength of gelatin films compared to synthetic polymers used in food packaging limits their applications. Several attempts have been made in order to overcome these drawbacks. Chemical

crosslinking improves mainly thermal and mechanical properties and imparts water resistance by introducing covalent stable bonds between the reactive side groups presents in gelatin chains [11]. Among the chemicals used to crosslink gelatin, glutaraldehyde (GTA) has been used extensively because it has the advantage of being a fast-acting hardener for cologeneous materials (gelation times of less than 1 min are reported for GTA concentrations between 10 and 20 wt.%), easily available and inexpensive [10–13]. Technical grade products based on crosslinked gelatin are widely used in many applications fields including medicine, pharmacy and packaging, and each one requires specific properties that should be well characterized.

Creep in polymers can be quite significant even at room temperature and is rapidly accelerated by an increase in temperature. The phenomenon of creep has to be carefully accounted for in many design problems. Thus, its characterization is important from the point of view of long-term performance of products under various environmental conditions. Such characterization is used for predicting the useful life of a product as defined by excessive creep deformation or creep rupture [14]. The creep performance is also of major importance in determining and explaining the molecular origins of viscoelasticity in these materials. Despite the extensive work on gelatin films, limited information is available concerning the effect of chemical crosslinking on the creep behavior. Apostolov et al. [15] have studied the creep behavior under bending deformation of native and diisocyanate crosslinked-gelatin films. Relaxation time and

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viscosity were found to be strongly dependent of the crosslinking density and the nature (i.e. chain length) of the hardening agent.

The aim of the present work is to evaluate the effect of the crosslinking degree on the short-time flexural creep behavior of glutaraldehyde–gelatin films (GTA–Ge). Experimental data were correlated with classical model using mechanical analogies and the accuracy of the predictions were evaluated.

## 2. Creep modeling

Creep measurements is a simple way to obtain information concerning the viscoelastic properties of materials, which can be correlated with structural features. From a more practical point of view, creep is also a common phenomenon for engineering applications where products are subjected to loads. Creep deformation is the time dependent strain under constant stress. Stress applied on a viscoelastic material is time and temperature dependent. The rheological response of a purely elastic material is instantaneous while that of viscoelastic material is time dependent [16].

There exist several models to describe the viscoelastic creep response of polymers and each has its own limitations [17].

One of the simplest approaches is the creep power law [18], which is expressed as follows:

$$\varepsilon(t) = \varepsilon_0 + At^n \quad (1)$$

where  $\varepsilon(t)$  is creep strain at time  $t$ ,  $\varepsilon_0$  the instantaneous initial strain,  $A$  the amplitude of transient creep strain and  $n$  is the time exponent. The instantaneous strain, the amplitude of transient creep strain and the time exponent are defined as creep parameters. Creep strain is presented as relative creep ( $\varepsilon_r$ ), a percentage of instantaneous elastic strain of material. Rearranging Eq. (1):

$$\varepsilon_r = At^n \quad (2)$$

$A$  and  $n$  are the creep parameters. Parameter  $n$  could be related to the viscous behavior of the material [19]. By applying logarithms to both sides of Eq. (2), a straight line is obtained and creep parameters can be determined by plotting  $\log \varepsilon_r$  versus  $\log t$ . This model was successfully used to explain the creep behavior of different polymers and composites such as polypropylene/wood-fibre composites [20], sisal fibre/cellulose derivatives-starch blends [21], sisal fibre/polycaprolactone-starch blends [22], polyimide-carbon fiber composites [23] and thermosetting foams [24].

The total mechanical response of a specimen includes perfect elasticity, coupling of elastic and viscous components, called anelasticity, and a total irreversible flow. The simplest model, where the anelastic component is characterized by a single characteristic time that describes this entire response, is the four-element model (a Maxwell and a Voigt elements in series). This approach is based on the contribution of elements representing the elastic (springs) and viscous (dashpots) behaviour. Basically, Burger's model is a series of combination of Maxwell and Kelvin–Voigt models [25]. A scheme representing the four-parameter model is given in Fig. 1. The total strain  $\varepsilon$  is given by

