JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 7 (1996) 305–307

Nonlinear viscoelasticity of Hydrothane®

S. IANNACE, L. AMBROSIO, A. D'AMORE, L. NICOLAIS
Department of Materials and Production Engineering and Institute of Composite Materials Technology, University of Naples "Federico II", P.le Tecchio 80, 80125 Naples, Italy

The nonlinear viscoelastic behaviour of Hydrothane®, a hydrophilic polyurethane used for biomedical applications, has been studied. The material has been tested in stress-relaxation experiments in a range of deformation up to 25%. Isochrone curves have been predicted by using the rubber elasticity theory and separating strain and time effect. Stress–strain curves obtained at different strain rates have been interpreted introducing strain rate dependent scaling factors.

1. Introduction

The mechanical behaviour of elastomeric materials is usually characterized by dissipative processes that can be observed through stress-relaxation experiments. Based on the de Gennes tube model, or repeating chain model [1, 2], polymeric materials display a rapid relaxation followed by long time effects which are governed by the movement of the polymer chains in the non-equilibrium shape of the tube, and further relaxation is then caused by renewal of the tube as the chain exits the deformed non-equilibrium tube. The magnitude of the relaxing stress is related to the fraction of the chain segment remaining in the tube.

Analysis of the viscoelastic behaviour is greatly facilitated if the material displays linearity, and the well-known Boltzmann equation can be used to describe the stress dependence on an applied strain ε:

$$\sigma(t) = \int_0^t E(t-\tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau \qquad (1)$$

where $E(t)$ is the stress-relaxation function.

However, study of the viscoelasticity of rubbery polymers is generally complicated by nonlinear behaviour that can be related either to the stress versus strain nonlinearity, or to the dependence of the relaxation spectrum on the state of strain, or both. This implies that, beyond the maximum strain which determines the extent of linearity of the material, $E(t-\tau)$ has to be replaced by $E[(t-\tau), \varepsilon(t-\tau)]$, due to the dependence of the relaxation function on the state of strain [3].

If the two effects can be separated and the relaxation spectrum is assumed to be independent of the state of strain, then a generalized measure of strain can be introduced into the Boltzmann superposition integral and $E(t, \varepsilon)$ can be factorized as

$$E(t, \varepsilon) = E(t)\,h(\varepsilon) \qquad (2)$$

then the effect of time and strain can be uncoupled in a linear relaxation modulus $E(t)$ and a nonlinear strain dependent function $h(\varepsilon)$, leading to a simplified integral expression [3–5]

$$\sigma(t) = \int_0^t E(t-\tau)h(\varepsilon)\frac{d\varepsilon(\tau)}{d\tau}d\tau \qquad (3)$$

An analogous integral approach was proposed by Lodge [6] who used the Finger tensor as a measurement of the deformation. Wagner [7] introduced a damping function $h(I_1, I_2)$, which is a function of the scalar invariants I_1 and I_2 of the Finger tensor, and determined an analytical form of $h(\varepsilon)$ containing two adjustable parameters which can be determined by the best fit of experimental data.

Uncoupling of strain and time has been considered in order to analyse the nonlinear behaviour of soft natural tissue [8] such as tendons [9] and ligaments [10–12]. The slope of the relaxation function determines the relative degree of viscoelasticity of these particular systems. One of the main problems encountered in the theoretical analysis of viscoelasticity of such tissues, and in general of rubbery polymers, is the difficulty in performing an infinite-rate ramp-and-hold relaxation test [10]. As a result, the initial part of the stress-relaxation curve is lost and therefore the viscoelastic analysis determines only the long-term behaviour.

In this work we analyse the viscoelastic behaviour of Hydrothane®, a novel polyurethane with hydrophilic characteristics and with good biocompatibility due to the absence of aromatic groups in the polymeric chain. Because of this combination of properties, it has the appropriate features for potential application as matrix in the design and preparation of artificial soft tissue prostheses. In a previous work [13] it was shown that the nonlinear behaviour of the stress–strain curve of artificial composite systems can be attributed to variations in the geometrical configuration during the loading process. In order to explain the role of this matrix nonlinearity on the nonlinear

This paper was accepted for publication after the 1995 conference of the European Society of Biomaterials, Oporto, Portugal, 10–13 September.

behaviour of such composites the viscoelastic behaviour of Hydrothane® used for preparation of artificial prostheses was analysed. The time–strain separability has been checked and a scaling approach was used to predict the strain rate dependence of stress–strain curves.

2. Materials and methods

Hydrothane® was supplied by Polymedica Inc.; films were prepared by casting from a solution of tetrahydrofuran at room temperature. The films (300 μm thick) were then kept under vacuum overnight at 40 °C to allow complete evaporation of the solvent.

Stress-relaxation experiments were carried out at 37 °C by means of a Dynastat Instrument (Imass). The samples were subjected to an initial elongation and then the stress was recorded at times to 4000 s.

Stress–strain curves were obtained by an Instron 4202 on dumbell-shape samples with crosshead speeds which correspond to strain rates of 1 and 10 min^{-1}.

