Microindentation into an Epoxy Composition to Assess the Influence of Aging on Mechanical Properties

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ABSTRACT: This work aims to apply the microindentation technique for assessing the influence of two aging factors—long-term weathering and long-term laboratory aging—on the time-dependent mechanical properties of an epoxy composition. The linear theory of viscoelasticity was taken as a background for the problem, and the time-independent Poisson ratio value was assumed to simplify the assessment. Two nano/microindenters were used (Hysitron Triboscan and Nano XP Indenter) at two different laboratories. Four special time-dependent loading histories were applied: indentation under a step load, indentation under a constant load rate, indentation with a fixed depth of penetration, and indentation under a constant rate of penetration. The short-term histories of the viscoelastic compliance of a common epoxy composition, affected by 5-year weathering or laboratory aging, measured using a microindentation technique were compared to the data derived from standard macro measurements. The findings suggest that a qualitative assessment of the influence of the investigated aging effects on mechanical properties can be handled using short-term microindentation data, but the data has to be freed of possible attendant factors, especially of the influence of polishing procedures accompanying the microindentation techniques, before comparing it with standard measurement data. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2090–2094, 2012

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INTRODUCTION

The nano/microindentation technique developed over the past two decades has been demonstrated to be effective also for time- or rate-dependent materials.[1–3] The solution of the load-displacement relation of a rigid, axisymmetric indenter pressed into a homogeneous, linearly elastic and isotropic half-space is taken as fundamental, with its upgrade to a linear viscoelastic half-space.[3–5] Microindentation with sharp-pointed indenters leads to relatively large deformations beneath the indenter tip, and so it can be expected that nonlinear effects appear during indentation.[5,6] Linearly viscoelastic analysis should thus be considered a first-order approximation for measuring linearly viscoelastic functions. However, one important simplification is commonly accepted when applying indentation into these materials—because of the relatively short time measurements used, the Poisson ratio of the tested material is assumed to be constant.[3–6]

It has been confirmed that a quantitative analysis of time-dependent load-depth curves, based on linear viscoelasticity theory, successfully yields rheological functions such as creep compliance $D(t)$ and relaxation modulus $E(t)$. The question therefore arises whether it is also possible to apply the microindentation technique for assessing the influence of aging factors on time-dependent mechanical properties.

The linearly viscoelastic indentation solution of the load-displacement $[P(t) - h(t)]$ relation for the indentation of a rigid, axisymmetric conical indenter with effective face angle α—which has been taken as an ideal model of similarly shaped sharp indenters—into a homogeneous, linearly viscoelastic, and isotropic half-space defined by the shear creep compliance $J(t)$, and Poisson ratio ν leads to relation (1)[3] for the depth of penetration $h(t)$

$$h^2(t) = \frac{\pi(1-\nu)\tan\alpha}{4}\int_0^t J(t-\tau)\left(\frac{dP(\tau)}{d\tau}\right)d\tau. \quad (1)$$

The complementary expression for eq. (1), given in terms of the relaxation modulus $E(t)$, leads to the relation (2) for acting force $P(t)$

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$$P(t) = \frac{2}{\pi(1-\nu^2)\tan\alpha}\int_0^t E(t-\tau)\left(\frac{dh^2(\tau)}{d\tau}\right)d\tau. \quad (2)$$

Because of the conditions stated earlier, direct measurements of the time-dependent mechanical characteristics of a quasi-homogeneous quasi-isotropic material can be made using eqs. (1) and (2) for monotonic loadings in the course of penetration.

This work aims to review the correctness of the approach by determining the viscoelastic compliances of fresh and aged material using microindentation and comparing received results with standard data known for the material from our previous measurements.

Surfaces of all materials are commonly prepared for indentation. The adjustment of the samples surface to make them flat usually involves basic polishing, polishing with suspensions of different particle refinement, and wetting with water. Therefore, the influence of the applied polishing procedure is also briefly discussed.

