

Creep Behavior of Wood Flour Composites Made from Linseed Oil-Based Polyester Thermosets

Mirna A. Mosiewicki, Norma E. Marcovich, Mirta I. Aranguren

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata - National Research Council (CONICET), Mar del Plata 7600, Argentina

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ABSTRACT: The creep behavior of new polymers prepared by free radical polymerization of styrene-crosslinked resins obtained from linseed oil and derived wood flour (WF) composites have been analyzed. Results of short-time flexural creep tests at different temperatures are reported. The effects of the wood flour content and temperature are discussed. The creep deformation is significantly reduced with the incorporation of wood flour, due to the excellent fiber/matrix interaction. The creep strain was modeled using the creep power law and the Burgers models. The parameters were determined from the best fitting of the experimental data using a nonlinear optimization method. Although both models gave a good description of the viscoelastic creep of the materials, the Burgers model was pre-

ferred because of its ability to predict recovery. A master curve was built using the time temperature superposition principle, and the time shifts were well fitted using Arrhenius model. There was a good superposition of the short-term master curve and long-term data for samples tested at the same time after preparation. A reduction of the creep deformation was observed when the responses of samples tested after 2 and 5 years from preparation were compared, which was attributed to aging derived from the oxidative crosslinking of linseed oil fragments in the network. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2626–2633, 2011

Key words: linseed oil resins; wood flour; creep; master curve; aging

INTRODUCTION

The development of polymers from renewable resources has become an important subject in both scientific research and commercial applications, mainly because of their low cost and ecofriendly nature in contrast with petroleum based polymers.¹ Thus, vegetable oils have been used as natural sources for the preparation of different polymeric resins^{2–5} during the last decade. Natural oils are triglycerides of fatty acids, which have between 0 and 3 carbon–carbon double bonds. In particular, linseed oil has been widely used as a drying oil in the painting industry because it contains a high percentage of linolenic acid, with three unsaturations per fatty acid chain.^{6,7}

Since the original unsaturations of drying oils do not participate in radical polymerizations, a more reactive unsaturated reactive can be obtained by functionalizing the linseed oil triglyceride molecules in two steps: glycerolysis to produce mainly a monoglyceride, followed by the reaction with maleic anhydride, to produce a maleinated monoglyceride with highly reactive C=C double bonds.^{5,8} The product is mixed with a reactive diluent such as styrene and cured in the presence of an initiator by free radical polymerization to obtain a crosslinked thermoset polymer.⁸ Some of the physical and mechanical properties of these new polymers can be improved with the addition of plant-based reinforcements/fillers, such as wood flour (WF), to obtain composite materials. One of the most important factors that affect the final characteristics of the composites is the fact that this matrix has carboxylic groups that can interact with the hydroxyl groups on wood flour giving a composite material with a very strong fiber/matrix interface.⁹

In previous publications, the mechanical and thermomechanical behavior of these materials⁹ have been presented and discussed, however, the creep behavior has not been extensively evaluated.

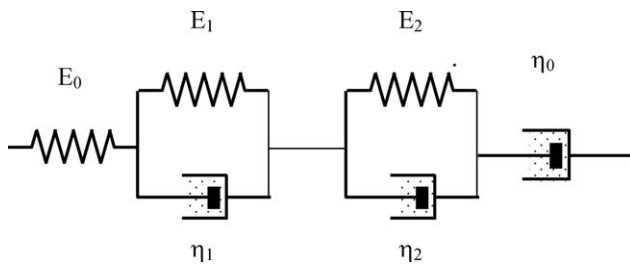
The aim of this work is to investigate the creep performance of woodflour-linseed oil based thermoset composites, since this viscoelastic behavior constitutes an important criterion for evaluating the

Correspondence to: M. A. Mosiewicki (mirna@fi.mdpl.edu.ar).

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Scheme 1 Mechanical analog for Burgers' model.

long-term performance in practical applications. In particular, the creep performance of the composite materials from linseed oil resins and wood flour was investigated taking into account the effects of filler content and testing temperature. The power law and Burgers models were used to predict the viscoelastic behavior of the composites. The time-temperature superposition principle was applied for the construction of a master curve from short-term creep tests and it was used to predict long term creep behavior. The effect of time after sample preparation (aging) on creep behavior was also evaluated.