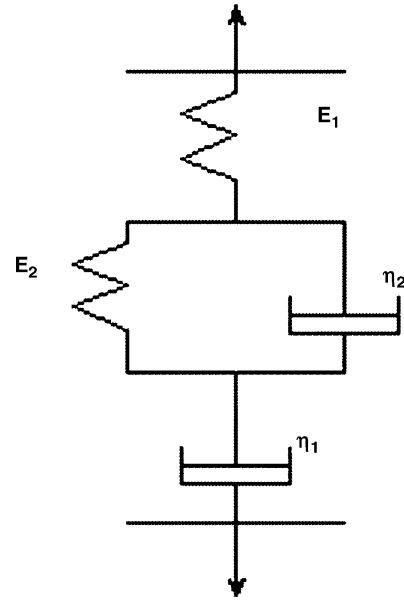


Fig. 1. Scheme of the Burger's model with spring and dashpot.

the following expression:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \quad (3)$$

where  $\varepsilon_1$  and  $\varepsilon_3$  are the elastic and viscous strain represented by Maxwell model and  $\varepsilon_2$  is the viscoelastic strain represented by the Kelvin–Voigt model. Eq. (3) can be expressed as:

$$\varepsilon = \frac{\sigma}{E_1} + \frac{\sigma}{E_2} \left( 1 - \exp\left(-\frac{tE_2}{\eta_2}\right) \right) + \frac{\sigma}{\eta_1} t \quad (4)$$

where  $E_1$  and  $\eta_1$  are the elastic and viscous component of Maxwell model,  $E_2$  the elastic,  $\eta_2$  the elastic and viscous component of Kelvin–Voigt model,  $\sigma$  the applied stress and  $t$  is the creep time. The relaxation time,  $\tau = \eta_2/E_2$ , is a measure of the time required to extend the spring up to its equilibrium length while retarded by the dashpot. Later deformation comes from the spring  $E_2$  and dashpot  $\eta_2$ , in parallel, and from the dashpot with viscosity  $\eta_1$ . At temperatures which are much lower than the glass transition temperature,  $T_g$  of the system, the viscosity parameters  $\eta_1$  and  $\eta_2$  are usually very large. In a time frame when a typical force–distance curve is measured, the effect of the elastic spring  $E_2$  is essentially blocked due to a much longer response time determined by  $\eta_2$ . Thus, the effective Young modulus of the system is  $E_1$ . As the temperature approaches  $T_g$ ,  $\eta_2$  decreases rapidly and the effect of  $E_2$  gradually comes into play. The parameters  $E_1$ ,  $E_2$ ,  $\eta_1$ ,  $\eta_2$  and  $\tau$  can be obtained from the best fitting of experimental data.

## 3. Experimental

### 3.1. Films preparation

Bovine hide gelatin (Ge) type B was kindly supplied by Roussetol (Argentina), Bloom strength 150 and isoionic point pH 5.3. Glutaraldehyde (GTA) solution (50 wt.%) was purchased from QBS (Argentina) and used as received.

Glutaraldehyde–gelatin crosslinked films (GTA–Ge) were prepared by adding the appropriate volume of GTA solution to the gelatin solution (10 vol.%), to obtain final GTA concentrations varying from 0.1 to 5 wt.%. In order to restrict the reordering of gelatin into a triple-helix, non-crosslinked gelatin films (Ge) were prepared by casting from an aqueous gelatin solution (10%, w/v) at 50 °C and under continuous stirring for 15 min. The resulting homogeneous solutions were poured into Teflon Petri dishes (10 cm of diameter) and allowed to react for a period of time. Crosslinked films were recovered after water evaporation at room temperature. Gelatin control films (Ge) were performed in a similar way but without adding any crosslinking agent.

### 3.2. Crosslinking density determination

In order to estimate the network crosslinking density, the number-average molecular weight of chain segments between two crosslinking points,  $M_c$ , was calculated from equilibrium water uptake experiments performed at 20 °C, according to the Flory–Renher equation [26]:

$$M_c = \frac{\rho V_1 (\phi_g^{1/3} - 2\phi_g/f)}{\chi \phi_g^2 + \ln(1 - \phi_g) + \phi_g} \quad (5)$$

where  $\rho$  is the density of the dry gelatin determined by picnometry,  $V_1$  the molar volume of the solvent,  $\chi$  the polymer–solvent interaction parameter and was taken from the literature ( $\chi = 0.49 \pm 0.05$ ) [15] and  $\phi_g$  is the volume fraction of the swollen gelatin. The gelatin volume fraction in the swollen samples ( $\phi_g$ ) was estimated assuming the following relationship:

$$\phi_g = \frac{W_0 \rho_w}{W \rho_g - W_0 (\rho - \rho_w)} \quad (6)$$

where  $W_0$  is the initial weight of the sample,  $W$  the weight of the swollen sample,  $\rho_w$  the density of the water at room temperature and  $\rho$  is the density of the dry and uncrosslinked gelatin film.