3. Results and discussion

The stress-relaxation experiments are presented in Fig. 1, where the engineering stress $\sigma(t)$ is reported versus $\log(t)$ for several stretch ratios λ. The data can be overlapped by a vertical shift, suggesting that the relaxation function can be considered independent of the state of strain.

The relaxation stress $\sigma(t)$ was interpreted using the following expression, which is equivalent to a series of Maxwell models, and was proposed by William and Watt [14, 15]

$$\sigma(t) = \sigma_0 \exp\left[-\left(\frac{t}{\tau}\right)^b\right] \qquad (4)$$

where $\tau = 2 \times 10^5$ is the mean relaxation time and the constant $b = 0.04$ takes into account the distribution of relaxation times.

The isochronal curves for time 10 s, 100 s and 1000 s, reported in Fig. 2, confirm the strain nonlinearity of the material investigated. The experimental data can be predicted, at low deformation, by the rubbery elasticity theory, which can be seen as a particular case of the more general stress–strain relationship developed by Rivlin [16, 17]. With the assumption of incompressibility and isotropy, he derived a generalized strain-energy function, which can be written in terms of the strain invariants:

$$W = \sum_{i,j,k=0}^{\infty} C_{i,j,k}(I_1 - 3)^i (I_2 - 3)^j (I_3 - 3)^k \qquad (5)$$

Considering only three terms of the above expression, the following relationship, which predicts reasonably well the stress–strain dependence of rubbers in a wide range of stretch ratios, can be written:

$$\sigma(\lambda) = \left(C_1 + \frac{C_2}{\lambda} + C_3\lambda^2\right)(\lambda - \lambda^{-2}) \qquad (6)$$

The Mooney–Rivlin equation [17] can be obtained if $C_3 = 0$ while for $C_2 = C_3 = 0$, it gives the equation of state for rubbery elasticity.

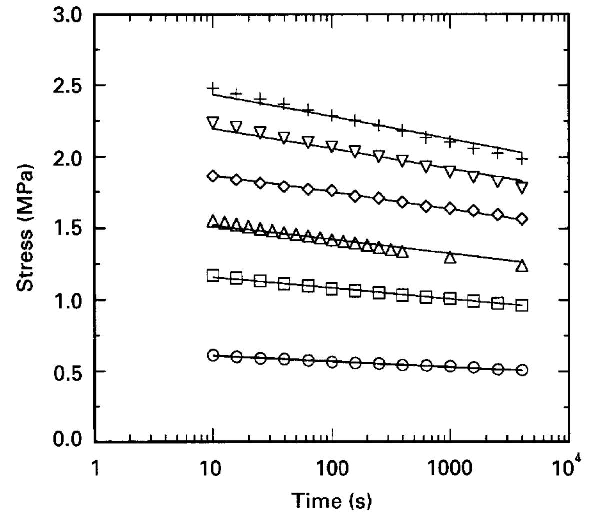

Figure 1 Stress relaxation data in simple extension for various values of stretch ratio λ: + 1.240; ▽ 1.170; ◇ 1.142; △ 1.106; □ 1.073; ○ 1.037.

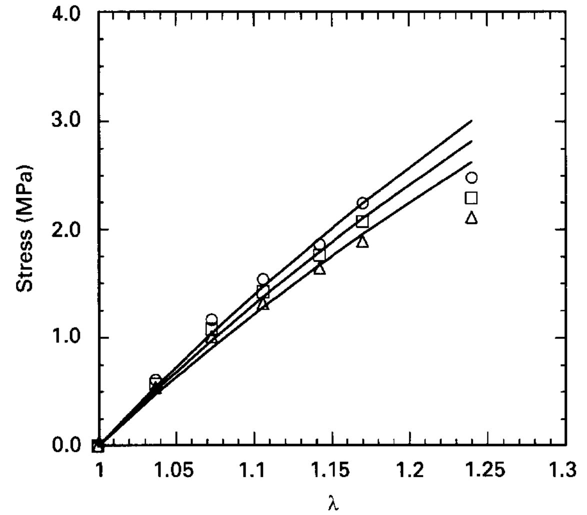

Figure 2 Isochrone curves obtained from the data of Fig. 1 at $t = 10$ s (○), 100 s (□) and 1000 s (△). Continuous curves were calculated using Equation 7.

Due to the low stretch ratio utilized in the stress-relaxation experiments, the isochronal curves reported in Fig. 2 were interpreted by the above equation with $C_2 = C_3 = 0$, with an additional term which takes into account the time-dependent effect:

$$\sigma(\lambda, t) = E(t)(\lambda - \lambda^{-2}) \qquad (7)$$

where $E(t)$ is a function of time as in Equation 4. The good prediction of the experimental results indicates that the assumption of strain–time separability can be considered valid, at least for the range of strain investigated.