Creep analysis

A simple way to simulate the viscoelastic behavior of a polymeric material is to use mechanical analogies that include the viscous performance of dashpot elements and the elastic response of spring elements. The particular Burgers model used in this work, a series combination of one Maxwell element and two Kelvin-Voigt elements, is shown in the Scheme 1.^{10,11}

The total strain, $\epsilon(t)$, is given by:

$$\epsilon(t) = \frac{\sigma}{E_0} + \frac{\sigma}{E_1} \cdot \left[1 - \exp\left(-t \cdot \frac{E_1}{\eta_1}\right) \right] + \frac{\sigma}{E_2} \cdot \left[1 - \exp\left(-t \cdot \frac{E_2}{\eta_2}\right) \right] + \frac{\sigma}{\eta_0} \cdot t \quad (1)$$

where σ is the constant applied stress, t is the time, E_0 is related to the instantaneous elastic response of the material, E_1 and E_2 are the elastic modulus of the springs, η_1 and η_2 are the viscosities of the dashpots in the Kelvin-Voigt elements and η_0 is the viscosity of the Maxwell element. Finally, the viscosity of the dashpot of the Maxwell element is related to the steady state creep, where the viscous flow is the predominant behavior. This last term is negligible in thermoset polymers, since the recovery should be, at least theoretically, complete.

These parameters were obtained from the best fitting of the experimental data, using the nonlinear least-squares Levenberg-Marquardt optimization algorithm.¹²

A simpler relationship of $\epsilon(t)$ with time was also used to explain the viscoelastic behavior of the materials, as follows¹³⁻¹⁵:

$$\epsilon(t) = a + b \cdot t^c \quad (2)$$

where a , b , and c are empirically determined parameters. This model, although less versatile, is simpler than the Burgers one and has just three fitting parameters. In some cases, the parameter "a" is close to zero and the simplification of Eq. (2) produces small variations on the "b" and "c" parameters.

$$\epsilon(t) = b \cdot t^c \quad (3)$$

If the creep load is suddenly removed at a given time ($t_r > 0$), the strain decreases with time, along a course called creep recovery. The rate of this shape recovery depends on the material viscoelastic properties. This test allows directly determining whether a material presents complete recovery or a permanent set remains after unloading. When working in the linear viscoelastic region, the creep recovery behavior can be predicted using the Boltzmann Superposition Principle,^{13,16} thus the creep recovery-strain predicted by the Burgers model, $\epsilon_r(t)$, is given by:

$$\epsilon_r(t) = \epsilon(t) - \frac{\sigma}{E_0} - \frac{\sigma}{E_1} \cdot \left[1 - \exp\left(-\frac{(t-t_r) \cdot E_1}{\eta_1}\right) \right] - \frac{\sigma}{E_2} \cdot \left[1 - \exp\left(-\frac{(t-t_r) \cdot E_2}{\eta_2}\right) \right] - \frac{\sigma \cdot (t-t_r)}{\eta_0} \quad (4)$$

The parameters obtained from fitting the creep deformation, $\epsilon(t)$, during the initial part of the tests, were utilized in this work to predict $\epsilon_r(t)$.

Generally, the creep deformation increases with temperature and time. If the material does not change its structure with time, the time-temperature-superposition (TTS) principle can be used to predict the long-term behavior from short-term measurements.¹⁶ The creep curves obtained at different temperatures are superposed by horizontal shifts along a logarithmic time scale ($\log a_T$) to obtain a master curve. This master curve can be used to predict the long time response of the material at the selected temperature. In the case of composite materials, this assumption cannot be taken as valid *a priori*, but instead its applicability should be investigated.

On the other hand, the functionality of a_T with the temperature, according to the Arrhenius expression, can be written as follows:

$$\log(a_T) = \frac{-E_a}{2.303R} \cdot \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (5)$$

where E_a is an activation energy and R is the universal gas constant, T is the test temperature and T_0 is the reference temperature.

EXPERIMENTAL

Materials

Linseed oil provided by Grainer S.A. (Entre Rios, Argentina) was used in this work. A resin was prepared from the chemical modification of the linseed oil. The synthesis of the resin corresponds to the glycerolysis of the linseed oil with excess of glycerol to obtain mainly a monoglyceride, followed by the reaction with maleic anhydride to produce a maleinated monoglyceride, as it has been previously reported.^{8,9}

The synthesized linseed oil-based resin was further crosslinked with styrene in a weight proportion resin/styrene 60 : 40. The crosslinking radical polymerization was carried out at 90°C for 1.5 h followed by postcuring at 150°C for 1.5 h with the addition of a thermal initiator, benzoyl peroxide (Lucidol 0.75, Akzo Chemical S.A.), 2.5% wt with respect to the total reaction mixture. The details of the synthesis and characterization of the matrix were carefully described in previous publications.^{8,9}

The composites were manufactured using the linseed oil-based thermoset with the addition of pine wood flour (J. Do Santos Freire, Buenos Aires, Argentina). Wood flour had average particle sizes ranging from 75 to 150 μm . Wood flour was dried at 75°C for 48 h in a vacuum oven.