### 3.3. Methods

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 calorimeter. Around 10 mg of sample were placed in an aluminum pan. Each sample was heated from 20 to 250 °C with a heating rate of 5 °C/min. The glass transition temperature  $T_g$  was taken as the temperature of the midpoint of the increment of the specific heat capacity,  $\Delta C_p$ , of the transitions.

The instantaneous elastic response and the viscoelastic properties were studied using quasi-static tests or DMA. A Perkin-Elmer dynamic mechanical analyzer (DMA 7-e) was used in the short-term creep tests. The experiments were carried out in the creep mode, using the three-point bending device with a specimen platform of 15 mm length under nitrogen atmosphere. Specimen dimensions were 15 mm  $\times$  10 mm  $\times$  0.2 mm. Creep devices were preconditioned for 30 min before the start of measurements. Experiments were performed for 45 min and at 30 °C.

## 4. Results and discussion

Crosslinked and control (un-crosslinked) gelatin films were obtained in similar conditions. It is important to keep in mind that control films must be obtained at higher temperatures than 35 °C (hot films) in order to prevent the triple-helix regeneration which may act as physical crosslinking points. On the other hand, it is well reported that gelatin gelation is a kinetic process and continues after the setting of the gel [27] Therefore, control and crosslinked films were kept in a desiccator at room temperature sufficient time before testing to prevent any further change during the experiments.

Glutaraldehyde (GTA) is a fast-acting hardener for collagenous materials (gelation times of less than 1 min are reported for GTA concentrations between 10 and 20 wt.%), easily available and inexpensive [11]. However, the above-mentioned advantages are counterbalanced with its suspected biological effect [28], which limits the application of the obtained materials. One way to overcome this drawback without losing mechanical properties is by lowering GTA concentrations, as it was demonstrated by Bigi et al. [12].

The reaction of gelatin with different amounts of GTA was carried out at 50 °C and at pH 6, in order to restrict the auto condensation of GTA which is favored in basic conditions. All crosslinked films were stiffer than gelatin films without chemical treatment used as control and turned yellowish, characteristic of the Schiff bases [11,12].

The results of the calculated average molecular weight between two crosslinking points,  $M_c$ , as a function of GTA concentration are summarized in Table 1. As seen from Table 1,  $M_c$  values decrease drastically with GTA content, due to the formation of a denser network. Percentages of crosslinking agent higher than 2 wt.% did not introduce bigger changes. Therefore, for GTA concentrations higher than 2 wt.%, no further reaction occurs. The high crosslinking density developed imposes a restriction in the mobility and a final conversion is reached. Similar results were reported by Fraga and Williams for cold water-fish gelatin crosslinked with formaldehyde [9]. The authors describe this effect as the same as the arrest of the reaction due to vitrification in thermosetting systems.

Thermal history has a great influence on the properties of gelatin films. Calorimetric experiments were carried out in the dynamic mode and under nitrogen atmosphere on control and crosslinked films in order to visualize the thermal behavior and stability. The glass transition temperature,  $T_g$ , values are

Table 1

Average molecular weight between crosslinking points ( $M_c$ ), crosslinking degree and glass transition temperature ( $T_g$ ) of glutaraldehyde-crosslinked gelatin films

GTA (wt.%)	$M_c^a$ (Da)	Crosslinking degree (%)	$T_g$ (°C)
0	37283	0	195
0.5	3779.8	76	201
1	1368.2	93	217
2	1024.8	97	nd
5	666.8	97	nd

nd, not determined.

