

Creep Enhanced Adsorption of Water or Aqueous Zinc Chloride Solution Increases the Creep Rate of Nylon 6,6

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ABSTRACT: The creep behavior of nylon 6,6 at 21°C was significantly altered when the local “dry” environment was changed to water mist or an aqueous zinc chloride mist. Nylon 6,6 was found to exhibit logarithmic creep because the relation between the log of the strain rate and the creep strain was linear with a negative slope. The effect of changing the creep environment from dry to wet, with the addition of moisture from an ultrasonic humidifier was to decrease the negative slope by 50–70% within 5–10 min. This effect could be interpreted as a decrease in modulus, which allowed for easier creep deformation. Based on the stress-free diffusivity of water in nylon and the dimensions of the test sample the time to saturate the sample was estimated to be about 100 h. Therefore, there appeared to be synergism between the creep deformation and the environment that dramatically enhanced the rate of saturation and slowed the decrease in the creep rate. The tentative explanation provided is that the aqueous solutions, by binding to the hydrogen bonds in nylon, are dragged into the sample during creep deformation, and the dragged-in aqueous solution then plasticizes nylon. This is analogous to the conclusion in another recent study that showed that deformation, during a hardness test, in the presence of aqueous zinc chloride, transported the solution species deeper into the sample than could be reasonably explained by ordinary diffusion processes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 494–497, 2001

Key words: creep; diffusion; moisture; ionic transport; hydrogen-bonded polymers

INTRODUCTION

The absorption of water by nylon decreases the modulus and yield stress, lowers the transition temperature, T_g , and increases toughness in proportion to the amount of water absorbed.^{1–3} The creep modulus of nylons is also lowered by water.⁴ Aqueous $ZnCl_2$ solutions decrease the modulus and yield stress more than water alone.^{5,6} The relevance of salt solutions lies in the fact that they can cause stress cracking of nylon by a plas-

ticization process,⁷ and when dehydrated, the residual salt content increases the modulus and yield strength and decreases the fracture toughness.⁶

A synergism between deformation and the uptake of water or salt solution was first demonstrated recently by Donovan.⁸ This work showed that indentation (i.e., a hardness test) of nylon 6 in the presence of aqueous $ZnCl_2$ solution decreased strain to failure by an order of magnitude during subsequent tensile deformation. When the same indentation was conducted in air, or when a drop of $ZnCl_2$ solution was placed on a smooth surface of the nylon 6 sample for the same time as it took to indent the sample, there was no effect

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on subsequent tensile deformation. In other words, localized plastic deformation by itself, or ZnCl_2 solution by itself did not affect tensile behavior, but when acting together, the effect was dramatic even though the indentation exposure time was the order of a minute or less. This study was reminiscent of a similar effect that has long been observed for the case of exposure of alloys to hydrogen containing environments. The role of plastic deformation in "dragging" hydrogen deep into the bulk of the alloys is now fairly well established.⁹⁻¹¹ Donovan⁸ concluded that there was a similar effect here, namely, that water and ZnCl_2 was being dragged into the polymer by a plastic deformation process. This result has major implications for mechanical behavior of polymers subjected to different environments. Localized deformation can drag the environment deep into components and cause changes in bulk mechanical properties, such as plasticization or embrittlement, within short time periods.

The following study further investigates the question of drag of environmental species into the bulk of polymer specimens by plastic deformation. In particular, we investigate whether drag can occur, not just under conditions of intense localized deformation, but also when slow bulk deformation occurs, as during creep. This is particularly important because many polymers experience measurable creep under normal service loads, even at ambient temperature. What role can this play when exposure to environments are involved? Accordingly, we have investigated the changes in creep deformation characteristics when water or water containing ZnCl_2 was introduced in the middle of an ongoing creep test of a nylon 6,6 sample to ascertain whether there was evidence of deformation related drag.