Compounding and molding

Composite materials were prepared by mixing the dried filler and the reactive mixture (linseed oil-based resin, styrene and benzoyl peroxide) in an intensive mixer at room temperature and 50 rpm. No appreciable reaction occurs under these conditions.^{9,14} The resulting paste was filled in a cylindrical metal mold (145 mm of diameter and about 3 mm of thickness), which was left open for 1.5 h at 50°C to decrease the viscosity of the reactive mixture and to facilitate the step corresponding to filling the mold. Then, the mold was closed and the temperature was increased to 90°C. The mixture was cured at this temperature for 1.5 h under pressure (4 MPa), and then postcured at 150°C for another 1.5 h. Samples were prepared with 0, 20, and 30 wt % of wood flour. All the specimens were dried at 75°C for 24 h in a vacuum oven prior to be tested.

Mechanical tests

Creep tests

The tests were carried out in a Perkin–Elmer dynamic mechanical analyzer (DMA 7) in creep mode (“instantaneously” applied stress-step), using the three point bending fixture with a specimen plat-

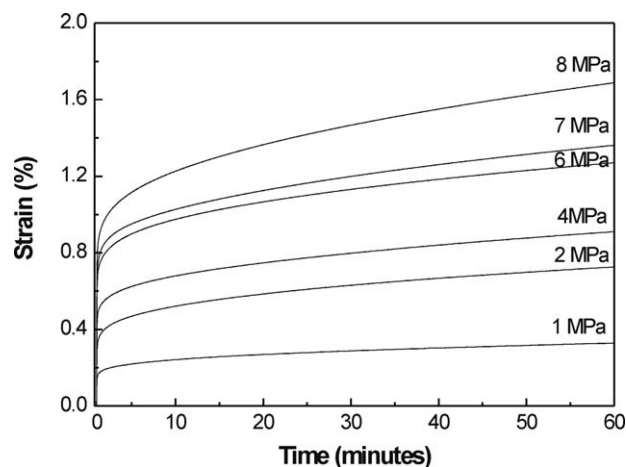


Figure 1 Strain (%) as a function of time at different stresses for the unreinforced linseed oil based polymer at 30°C.

form of 15 mm length under nitrogen atmosphere. The stress range selected for running the tests needed to identify the linear viscoelastic (LVE) range were chosen below the ultimate stress of the unreinforced material tested in three points bending until failure. The rest of the creep tests were run at a fixed stress of 7 MPa (LVE range). The sample dimensions were $\sim 20 \times 2 \times 3 \text{ mm}^3$ and the linear dimensions were measured up to 0.01 mm. Short-time creep tests were conducted during 60 min, using samples prepared 2 years before testing, while long-term creep tests were carried out for 7 h, using specimens prepared 5 years ago.

RESULTS AND DISCUSSION

To ensure working in the linear viscoelastic range, the unfilled specimen (which corresponds to the sample that shows larger creep deformations under any given test conditions) was tested in creep mode at 30°C during 60 min applying different stresses. Figure 1 shows the corresponding strain versus time curves. All the curves show similar characteristics: instantaneous elastic strain on loading, a transition zone of decreasing creep rate and eventually, an incipient steady creep region. As it was expected, higher applied stress leads to larger creep strain. In Figure 2, the creep strain experienced by the unfilled matrix at 60 min testing was plotted as a function of the applied stress (testing temperature = 30°C). If the response of the material is in the linear viscoelastic range (small deformations), the relation between stress and strain is linear, since the compliance (strain/stress) depends only on time (which was selected as 60 min) and not on the magnitude of the deformation. Thus, from the analysis of the isochronous tests, a stress of 7 MPa was selected to