<sup>a</sup> Estimated from Eq. (5).

summarized in Table 1. Control gelatin film shows endothermal events, which can be related with its structure. Gelatin can be visualized as a block copolymer build up from triads of  $\alpha$ -aminoacids with glycine (Gly) at every third position (soft blocks) and triads of hydroxyproline (Hypro), proline (Pro) and glycine (rigids blocks). The devitrification of each block can be associated with a  $T_g$  value. In mammalian gelatins the rigid blocks prevail over the soft ones. Thus the second  $T_g$  (195 °C, Table 1) represents the overall glass–rubber transition of the material [9]. In cold gelatin films, a third complex transition may appear. This last is related with the denaturation of the triple helix which is absent in hot films. On the other hand, GTA–Ge films show also two glass transition temperatures (soft and rigid blocks, respectively) and do not show melting behavior which is restricted by crosslinking. The second glass transition temperatures are more visible, being in the range of 201–211 °C (Table 1). Concentration of GTA higher than 1.5 wt.% produced highly crosslinked films (see  $M_c$  values in Table 1) and the second glass transition temperature is superimposed with thermal degradation around 230 °C.

Crosslinking degree and thermal properties allowed us to select the formulations and temperature for the creep experiments. Highly crosslinked films (i.e. GTA content higher than 1.5 wt.%) were extremely brittle and were not able to be tested. Thus, creep test were performed on gelatin films with GTA content varying from 0 to 1 wt.% GTA.

Short-time creep measurements at different temperatures are usually preformed in order to predict long-term creep behavior by using time–temperature superposition principle. This principle assumes that polymer structure and morphology do not change with time. However, superposition is often not observed because the structure of the sample will vary with the temperature, resulting in different creep responses. Proteinaceous materials, may suffer structural and morphological changes even at low temperatures, thus the initial assumption of the model is not longer valid. For the case of gelatin gels (without any crosslinking agents), changes in temperature may induce renaturalization or denaturalization of the triple helix, which in turn conduct to morphological changes. This limited stability restrict temperature range and then, time–temperature superposition cannot be applied. Therefore, creep analysis were performed at 30 °C, below both glass transition temperature and near that used for conditioning the samples.

In order to determine the creep behavior within the elastic range, isochronous tests were conducted on un-crosslinked gelatin films (control) at 30 °C during 45 min and under different tensions. The curves were linear up to certain stress and strain levels. Fig. 2 shows the results of the strain versus time for different stress values. The results were analyzed by applying the Norton equation:

$$C = B\sigma^m \quad (7)$$

where  $C$  is the strain rate or creep velocity (mm/s),  $\sigma$  the applied stress (MPa),  $B$  the material and temperature dependent constant and  $m$  is the material constant. Fig. 3 represents a log–log plot of Eq. (7). A value of  $m$  near the unity ( $m_{\text{experimental}} = 1.18$ ) indicates that measurements are within the linear elastic range.

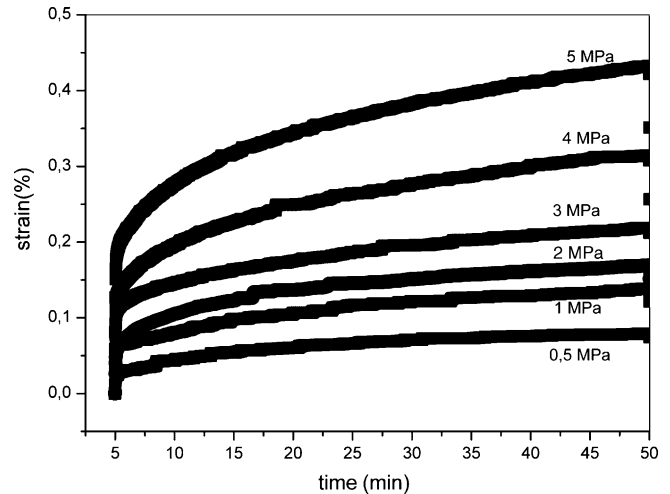


Fig. 2. Strain vs. time deformation at different stresses for uncrosslinked gelatin films at 30 °C.

Therefore, a constant stress of 1 MPa was selected to analyze all the samples.

The effect of crosslinking on the creep response at 30 °C is shown in Fig. 4. The final creep response in the crosslinked samples is significantly lower than in the control film. This finding may be related to a reduced viscous flow of the matrix due to crosslinking. The deformation decreases as a consequence of the increment in rigidity induced by crosslinking. Then, the effect of adding GTA is to stiff the material, in agreement with a more reticulated material.

