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Effects of temperature on the relaxation behavior of poly(lactic acid)

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A series of tensile loading–unloading and relaxation tests, under stretching and retraction cyclic deformation conditions, were conducted between room temperature and 50°C.

Poly(lactic acid)—PLA—is a bioabsorbable, biocompatible, and biodegradable polymer that is widely used in medical applications for the manufacture of porous scaffolds, bone-fixation devices, interference screws, drug-eluting stents, sutures, and suture anchors.[1–3] Despite the widespread use of PLA in biomedical applications, to the best of our knowledge, a comprehensive analysis of the relaxation behavior of PLA under cyclic deformation has not yet been performed. Such analysis is particularly required, however, because some PLA applications (i.e., composite sutures and suture anchors) are conventionally tested under such cyclic loading conditions.[4,5]

In this work,[6] we have therefore conducted a number of experiments on PLA under uniaxial tensile loading–unloading conditions, as well as relaxation tests under both tension and retraction. For the study, we purchased PLA Polymer 4042D (with density of 1.24g/m^3) from NatureWorks LLC and used an injection-molding machine to mold the material into tensile dumbbell-shaped specimens. In addition, we used an Instron 5568 universal testing machine to perform the mechanical tests in accordance with ASTM standard D-638 at a range of temperatures between room temperature and 50°C. In total, our experimental program involved four series of loading–unloading/relaxation tests (using a cross-head speed of 1mm/minute) at temperatures of 23, 30, 35, 40, 45, and 50°C.

In the first series of tests (i.e., loading–unloading), we stretched a PLA specimen up to a maximum strain (ε_{max} of 0.015 and unloaded it with a minimum stress (σ_{min}) of 1MPa. From the results (see Figure 1) we can draw a number of conclusions. First, we find that the effect of temperature (T) on the mechanical response is relatively weak at T≤35°C, but becomes noticeable at temperatures above this threshold. We also observe that in the low-temperature region (i.e., T≤35°C), the stress–strain curves are similar and the residual strain (ε_{min}) is small.

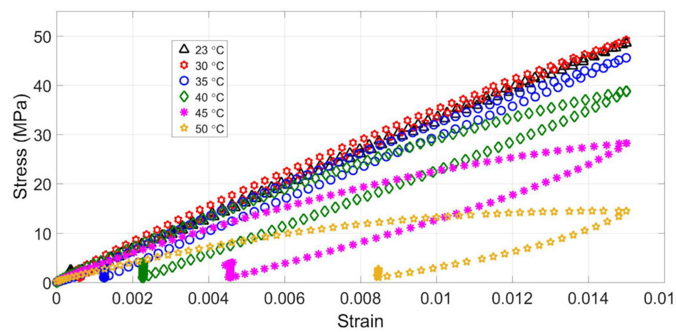

Figure 1. *Experimental results from loading–unloading tests of poly(lactic acid), PLA, at various temperatures (i.e., 23–50°C). For these tests, the sample was stretched with a maximum strain (ε_{max}) of 0.015 and unloaded with a minimum stress (σ_{min}) of 1MPa.*

In contrast, in the high-temperature region (T≥35°C), the loading and unloading paths are substantially different, and the ε_{min} is close to ε_{max}.

For the second test series (relaxation under retraction), we also stretched the sample with ε_{max} of 0.015 and retracted it with σ_{min} of 1MPa. We then fixed the strain and monitored the evolution of the stress (σ) with time (t). The stress–time curves we thus obtained (see Figure 2) show a strong temperature effect for the relaxation behavior of PLA. Our results indicate that in the low-temperature region, stress increases monotonically with relaxation time (inverse relaxation). In the high-temperature region, however, we find that the σ–t dependence becomes non-monotonic (mixed relaxation), with the position of the stress peak decreasing markedly with T.

The results from our third series of tests (loading/partial unloading–relaxation) are shown in Figure 3. For these experiments, we again stretched the sample with ε_{max} of 0.015. We also retracted the specimen with a σ_{min} that was about 0.5 times σ_{max} (we conducted the tests at σ_{max} of 25, 24, 22, 20, 12, and 8MPa). From these measurements, we observe mixed relaxation in the low-temperature region, but only

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simple relaxation in the high-temperature region. In addition, at temperatures below 35°C, the position of the peak in the relaxation diagrams decreases strongly with T. On the basis of this result, we hypothesize that mixed relaxation occurs at all temperatures, but that the temporal length of the peak conditions in the high-temperature region is shorter than one second. Our results also indicate that the evolution of stress with relaxation time is insignificant at T≤35°C.