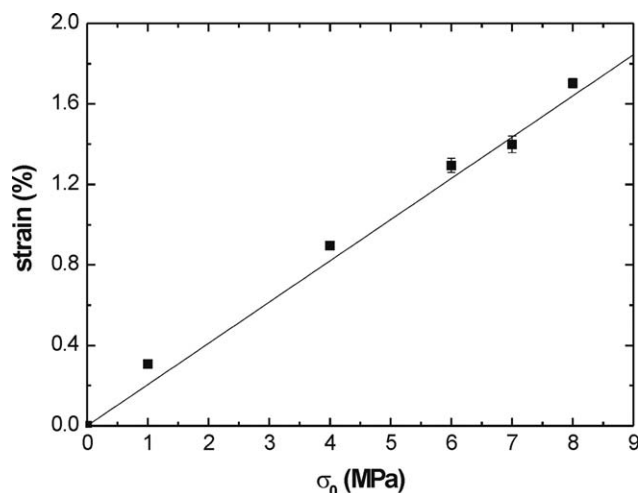


Figure 2 Creep deformation of unreinforced linseed oil based polymer after 60 min of applied load at 30°C.

perform all the rest of the creep tests, ensuring testing all the samples in the linear viscoelastic range.

Effect of the wood flour addition

The final properties of composite materials depend on the individual properties of the components as well as on the interactions developed at the interface. Figure 3 shows the effect of the incorporation of wood flour to the linseed oil-based matrix on the creep behavior at 20°C [Fig. 3(a)] and 30°C [Fig. 3(b)]. The addition of 20 wt % of particles reduces significantly the deformation of the material as compared with the neat polymer, as it was expected due to the higher rigidity of the filler/reinforcement. By further increasing the filler/reinforcement concentration to 30 wt %, an additional decrease of creep deformation is observed, but the incremental effect is smaller.

In general, when the filler wetting and dispersion in the polymeric matrix are carried out efficiently, the rigidity of the composites increases with filler concentration. In the present case, the interaction filler-matrix is excellent, as it was previously reported,⁹ due to the H-bonds formed between the hydroxyl groups of the wood flour and the hydroxyl and carboxylic groups present in the synthesized resin. Thus, the creep resistance is expected to increase due to the presence of the strongly interacting wood flour, which reduces the mobility in the molecular segments of the matrix.

The creep behavior of materials at 10, 20, 30, and 40°C was modeled using Eq. (1) and the corresponding parameters were obtained from the best fitting curve. Figure 3(a) shows the experimental results at 20°C (points) and the fitted curves obtained applying the Bürgers model (solid line). Table I summarizes the values of the calculated parameters

obtained from the fitting of the experimental creep data of the composites containing different wood flour concentrations and measured at different temperatures.

At any given temperature, the values of all the parameters (E_0 , E_1 , E_2 , η_0 , η_1 , and η_2) increase with the wood flour concentration. These results are in agreement with the increased rigidity of the composites as the concentration of wood flour increased, analogously to the results previously reported for the bending properties of these materials.⁹ The nonrecoverable creep, represented in the model by the response of the dashpot connected in series, is inversely related to the viscosity η_0 . The results show that this parameter increases with wood flour content in correlation to the decreasing permanent deformation of the composites, which was attributed to the effect of the presence of the rigid particles. The instantaneous elastic deformation of the material is reduced as