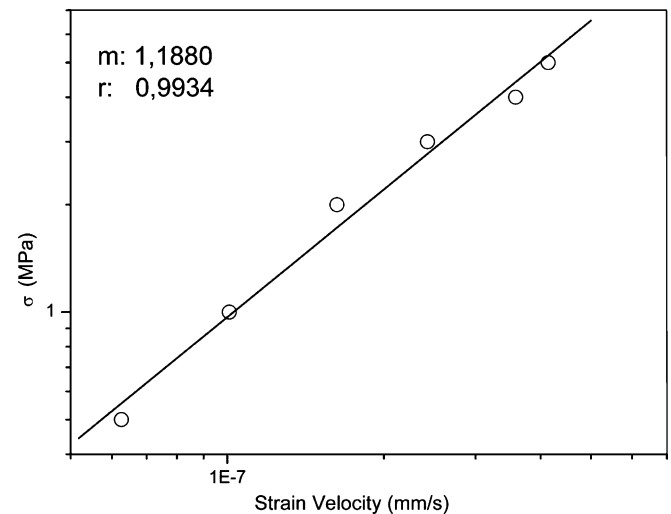


Fig. 3. Log–log plot of applied stress vs. creep velocity for gelatin films to determine the elastic range conditions.

Table 2

Creep power law fitting results for glutaraldehyde-crosslinked gelatin films at 30 °C

GTA (wt.%)	A	n	R <sup>2</sup>
0	0.767	0.383	0.998
0.5	0.767	0.260	0.986
1	0.879	0.243	0.995

Table 3  
Burger’s model fitting results for different GTA concentrations and at 30 °C

GTA (wt.%)	$E_1$ (MPa)	$\eta_1$ (MPa min)	$E_2$ (MPa)	$\eta_2$ (MPa min)	$\tau$ (min)
0	26.53 ± 0.09	817.10 ± 9.79	28.28 ± 0.49	326.81 ± 3.55	11.6
0.5	30.58 ± 0.21	1184.70 ± 16.25	66.93 ± 1.75	510.78 ± 21.49	7.6
1	34.10 ± 0.10	1811.89 ± 13.80	81.12 ± 0.93	607.15 ± 11.58	7.5

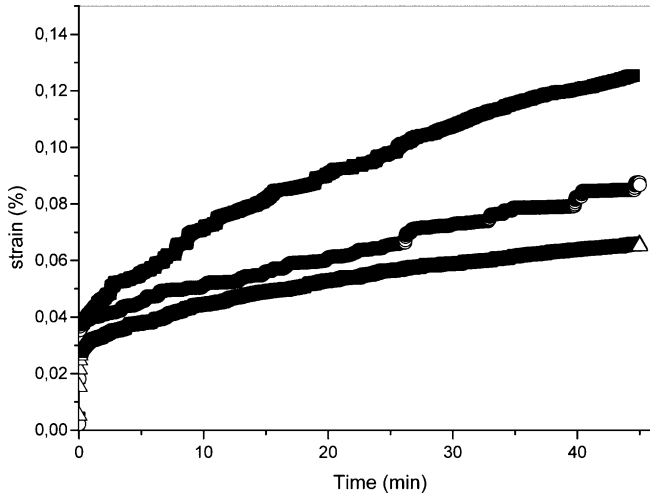


Fig. 4. Effect of crosslinking on the creep response at 30 °C and  $\sigma$  1 MPa. (■) Ge; (●) 0.5 wt.% GTA-Ge; (▲) 1 wt.% GTA-Ge.

The creep power law (Eq. (3)) was used to fit the experimental data and are represented together in Fig. 5. Prediction agrees well with experimental data in the range of GTA analyzed. The values of  $A$  and  $n$  obtained are summarized in Table 2. As GTA increases,  $n$  value decreases. This is an indication that creep resistance increases with crosslinking. Even if power-law model results in a very good fit of the data, does not offer the possibility of predicting other viscoelastic properties as the Burger’s model.