EXPERIMENTAL

Standard $\frac{1}{2}$ " \times $\frac{1}{8}$ " cross-section nylon 6,6 tensile samples of 2" gage length were first dried in a vacuum oven at 60°C for approximately 18 h. The samples were then tested in an Instron (model 4411) tensile test machine at a constant load corresponding to an initial applied stress of 50 MPa. The macroscopic yield stress for this material was about 70 MPa.¹² The strain was measured by an Instron extensometer attached to the gage length of the specimens. The specimens were surrounded in a sealed plastic enclosure that was connected to a household humidifier that provided a stream of

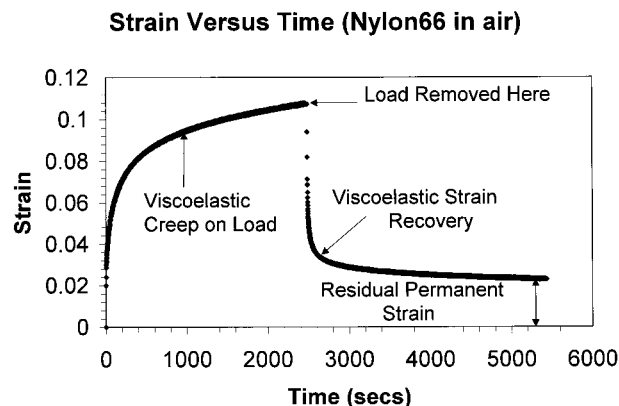


Figure 1 Strain vs. time of nylon 6,6 in air environment at a constant applied stress of 50 MPa.

ambient temperature water mist or water mist containing ZnCl_2 . The ZnCl_2 containing mist was produced by filling the humidifier with a 0.17 *N* solution of ZnCl_2 . Measurement of the mist temperature indicated that it was within 1°C of the measured ambient temperature. The humidifier was turned on after the first 10 min of creep at ambient temperature. Exposure to the vapor was then continued for a period of 30–40 min, after which the load was removed and the strain recovery of the specimen was monitored in the presence of the environment. Strain data was acquired by a computer using a standard Labview software program. Three samples were tested: one in ambient air with no exposure to mist, one exposed to water mist alone, and a third exposed to a ZnCl_2 containing mist.

RESULTS AND DISCUSSION

Figure 1 shows the baseline, or reference, creep, and strain recovery behavior in the absence of exposure to mist from the humidifier. The initial elastic strain was about 3%, consistent with previous results,¹² while the creep strain was substantially more. As can be seen, when the load was removed, much of the creep strain was recovered, indicating that it was viscoelastic in nature, while the nonrecoverable, or viscous, component was found to be about the same as the elastic strain. What was notable (see Fig. 2) was that when the natural log of the creep strain rate was plotted as a function of the creep strain, a straight line behavior was observed, which indicated that the creep strain rate dropped exponentially as the creep strain.

Nylon 6,6 Ambient Air Environment

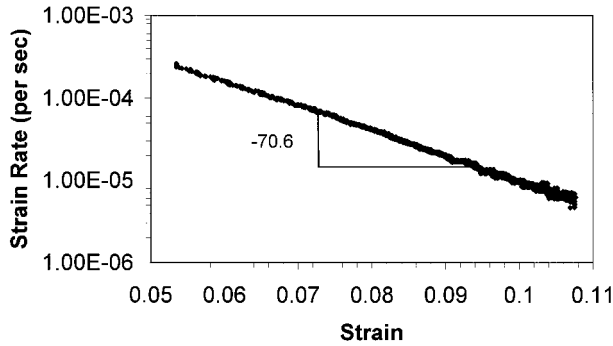


Figure 2 A semilog plot of the strain rate vs. strain during the loading phase of nylon 6,6 in air (shown in Fig. 1). The slope of the straight line of -70.6 was obtained by linear regression of all data shown.