Material

The selected characteristic representative of the viscoelastic material mentioned earlier is an epoxy resin mix consisting of solvent-free low-viscosity bicomponent pigmented systems on the basis of a low-molecular weight epoxy resin with a content of nontoxic reactive diluents, additives, pigments, fillers, and auxiliary admixtures, hardened by a cycloaliphatic polyamide. The quasi-homogeneous and quasi-isotropic material is used for surfacing a range of building substrates such as concrete, plaster, steel, and stone. It is well suited for the manufacture of self-leveling flooring top layers and can be blended with fillers to form toweled polymer mortar or polymer concrete mixes. The material is produced by the Czech firm COMING, join-stock company, Prague, with a trade name Comflor.

The samples were made by mold casting from one mixing, cured at room temperature, and postcured at 90°C for 4 h. This type of posture followed by slow cooling to laboratory temperature is indicated as rejuvenation (REJ). To assess the effect of aging (A), the physical aging time—5 years storage in a black box under laboratory conditions (LAs) or 5 years weathering [climatic aging (CA) according to the Czech Standard CSN 64 0771 "Outdoor weathering test of plastics"]—were identical for the corresponding series of measurements.

APPARATUS AND PROCEDURES

Microindentation

Two nano/microindenters with distinct loading possibilities, each equipped with a Berkovich indenter of effective cone angle α, were used at two different laboratories—the Hysitron Triboscan at the Czech Technical University in Prague (CTU) and the Nano XP Indenter at the University of West Bohemia (UWB) in Plzen. The reason for using two pieces of equipment at two different laboratories was partly to widen the time interval of the indentation creep from 50 s at CTU to 300 s at UWB and partly to check whether dissimilar test conditions (loads and loading rates) might influence the results. All tests were performed in LAs, with constant relative humidity and temperature control (T = 22–23°C and 50% relative humidity). The indentation proceeded mainly under a step load (an indentation creep test with a constant load)

$$P(t) = P_0 H(t) \quad (3)$$

where $H(t)$ is the Heaviside unit step function with series of 5 × 5 or 6 × 8 indents. The creep compliance $D(t)$ can then be directly deduced[3] from the equation

$$D(t)\frac{2h^2(t)}{\pi(1-\nu^2)P_0\tan\alpha}. \quad (4)$$

Equation (4) implies zero instantaneous compliance at time $t = 0$, because the displacement into the surface $h(t)$ is also zero at the time. An ideal step load history (4) cannot ordinarily be generated in laboratory tests. Instead, ramp loading is used with a short rise time t_0 and a constant load thereafter. The constant loads P_o and loading rates dP/dt were as follows:

10 mN and 10 mN/s with $t_0 \sim 1$ s and the indentation creep duration $t_c \sim 50$ s at CTU and 200 mN, 34 mN/s with $t_0 = 6$ s and indentation creep duration $t_c \sim 300$ s at UWB.

Because of these conditions, we reject from the analysis five times interval t_0 after the constant load is reached. It is assumed, however, that after passing this initial loading period, the creep compliance approaches values representing the linear viscoelastic behavior.

The following three monotonic time-dependent loading histories can be also applied for direct measurements of the time-dependent mechanical characteristics:

i. Indentation under a constant load rate, $P(t) = \dot{P}_0 t H(t)$, which leads, using eq. (1), to

$$D(t)\frac{4h(t)}{\pi(1-\nu^2)\tan\alpha}\left(\frac{dh}{dP}(t)\right). \quad (5)$$

ii. Indentation with a fixed depth of penetration (indentation relaxation), $h(t) = h_0\, H(t)$ with the relation to relaxation modulus $E(t)$[3,4]