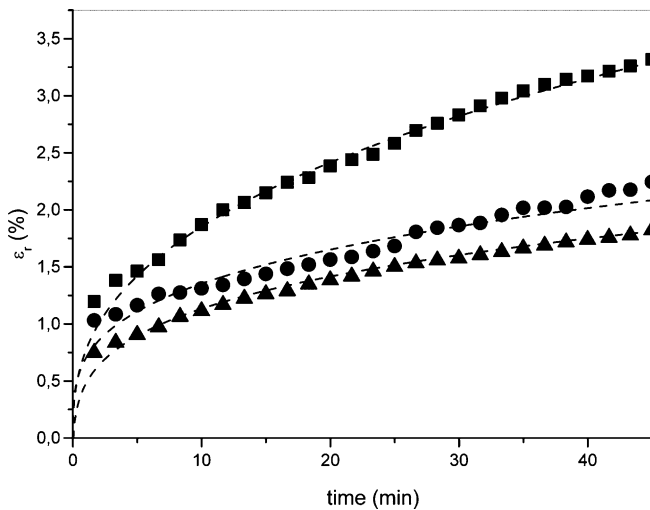


Fig. 5. Relative creep curves of glutaraldehyde-crosslinked gelatin films exposed to 30 °C and  $\sigma$  1 MPa. Experimental data: (■) Ge; (●) 0.5 wt.% GTA-Ge; (▲) 1 wt.% GTA-Ge. Dashed lines correspond to creep power law’s predictions.

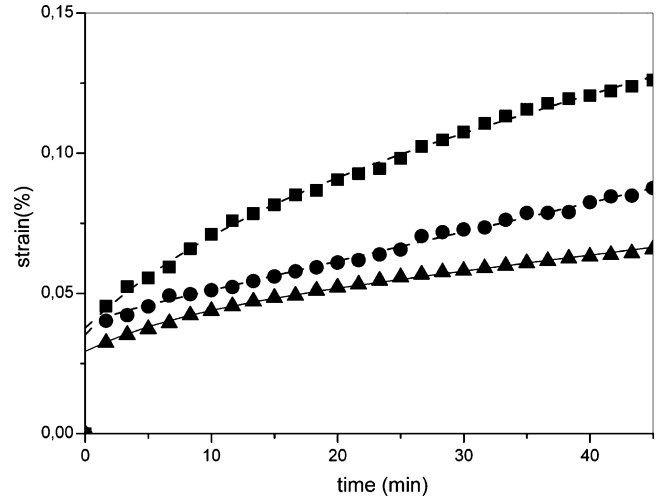


Fig. 6. Strain vs. time of deformation of glutaraldehyde-crosslinked gelatin films  $T$  30 °C and  $\sigma$  1 MPa. Experimental points: (■) Ge; (●) 0.5 wt.% GTA-Ge; (▲) 1 wt.% GTA-Ge.

Experimental data were also correlated by using the four-parameter model (Eq. (4)). Fig. 6 shows the comparison between experimental (symbols) and predicted (dashed lines) curves for different GTA concentrations and at 30 °C. As can be concluded from Fig. 6, the model fits well within the entire time range of the experiment. The predicted values of  $E_1$ ,  $E_2$ ,  $\eta_1$ ,  $\eta_2$  and  $\tau$  were obtained as the best fitting parameters and are summarized in Table 3. As GTA concentration increases the elastic modulus of the Maxwell element ( $E_1$ ) increases (the immediate creep deformation decreases) as well as the viscosity ( $\eta_1$ ) (the steady state creep decreases). Contrary, the relaxation time decreases. This parameter characterizes the elastic relaxation. The presence of chemical crosslinkages decreases the viscous creep and enhances the elastic contribution.

### 5. Conclusions

Gelatin-based materials would be considered as potential candidates to develop environmentally sound packaging materials. Crosslinking is necessary in order to enhance the mechanical, thermal and water resistance properties of the produced films.

Gelatin was successfully crosslinked with low glutaraldehyde concentrations in order to produce highly crosslinked materials but keeping the GTA concentrations as low as possible in order to prevent the potential migration of the crosslinking agent.

The creep behavior of glutaraldehyde-crosslinked gelatin films was evaluated by short-time flexural tests. There is a good correlation between the creep response and the degree of

crosslinking. A higher degree of crosslinking (i.e. more denser network) lowers the creep response, which is an indication that crosslinking improves the film stiffness.

Experimental data were correlated by using two different approaches, the power-law and four-parameters models. Results indicated that both models fit adequately creep short-term experimental data, but it must be taken into account that the predicted parameters do not have the same physical significance. However, they give a complementary information. On one hand, the creep power-law is the simplest model, which has the ability of predicting the parameter  $n$  which can be related to the creep resistance. On the other hand, Burger's model analysis revealed an increase in the elastic modulus and a decrease in the relaxation time for Ge-GTA films compared to the control films, according with the increasing crosslinking density. It is important to remark that these parameters are mathematical results of fitting experimental data with a particular equation which is only an approach to describe the system under study.

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