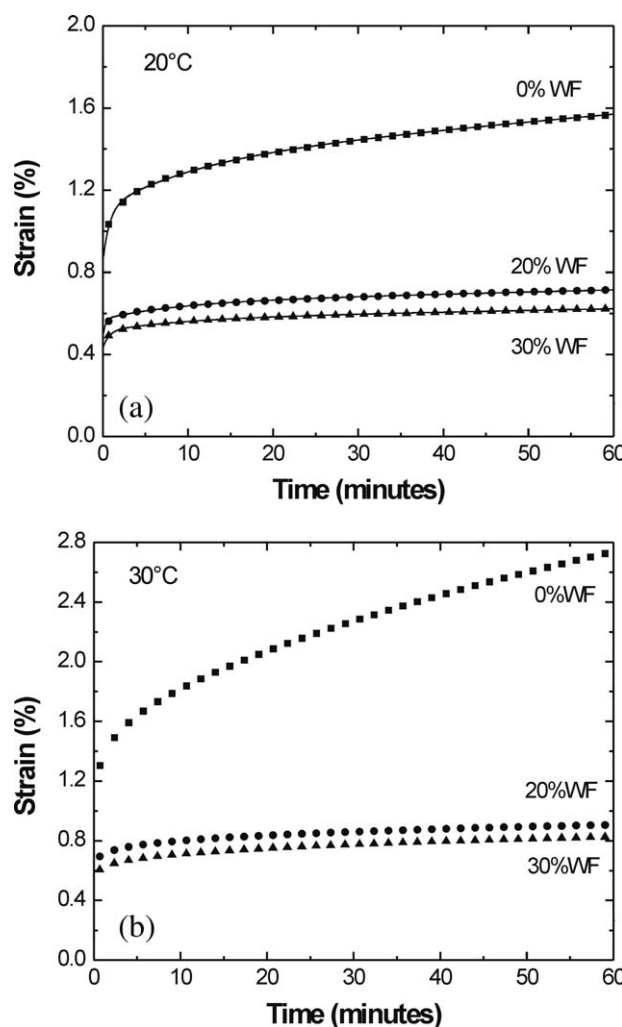


Figure 3 a) Experimental creep results of unreinforced polymer and wood flour composites at 20°C (points) and the fitted curve obtained applying the Bürgers model (solid lines). b) Experimental creep results of unreinforced polymer and wood flour composites at 30°C.

TABLE I
Bürgers and Power Law Fitting Parameters

Temp. (°C)	WF (wt %)	Bürgers model						Power law	
		E_0 (GPa)	E_1 (GPa)	E_2 (GPa)	η_1 (Pa·s)	η_2 (Pa·s)	η_0 (Pa·s)	b	c
10	0	0.87	4.74	5.88	3.54×10^{12}	6.40×10^{11}	2.14×10^{13}	0.6097	0.0805
	20	1.56	11.94	12.57	7.68×10^{12}	6.35×10^{11}	8.52×10^{13}	0.3995	0.0486
	30	1.67	17.42	15.70	11.25×10^{12}	13.18×10^{11}	9.13×10^{13}	0.3679	0.0452
20	0	0.82	2.89	2.71	1.94×10^{12}	1.26×10^{11}	1.14×10^{13}	0.6796	0.1010
	20	1.46	8.67	7.56	4.77×10^{12}	1.28×10^{11}	4.12×10^{13}	0.4335	0.0605
	30	1.63	11.54	8.35	6.85×10^{12}	3.51×10^{11}	5.20×10^{13}	0.3892	0.0570
30	0	0.80	1.41	1.37	1.04×10^{12}	4.02×10^{10}	2.93×10^{12}	0.5482	0.1909
	20	1.30	6.65	4.14	3.23×10^{12}	8.08×10^{10}	2.61×10^{13}	0.4450	0.0798
	30	1.52	6.17	4.21	3.96×10^{12}	9.08×10^{10}	2.86×10^{13}	0.4342	0.0779
40	0	—	—	—	—	—	—	—	—
	20	1.19	3.04	2.80	2.01×10^{12}	6.85×10^{10}	1.60×10^{13}	0.5213	0.1038
	30	1.30	2.98	2.79	1.87×10^{12}	7.14×10^{10}	1.78×10^{13}	0.4937	0.1048

more wood flour is incorporated into the composite and this is correlated with the modulus of the Maxwell spring in the model.

Figure 4 shows the comparison of experimental results and curves calculated using the power law model. Although the Bürgers as well as the power law models give very good fitting of the data, the power law model is simpler and requires less fitting parameters (Table I). However, it offers neither the possibility of prediction of other linear viscoelastic properties like the Bürgers models does, nor a good description of the recovery process. The nonlinear optimization fitting algorithm indicates that the parameter "a" of the power law model is close to zero, so that relatively small variations of the parameter "b" and "c" are observed if the Eq. (2) is simplified taking "a" identically equal to zero. The parameter "b" is in this case related to the elastic initial response of the material, and the parameter "c," related to the viscous creep response.

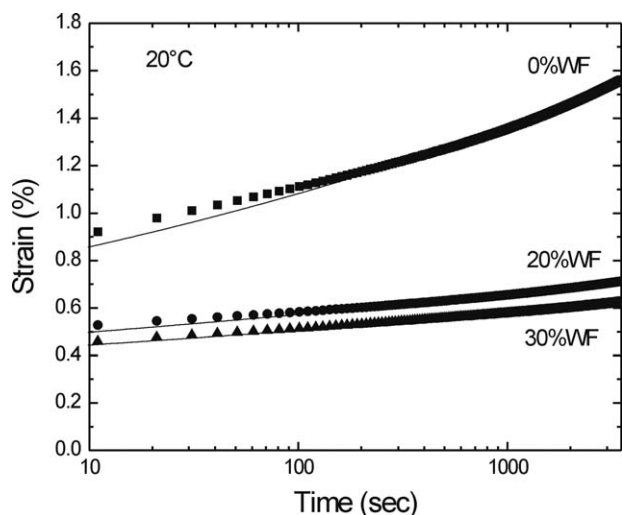


Figure 4 Comparison of experimental (points) and predicted (solid lines) creep using power law model for the unreinforced polymer and composites at 20°C.

