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Validity of predictive models of stress relaxation in selected dental polymers

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ABSTRACT

Objective. The goal of this investigation was to assess validity of predictive models of stress relaxation in dental polymers when applied to extended master curves generated from short time experimental data by WLF time temperature superposition method.

Methods. The stress relaxation modulus changes with time at three different temperatures near the ambient body temperature were determined for selected mono-methacrylate (PEMA and PMMA) and dimethacrylate (bis-acryl) dental polymers. WLF time–temperature superposition procedure of logarithmic shift of the data from other temperatures to those at 37 °C was used to generate extended master curves of relaxation modulus changes with time. The extended data were analyzed for conformity to three different predictive models of stress relaxation including Maxwell, KWW stretched exponential function and Nutting's power law equation.

Results. Maxwell model was found to be a poor fit for the extended data in all polymers tested, but the data showed a much better fit for KWW ($0.870 < R^2 < 0.901$) and Nutting's ($0.980 < R^2 < 0.986$) models. The non-exponential factor β in the KWW function and the fractional power exponent n in Nutting's equation were both significantly different for PEMA based system when compared to that of PMMA and bis-acryl systems.

Significance. The mean values of β in KWW function and power exponent n in Nutting's equation for PEMA resin is consistent with significant viscoplastic contribution to its deformation under stress unlike in PMMA and bis-acryl resin systems. This may have significant bearing for PEMA use in medium to longer term stress-bearing applications even as a temporization material.

1. Introduction

Hookean springs and Newtonian dashpots are conventionally used to model the elastic, viscoelastic and viscoplastic mechanical behavior of polymers under applied stress or strain [1]. In this approach, the spring under stress represents elastic deformation, the dashpot viscous deformation, Maxwell element (spring and dashpot in series) a combination of elastic and viscoplastic deformation, and a Voigt element (spring and dashpot in parallel) time dependent recoverable (viscoelastic) deformation. Typical real polymers combine elastic, viscoelastic and/or viscoplastic deformation in their mechanical behavior under stress within the linear viscoelastic region, and two or more of these elements are therefore necessary to model the cumulative deformation behavior. Examples of such models for typical polymers are the three element standard linear solid model (which combines a spring

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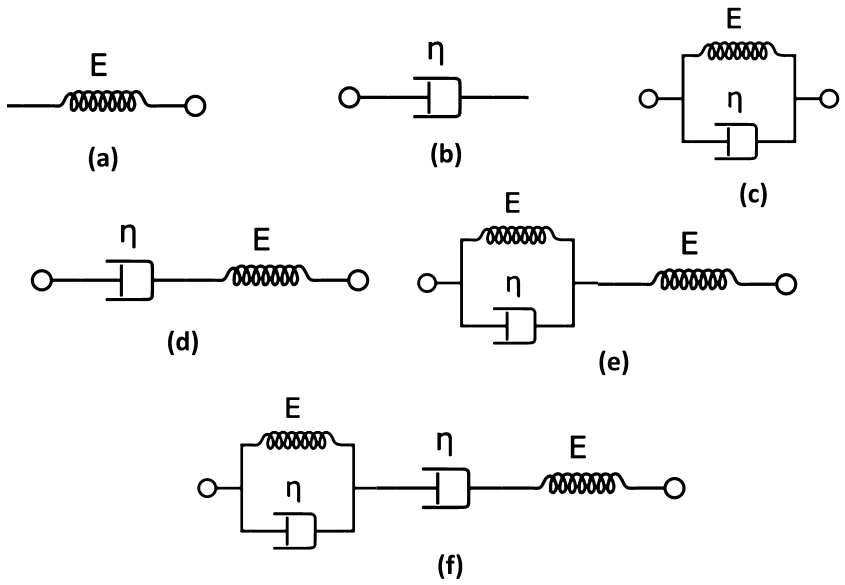