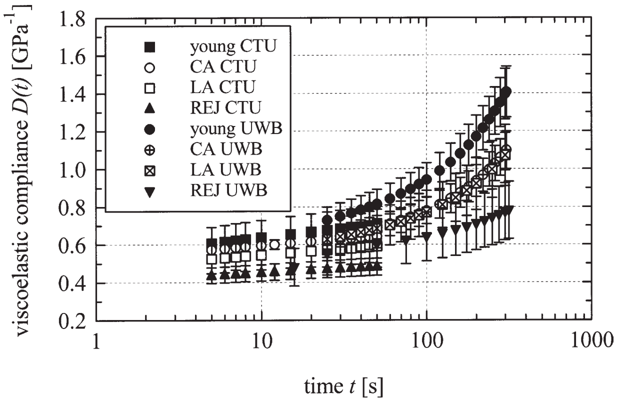

Figure 1 Short-term creep compliance histories $D(t)$ measured by instrumented indentation tests.

$$E(t)\frac{\pi(1-\nu^2)\tan\alpha}{2h_0^2}P(t) \tag{6}$$

and

iii. Indentation under constant rate of penetration v_0, $h(t) = v_0\ t$, which leads to the equation

$$E(t)\frac{\pi(1-\nu^2)\tan\alpha}{4v_0^2}\frac{d^2P(t)}{dt^2} \tag{7}$$

Application of the monotonic loadings with a constant load rate or a constant rate of penetration extends to shorter times the time interval for receiving reasonable data using microindentation[3,7] and so can partly compensate the loss of the corresponding data related to the application of ramp loading instead of step loading.

Four subgroups of samples were measured according to the purposes of the work:

a. samples immediately after postcuring, not influenced by physical or chemical aging (REJ)
b. samples after physical aging (LA)—5-year storage in a black box under LAs
c. samples after 5 years exposure to climatic factors (weathering) comprising daily and seasonal cycles (CA), and
d. "young" samples after physical or climatic aging for less than 1 year.

Standard measurements

Long-term experiments were performed on the same subgroups of samples in series comprising at least three samples at a stable temperature of 20°C with 60–250 days active loading.

The prismatic samples $4 \times 4 \times 12$ cm^3 were made by mold casting from a single mixing, cured at room temperature, and postcured at 90°C for 4 h (REJ). Compressive stress σ_o amounting to 0.2 of strength in compression σ_p was applied. The measured values enabled creep compliance D_c to be determined according to the equation

$$\begin{aligned} D_c(t) &= \varepsilon_c(t)/\sigma_0 \\ D(t) &= D(0) + D_c(t) \end{aligned} \tag{8}$$

where ε_c (t) is the viscoelastic creep strain formed for the duration of the constant stress σ_o. Total deformation $\varepsilon(t)$ is the sum of the elastic and inelastic parts $\varepsilon(t) = \varepsilon_e + \varepsilon_c\ (t)$ and Young's modulus $E(0)$ for temperature 20°C [$E(0) \approx 3.5$ GPa $\rightarrow D(0) \approx 0.286$ GPa^{-1}] is defined by the equation $E(0) = d\sigma_o/d\varepsilon_e$.

RESULTS AND DISCUSSION

Short-term creep compliance histories $D(t)$ of the material measured by instrumented indentation tests according to eq. (4) are shown in Figure 1. The empty circular marks hold for 5-year CA, the empty square marks indicate 5-year LA, the full triangle marks represent REJ material, and the others hold for young samples. Two groups of histories are presented—defined in the time interval from 5 to 50 s based on the CTU data and in the time interval from 25 to 300 s for the measurements at UWB. The values derived at two different laboratories under dissimilar conditions (loads and loading rates) correlate well. The ranking of the compliance data from the highest to lower values is as follows: young (check) samples, CA, LA, and REJ.