Table I shows that parameter "b" decreases as more wood flour is incorporated in the polymeric matrix, which is due to the lower initial deformation associated with the higher rigidity of the composites. The same trend is observed in parameter "c," it decreases as wood flour content increases. This clearly denotes that the rate of viscous creep is very much reduced because of the addition of WF.

Creep and creep recovery

The complete recovery of the thermoset polymers is expected at equilibrium.¹⁷ In our case, when the samples are unloaded after 60 min testing, they recover instantaneously the initial elastic strain. However, a retarded slower recovery continues, leaving a constant permanent deformation. Thus, although low strains were used in this work, permanent deformations were recorded in all the materials, as can be noticed from Figure 5. This behavior can be attributed

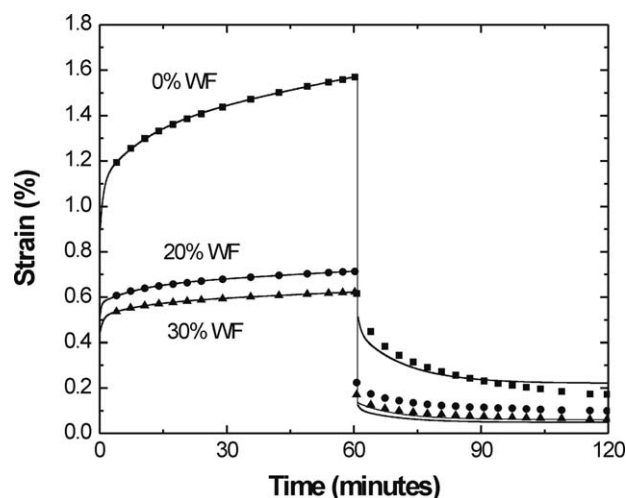


Figure 5 Creep and creep recovery of the unreinforced polymer and composites at 20°C. Experimental results (points) and Bürgers model (solid lines).

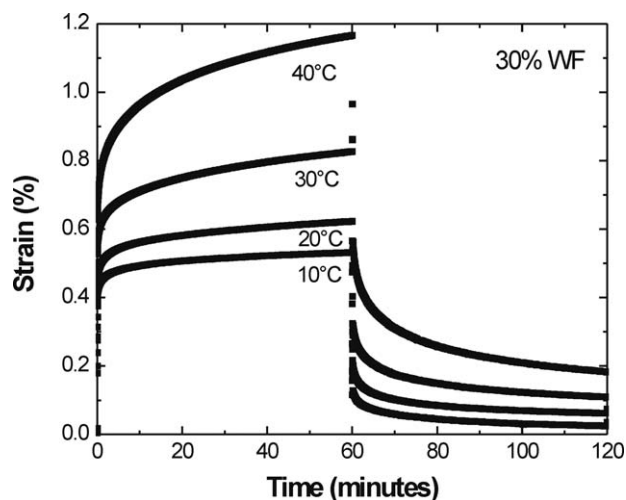


Figure 6 Creep of the composite with 30 wt % of wood flour at different temperatures.

to the nonreacted (dangling chains) or lightly cross-linked fatty acid chains that can be irreversibly deformed when the stress is applied and cannot recover their original conformations or locations as the load is removed during the recovery part of the test.¹⁸ As it was discussed in a previous publication, after the chemical modification of the linseed oil, highly reactive carbon-carbon insaturations are introduced by means of a maleinization reaction. However, up to two fatty acid chains per molecule with less reactive carbon-carbon double bonds can remain pendant in the crosslinked network having a plasticizing effect on the polymer. The wide thermal transitions measured by dynamic-mechanical tests are in agreement with a morphology corresponding to a heterogeneous network with various relaxation mechanisms.⁹ The creep rate after the initial response is reduced by the addition of WF, but as discussed above the viscous creep leads to the appearance of a nonrecoverable deformation. The consequence of WF addition appears as an increase of the viscosity, η_0 , of the Maxwell dashpot, related to the reduced mobility of the chains in the rigid filled composites and in agreement with the decreasing permanent deformation of the composites.

The parameters calculated from fitting the creep deformation (Table I) were used in Eq. (4) to predict the recovery part of the curves. The recovery predictions for the different composites are also shown in Figure 5. Considering that the recovery part of the test is a prediction (not a fitting), the agreement between theoretical calculation and experimental results is good.