Our results indicated that the slope, S , of the curve in Figure 2 can be given by

$$S \approx E/\sigma \quad (1)$$

Where, E is the Elastic Modulus ($3.3\text{--}3.5 \text{ GPa}^{13}$) and σ is the applied stress (50 MPa). This can be seen by comparing this ratio with the value of the slope, S , indicated on Figure 2. A smaller value for S would mean a smaller decrease in the creep rate with creep strain, that is, the material behaves in a more plasticized fashion. Because a more plasticized material is known to have a smaller modulus,⁸ eq. (1) is, therefore, physically consistent. In what follows, Figure 2 is used as a reference to compare the effects of water and ZnCl_2 solution on the creep process.

Figure 3 shows the semilog plot of creep rate versus strain, corresponding to Figure 2, but for the case when water mist is introduced. The arrow on the figure indicates when the mist was introduced into the plastic enclosure. It is evident that the data shows a linear behavior prior to water exposure just as in the case of Figure 2 when testing was done in air. Once water is introduced, there was transient increase in creep rate that, within 5–10 min, restabilizes to a linear relationship with a new but distinctly smaller slope. The initial slope and the restabilized slopes are both shown on the figure. The initial slope prior to water exposure was about 14% lower than was found in Figure 2. Using eq. (1), the initial slope prior to water exposure gave a modulus of 3 GPa for nylon 6,6, which is still within the scatter band for the elastic modulus of nylon 6,6 in nor-

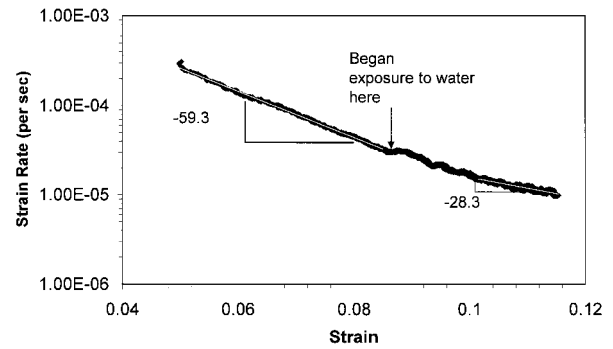
Nylon 6,6 H₂O environment

Figure 3 A semilog plot of the strain rate vs. the strain during the test where water mist was introduced at the point in time indicated by the vertical arrow in the figure. The slopes before and after water introduction, obtained by linear regression, are indicated on the figure. See text for discussion.

mal ambient air. However, it is notable that within a few minutes of water mist exposure the slope of the line decreased by 52%. The lower restabilized slope corresponded to a modulus value of only 1.4 GPa , significantly below the modulus range for nylon 6,6 in air. This indicated a significant degree of plasticization of nylon 6,6 as a result of water absorption that is consistent with previous studies of plasticization of the polymer by moisture.

Figure 4 is the corresponding plot for the case when water mist containing ZnCl_2 was intro-

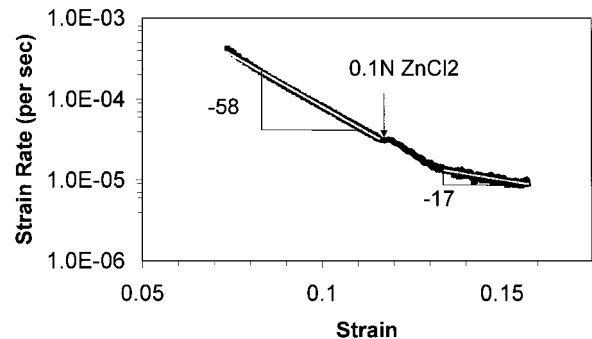
Nylon 6,6 0.1N ZnCl₂ solution

Figure 4 A semilog plot of the strain rate vs. strain as was done in Figure 3, but this time the arrow on the figure indicates when the specimen was exposed to water mist containing ZnCl_2 . Observe the much greater decrease in the magnitude of the slope with exposure to the ZnCl_2 containing water mist when compared to Figure 3 for water mist alone. See text for discussion.

duced during creep. Once again, for this case, the initial slope was within the expected scatter. However, once the ZnCl_2 containing mist was introduced, the slope decreased by 71%, giving a modulus value of only 0.85 GPa using eq. (1). Thus, there was a 50% larger effect on softening of the nylon 6,6 polymer by ZnCl_2 solution than by water alone. In an earlier independent study,⁸ the elastic modulus was found to decrease by an additional 50% in ZnCl_2 solution when compared to that by water alone. Our result is remarkably consistent with this previous result, and, furthermore, provides additional support for the applicability of eq. (1).