Non-equilibrium stress–strain curves can be calculated from experimental stress-relaxation data by applying the Boltzmann superposition principle. However, the description of nonlinear behaviour requires knowledge of the function $h(\varepsilon)$, which has to be evaluated by vertically shifting the experimental stress-relaxation curves. Moreover, if the Wagner damping function $h(I_1, I_2)$ or any other analytical form of $h(\varepsilon)$ is used to fit the data, then stress-relaxation

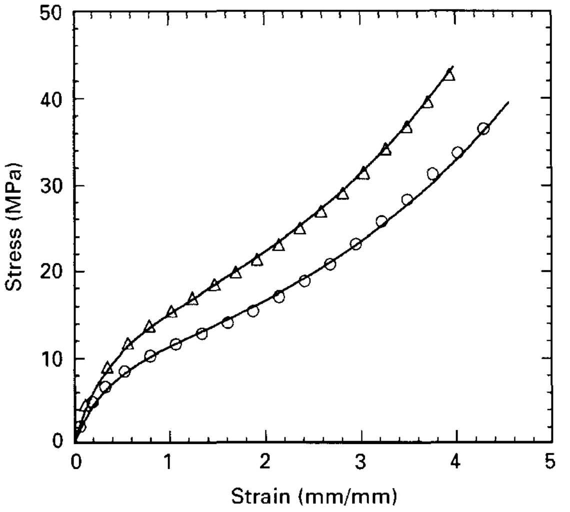

Figure 3 Comparison between experimental and predicted stress–strain curves. Strain-rate scaling effects were calculated using Equation 8: △ 10 mm^{-1}, ○ 1 mm^{-1}.

experiments must cover a wide range of deformation in order to predict the stress–strain curves.

Stress–strain curves at two different strain rates are reported in Fig. 3. The experimental data were interpolated using the complete form of Equation 6 multiplied by a scaling factor that takes into account the strain rate $\dot{\varepsilon}$:

$$\sigma(\lambda) = (\dot{\varepsilon}\tau)^b \left[C_1 + \frac{C_2}{\lambda} + C_3\lambda^2 \right] (\lambda - \lambda^{-2}) \quad (8)$$

Scaling factor $(\dot{\varepsilon}\tau)$ can be derived solving the Boltzmann integral (Equation 1) using for $E(t)$ an exponential function with a single relaxation time. Replacing the quantity (t/τ) with $(t/\tau)^b$ of the William–Watt equation, a generalized expression $(\dot{\varepsilon}\tau)^b$ for the scaling factor is obtained and has been used successfully for glassy polymers [15]. The application of such an approach to rubbery materials can be considered as a further generalization, and is successfully confirmed by comparing (Fig. 3) the experimental results with the theoretical predictions (Equation 8) obtained with $C_1 = 0.80$, $C_2 = 2.89$, $C_3 = 0.044$.

4. Conclusions

From the experimental data and comparison with the theoretical expressions, it is concluded that in the range of strain investigated, the effect of time and the effect of strain can be separated. Isochrone curves at small deformations can be predicted by equations derived from the theory of rubbery elasticity, in which the time-dependent function can be calculated independently by means of stress-relaxation experiments. These results can be then used in a generalized form of the Mooney–Rivlin equation to predict the strain rate dependent effect in stress–strain curves.

Acknowledgements

The authors wish to thank Ms M. Geremicca for her contributions to most of the experimental work and PolyMedica Biomaterial, Inc. for supplying the materials.

References

1. J. D. FERRY, "Viscoelastic properties of polymers" (Wiley, New York, 1980).
2. M. DOI and S. F. EDWARDS, "The theory of polymer dynamics" (Clarendon Press, Oxford, 1986).
3. C. M. ROLAND, *Rubb. Chem. Technol.* **62** (1989) 880.
4. W. V. CHANG, R. BLOCH and N. W. TSCHOEGL, *J. Polym. Sci.* **15** (1977) 923.
5. K. OSAKI and M. KURATA, *Macromol.* **13** (1980) 671.
6. A. S. LODGE, "Elastic liquids" (Academic Press, London, 1964).
7. M. H. WAGNER, *Rheol. Acta* **15** (1976) 136.
8. Y. C. FUNG, "Biomechanics: mechanical properties of living tissues" (Springer-Verlag, New York, 1993).
9. R. C. HAUT and R. W. LITTLE, *J. Biomech.* **5** (1972) 423.
10. R. C. HAUT, in "The anterior cruciate ligament: current and future concepts" D. W. E. A. Jackson, (Raven Press, New York, 1993).
11. S. L. Y. WOO, M. A. GOMEZ and W. H. AKESON, *J. Biomech. Eng.* **103** (1981) 293.
12. H. C. LIN, M. K. W. KWAN and S. L. Y. WOO, *Adv. Bioeng.* **3** (1987) 5.
13. S. IANNACE, G. SABATINI, L. AMBROSIO and L. NICOLAIS, *Biomaterials* (in press).
14. G. WILLIAM and D. C. WATT, *Trans. Faraday Soc.* **66** (1970) 80.
15. S. MATSUOKA, in "Failure of plastics", edited by W. Brostow and R. D. Corneliussen (Hanser, Munchen, 1986).
16. R. S. RIVLIN, *Trans. R. Soc. (London)* **A241** (1948) 379.
17. L. H. SPERLING, "Introduction to physical polymer science" (Wiley, New York, 1986).

Received and accepted
7 September 1995