Effect of temperature

In general, higher temperatures increase the creep rate limiting the applicability of the material. Figure 6

illustrates the strong temperature dependence of the creep behavior of the composite containing 30 wt % wood flour. The instantaneous deformation, as well as the viscous creep, increase with temperature, as it was expected because of the higher mobility of the molecules. While the composites prepared with 20 and 30 wt % of wood flour tested at 10, 20, 30, and 40°C were found to be in the linear viscoelastic range, the behavior of the unreinforced material at the highest temperature is outside this range (large deformations are reached during the test and the compliance of the material becomes a function of both time and level of deformation or stress during the last part of the test) and thus, it is not reported in Table I.

The nonlinear behavior at 40°C can be explained by reference to previous studies which showed that the glass transition temperature of the unfilled cross-linked polymer (recently prepared sample) was centered at 73°C (measured at the maximum of $\tan \delta$ in a dynamic mechanical test), exhibiting a broad transition that showed relaxation mechanisms already active at temperatures as low as 40°C, leading to large creep deformations.⁹

The Burgers parameters included in Table I show that as the temperature increase, E_0 , E_1 , E_2 , η_1 , η_2 , and η_0 values decrease. The rigidity of the materials decreases with temperature and consequently, the creep deformation increases.

The behavior of the Power law parameters (Table I) is also consistent with the previous discussion: higher temperatures produce higher “ b ” parameters due to higher initial elastic response. The parameter “ c ” also increases with temperature denoting that the rate of steady creep is also increased.

Time-temperature superposition and validation of the prediction for long term creep

The TTS principle was utilized to predict long-time creep behavior using a master curve produced from the short-term creep tests performed at different temperatures. Although this technique cannot be assumed to be applicable *a priori* in multiphase systems, it has been shown to be effective in the characterization of different composite materials.^{10,19–21} To predict long-term data, the creep data at various temperatures were shifted according to the TTS principle. The reference temperature selected was 20°C. The “master curve” constructed from short-term data (samples tested 2 years after preparation) for the composite containing 30 wt% wood flour is shown in Figure 7.

The same work was carried out on the same samples tested 5 years after curing and a master curve was also constructed. The creep of the composite sample containing 30% WF was also measured over

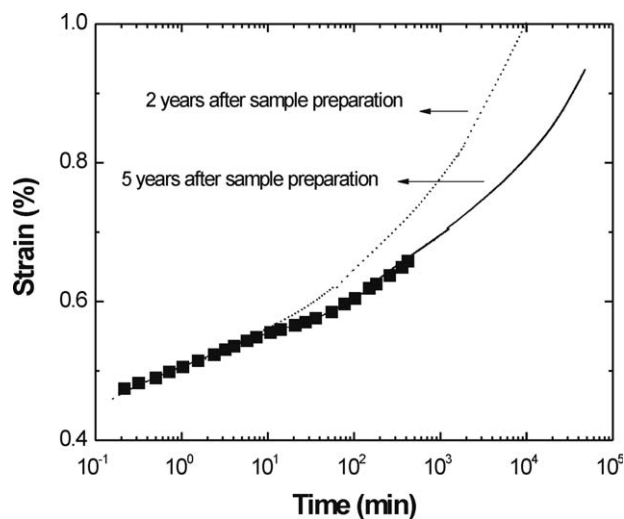


Figure 7 Short-term master curves (5-years aged sample, solid line and 2-years aged sample, dotted lines) and experimental results from long-term creep data (5-years aged sample, points) for the composite with 30 wt % wood flour. Experimental long term creep results were obtained at 20°C, which is the reference temperature for the two master curves.

a period of 7 h to check the prediction obtained from using the short time-master curve. Figure 7 also shows the comparison between the long term experimental deformation and calculated master curve (both corresponding to the 5-years-aged material). The agreement of predicted and experimental results is quite good, which indicates that the material is stabilized and thus, prediction from the master curve is possible.