Long-term (250-day) histories of standardly measured viscoelastic compliance $D_c(t)$ are presented in Figure 2. The full circular and triangular marks hold for rejuvenated and young (check) samples, empty squares indicate the results for samples after CA, and empty circular marks hold for samples after LA. The ranking in a similar sequence is now: young (check) samples, REJ, CA, and LA. The differences

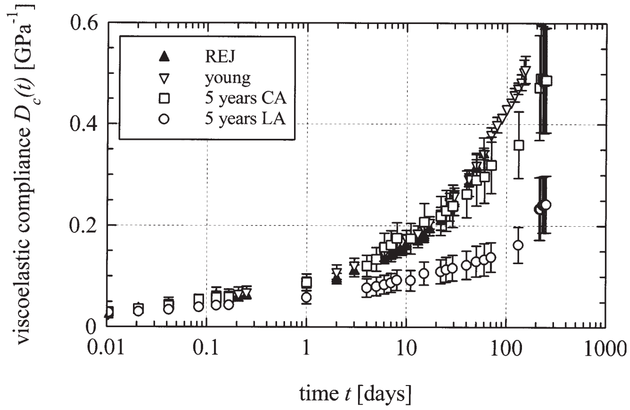

Figure 2 Long-term histories of standardly measured viscoelastic compliance $D_c(t)$.

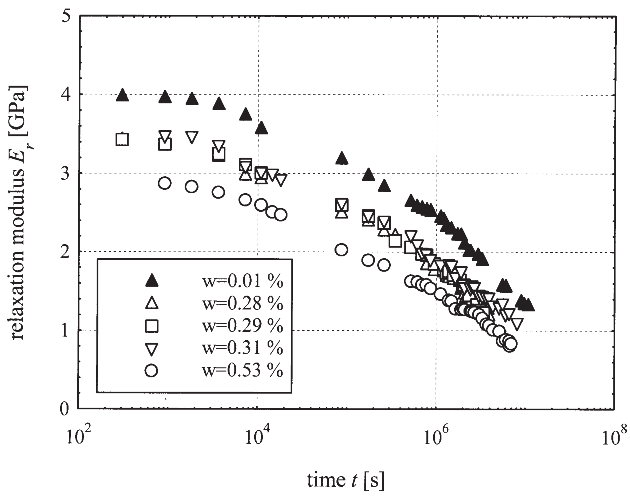

Figure 3 Histories of the relaxation modulus of the material at three different levels of moisture content w (%) and $T = 20°C$.

between the behavior of the young and REJ samples are negligible, and a more marked difference in viscoelastic compliance data among the tested types of samples is revealed for time data of 1 day and more. In comparison with the behavior of rejuvenated or young material, both climatic aging and laboratory aging have a more positive influence on the long-term data. Indoor applications with no fluorescent light seem to be optimal for the tested composition and the analyzed influence agents.

The main difference between the two viscoelastic compliance histories of microindentation and standard data is the position of the viscolelastic compliance values for the REJ samples. The reason lies in the polishing procedure accompanying microindentation. The surfaces of all groups of samples are influenced by the identical polishing procedure. The positive influence of REJ in Figure 1 is due to the postcure realized after surface polishing of a sample, which is attended by lower moisture content and accordingly lower compliance. Effects of moisture on the viscoelastic compliance of the tested epoxy resin have been measured by some authors of the work.[8] A modified result of their investigation is presented in Figure 3.

Two subgroups of samples were used for moisture effect measurements: (a) samples after postcuring, not significantly influenced by physical and chemical aging with moisture content $w = 0.01\%$ and (b) samples subjected to the programmed effect of moistening in distilled water at temperature $T = 20°C$. Lower moisture content leads to higher relaxation modulus values and consequently to lower viscolestic compliance. At the very beginning, the ratio between the relaxation moduli of the REJ and moistened samples reads as 1.4. This could clarify the results for rejuvenated samples, which are at first sight surprising (see Fig. 1).