In the final test series (relaxation under tension)—see Figure 4—we stretched the sample with $\varepsilon_{\max}$ of 0.015 (as in the previous series), but did not subject it to any unloading. The results show that at all temperatures σ decreases monotonically with t. Furthermore, we observe that this decay is rather modest in the low-temperature region, but that it becomes pronounced at temperatures below 35°C. We also find that given a specific relaxation time, an increase in temperature gives rise to a strong decrease in stress.

In summary, we have conducted a series of tensile loading–unloading and relaxation tests on PLA samples at different temperatures (up to 50°C). Overall, we note two characteristic features of

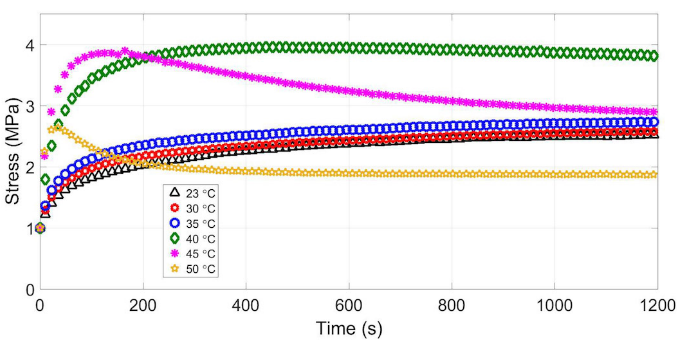

__Figure 2.__ Results (stress as a function of relaxation time) from the relaxation under retraction tests for PLA, at a range (23–50°C) of temperatures.

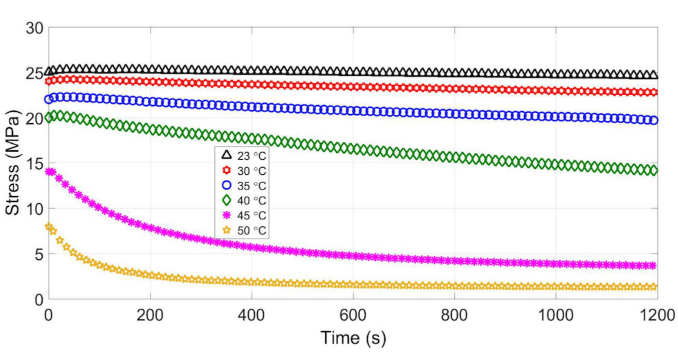

__Figure 3.__ Experimental data (stress versus relaxation time) from the PLA loading/partial unloading–relaxation tests (at 23–50°C).

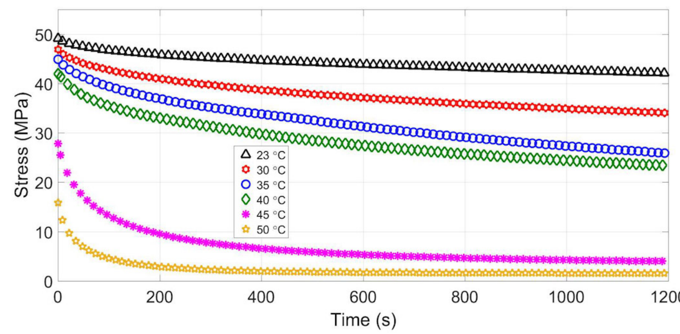

__Figure 4.__ Stress–relaxation time data obtained during the PLA relaxation (under tension) tests at 23–50°C.

the time-dependent response of the PLA samples. First, we observe a change in relaxation evolution—from monotonic decay (simple relaxation), to non-monotonic decay (mixed relaxation), to monotonic increase (inverse relaxation)—when the minimum stress under retraction decreases (at constant temperature). We also find that—with increasing temperature—the inverse relaxation after unloading (i.e., to zero stress) evolves into mixed relaxation, with a pronounced shift of the peak position to smaller relaxation times. We have also derived constitutive equations for the observed PLA mechanical behavior and have used numerical simulations to verify the ability of our model to predict the time-dependent response of the polymer under cyclic deformation conditions.[6] As part of our future work, we will conduct creep and cyclic fatigue tests at high temperature to provide detailed information about the damage behavior of PLA.

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