The horizontal shift values, a_T , utilized for the construction of the two master curves were well correlated using the Arrhenius Eq. (5) as it is shown in

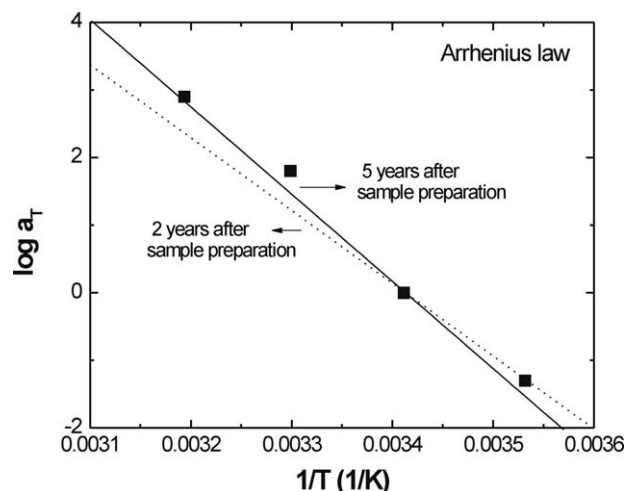


Figure 8 Experimental shifts ($\log a_T$) (points) used in the construction of the creep master curves and calculated Arrhenius' fittings (5-years aged sample, solid line and 2-years aged sample, dotted lines).

TABLE II
 E_a/R Value from the Arrhenius Equation as a Function of the WF Content

WF (wt %)	E_a/R (K)
0	21,385
20	23,252
30	24,808

Figure 8 for the composite with 30 wt % WF. The E_a/R values calculated from the Arrhenius equation as a function of the WF content (samples tested 2 years after preparation) are shown in Table II. The activation energy increases with WF concentration due to the increased creep resistance resulting from the addition of the rigid particles. The effect of aging is discussed in the following section.

Aging effect

The effect of room temperature aging on the creep response of the 30 wt % composite was evaluated by comparing the performance of samples tested 2 years and 5 years after curing. The experimental creep curves obtained for the composite are shown in Figure 9. For all the testing temperatures, it is clear that the creep deformation decreases as the time after sample preparation increases, which was attributed to aging effects, as it was reported in a previous work focused on linseed oil based thermoset.^{22,23} It is known that the highly unsaturated linolenic acids in the linseed oil are responsible for the drying properties in this vegetable oil and the reason why it has been widely used in the painting industry.^{6,7} Even after chemical modification by glycerolysis and maleinization, carbon-carbon double bonds from the original fatty acid chains remain in the

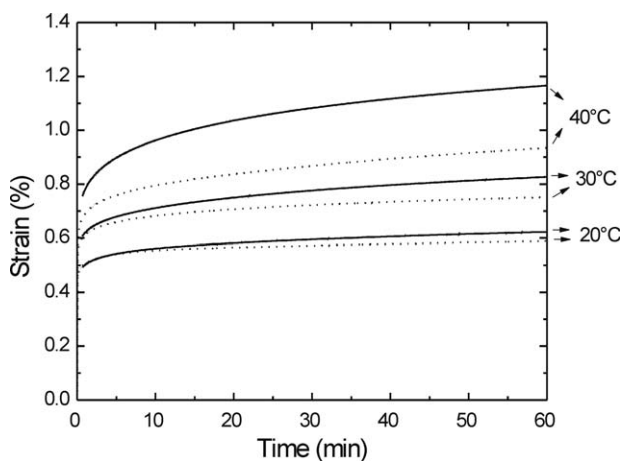


Figure 9 Experimental creep results for the composite with 30 wt % wood flour tested at different temperatures and different time after preparation: Solid lines: 2 years; dotted lines: 5 years.

polymer structure. The action of atmospheric oxygen on these unsaturations produces chemical changes by slow oxidative crosslinking reactions in these polymers, which in turn affect the properties of the cured materials.

The fittings of the 2 and 5-years shift factors, a_T , to an Arrhenius Eq. (5) for the composite with 30 wt % WF, leads to E_a/R values of 24,808 and 29,727 K, respectively. The increase in activation energy with time supports the fact that aging increases the creep resistance of the material, in agreement with the above discussed characteristics of drying oils.

CONCLUSIONS

The creep behavior of new polymers and composites based on linseed oil resins and wood flour was studied. Short-time creep results showed that the creep deformation is significantly reduced with the incorporation of wood flour due to the excellent interaction fiber/matrix.

The power law and the Burgers models were able to describe the viscoelastic behavior of the unreinforced polymer and the composites. Two Kelvin-Voight elements were necessary to adequately fit the experimental curves obtained during creep and creep recovery. The simpler power law offered a good fit only of the creep part of the test.

A master curve was built using the time temperature superposition principle and it was used to predict long-term creep behavior of the 5-year aged 30 wt % composite.

The creep deformation of the samples decreases when they are tested at increasing times after curing. This effect was attributed to the aging of the linseed oil based polymer.

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