The observation of plasticization in and of itself is not new, although its manifestation in creep does appear to provide some new insights. What is unique about the present results is the kinetics of the response when water is introduced. The diffusivity of water molecules into nylon is $14 \times 10^{-13} \text{ m}^2/\text{s}$ at 40°C . In the presence of 1 *N* ZnCl_2 this value is about $4 \times 10^{-13} \text{ m}^2/\text{s}$. Using this value for a $\frac{1}{8}$ -inch thick sample, bulk penetration would be predicted to require 100–400 h at 40°C . Thus, the observed changes in the bulk creep response (on the order to 5–10 min, as shown in Fig. 3 and Fig. 4) cannot be rationalized as occurring due to normal diffusion of water into the samples. We conclude that the water molecules were dragged into the bulk rapidly by the molecules as they displaced during the creep process. We believe this is a plausible process because both water and water containing the ZnCl_2 are polar groups and can attach to the hydrogen bonds on the nylon molecules. The transient period observed in Figure 3 and Figure 4 just after the environment is introduced is then the period when water and ZnCl_2 are being dragged into the sample and the bulk has not yet been saturated. Once saturation occurs, a new (and lower) slope would be observed.

Further study is needed to understand the role of plastic deformation on enhancing transport of

solute species in polymers. For example, the charge to size ratio of the solute cation is known to play a role in both the diffusivity of aqueous salts and also the embrittlement of polymers by aqueous salts.⁸ The dependence of strain-induced transport on solute type could provide additional insights into the details of the transport mechanism. There are also questions as to how this process is influenced by the degree of crystallinity in the polymer, and what the apparent binding energies would be of the solutes to the displacing polymer molecules.

REFERENCES

1. Kim, H. G.; Harget, P. J. *J Appl Phys* 1979, 50, 6072.
2. Bianchi, E.; Valenti, B.; Greppi, G.; Tealdi, A.; Ciferri, A. *Macromolecules* 1976, 9, 117.
3. Frasci, A.; Martuscelli, E.; Vittoria, V. *Polym Lett* 1971, 9, 561.
4. Tang, H. H. Y.; Williams, H. L. *J Appl Polym Sci* 1990, 40, 495.
5. Burford, R. P.; Williams, D. R. G. *J Matl Sci* 1979, 14, 2881.
6. Li, H. PhD Thesis, University of Massachusetts at Amherst, Amherst, MA, (1996).
7. Dunn, P.; Sansom, G. F. *J Appl Polym Sci* 1970, 14, 1799.
8. Donovan, J. A. Indentation Enhanced Adsorption of Aqueous Zinc Chloride Prevents Drawing of Nylon 6, *Procd. of 10th International Conf. on Deformation, Yield and Fracture of Polymers*, (April 1997) UK, Inst. of Mat. London, 258–261.
9. Donovan, J. A. *Met Trans A* 1976, 7A, 145.
10. Nair, S. V.; Tien, J. K. *Met Trans A* 1985, 16, 2333.
11. Nair, S. V. In *Fracture Mechanics, Microstructure, Micromechanisms*, Nair, S. V.; Tien, J. K.; Bates, R. C.; Buck, O., Eds.; ASM International: Metals Park, OH, USA, 1989, pages 169–199.
12. Nair, S. V.; Wong, S.-C.; Goettler, L. A. *J Matl Sci* 1997, 32, 5335.
13. *Modern Plastics Encyclopedia*; McGraw-Hill: New York, 1988.