Fig. 1 – Typical mechanical models used to characterize polymer deformation (a) spring (elastic deformation), (b) dashpot (viscoplastic deformation), (c) Voigt model: spring and dashpot in parallel (viscoelastic deformation), (d) Maxwell model: spring and dashpot in series (elastic and viscoplastic deformation), (e) three element solid linear model: spring attached to a Voigt model in series (elastic and viscoelastic deformation) and (f) Burger's model: series combination of Voigt and Maxwell model (elastic, viscoelastic and viscoplastic deformation).

and a Voigt element), and the four element Burger's model in which a Maxwell and Voigt element are combined. Fig. 1 shows the different basic types of mechanical models used to model mechanical behavior.

The time–temperature superposition (TTS) is an important tool to estimate a longer term polymer viscoelastic behavior at a use temperature from short term measurements over a range of temperatures [2–4]. In this approach, data from short time isochronal measurements at different temperatures are used to extrapolate a much longer term isothermal set of data at a use (or service) temperature. Two equations are used to predict TTS behavior in polymers. One is the William–Landel–Ferry (WLF) equation and the other, the Arrhenius equation. Arrhenius equation is typically used to follow secondary transitions and melt viscosity changes, while, over the years, WLF equation has been successfully applied to follow time–temperature superposition in creep, stress relaxation and dynamic mechanical properties at and near the glass transition temperature in many polymers. We have previously shown that the dental polymers typically follow WLF equation for TTS near the body temperature, and that this is a very powerful approach to extend short time deformation measurements at different temperatures to assess longer term isothermal deformation events at 37 °C [5].

A valuable mechanical approach to study time dependent mechanical behavior of polymers is through a stress relaxation test. In this test, the polymer specimen is subjected to a step strain perturbation by the instantaneous application of a constant strain and the stress required to maintain the constant strain is monitored as a function of time. Taking Burger's model as a typical mechanical analog of a polymer mechanical behavior under stress, we can consider the Voigt element and the Maxwell element as potentially contributing to the time dependent stress changes in the polymer. The Burger's model contains two energy storage elements, namely the Voigt element and the spring in the Maxwell unit. It also contains one energy dissipation unit, namely the Maxwell dashpot. The stress dissipation that occurs in the stress relaxation test is associated only with the Maxwell unit since only an unconstrained dashpot can dissipate stress through energy loss. A constitutive relation between stress relaxation modulus ($E(t)$) and time (t) using the Maxwell model is therefore often used to characterize time dependent changes in stress relaxation modulus. This constitutive relation is given by:

$E(t) = E_o \cdot e^{(-t/\tau)}$, where $E(t)$ is the transient relaxation modulus at time t, E_o is the initial relaxation modulus immediately on application of deformation, τ the relaxation time. The Maxwell model is only obeyed when there is a single relaxation process. Most real polymers show a broad continuous relaxation spectrum, and this is attributed to the relaxation process occurring by an array of Maxwell units in parallel [6]. The Kohlrausch–Williams–Watt (KWW) stretched exponential relaxation function has been used to explain relaxation phenomena, and many aspects of its application has been highlighted in several theoretical, experimental and review articles [7–15]. In this approach, the relaxation function φ as a function of time ($\varphi(t)$) is given by $\varphi(t) = \exp-(t/\tau_{K\omega\omega})^{\beta}$, where β is a fractional power exponent known as non-exponential factor and $\tau_{K\omega\omega}$ is the KWW relaxation time. In the case of transient relaxation modulus changes with time, the ratio of KWW relaxation function at time t to that at $t = 0$ is given by, $E(t)/E_o = \exp-(t/\tau_{K\omega\omega})^{\beta}$. A $\log\{\log(E_o/E(t))\}$ vs. $\log(t)$ plot is expected to be linear with slope β and intercept $-\beta\log\tau_{K\omega\omega}$. The non-exponential factor β in the KWW stretched relaxation function is considered to control the breadth of the continuous relaxation spectrum responsible for the overall relaxation