The polishing procedure generally reduces the relaxation modulus values and, according to the Boltzmann inequality, increases the viscoelastic compliance values. This is documented in Figure 4 that compares the short-term histories of the relaxation modulus $E(t)$ defined from penetrations into a rough and polished surface of the tested material. The measurements were made[7] applying instrumented indentation tests with a fixed penetration depth {indentation relaxation according to eq. (6) or a fixed penetration rate [eq. (7)]}. Three different rising times t_0 ($5\ s \leq t_0 \leq 30\ s$) to the max load 10 mN and three different rates of penetration v_0 ($113\ nm/s \leq v_0 \leq 1691\ nm/s$) are indicated. Full square marks represent the results of indentation into a rough unpolished surface. The polishing that was used

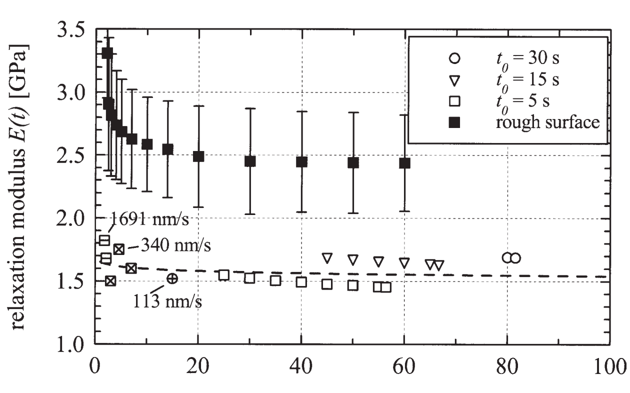

Figure 4 Comparison of relaxation modulus values of the tested material measured by instrumented indentation tests into a rough unpolished surface (full marks) and into a standard polished samples (all other marks).

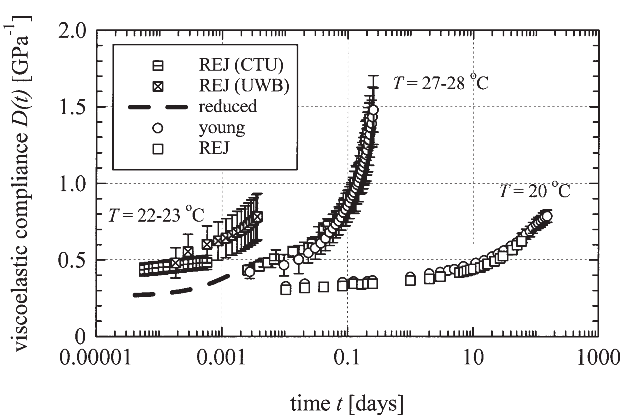

Figure 5 Histories of viscoelastic compliance $D(t)$ of rejuvenated samples measured by standard macro creep tests (empty marks) at two different temperatures and comparable data derived from instrumented indentation tests (crossed marks and dashed line) according to eq. (4) at CTU and UWB.

evidently reduces the relaxation modulus values of the tested material on an average 1.6 times in the relevant time interval and naturally increases the viscoelastic compliance values minimally in the same manner, taking into account the conservative form of the Boltzmann inequality. Values of relaxation modulus are weakly dependent on loading rates during the rise time, which indicates that a nonlinear viscoelastic response is involved.

Figure 5 shows the average viscoelastic compliance values of all comparable subgroups of rejuvenated samples including all tests that were carried out. The marks represent data from performed measurements, and the dashed line shows reduced values of the viscoelastic compliance defined from microindentation data with the application of the tested influence of a polished surface on the results. The figure also illustrates a relatively considerable influence of temperature on the measured characteristics and satisfactory agreement between standard and microindentation measurements when affecting factors are taken into account.

CONCLUSIONS

The courses of the short-term creep compliance histories of the tested material derived from microindentation data at two different laboratories under dissimilar conditions (loads and loading rates) correlate well. Both physical aging and climatic aging for less than 1 year have a negligible influence on the viscoelastic compliance values. A qualitative assessment of the influence of the investigated aging factors—long-term weathering or long-term laboratory aging—on the mechanical properties of the epoxy composite can be handled using short-term creep microindentation data, but the real time-delayed behavior needs long-term tests to make it evident. Physical aging (5-year storage in a black box under LAs) has the most favorable influence on the time-dependent mechanical properties. Short-term data defined using microindentation are influenced by the polishing procedures accompanying microindentation techniques and has to be freed from these effects before it is compared to the standard measurement data.

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