Introduction

Traditionally composites have been designed using trial and error methods which results in an expensive development process. This is particularly true for the development of manufacturing processes, where many expensive experimental loops are necessary before an efficient process is established.\(^1\)

Therefore, the present trend in composites design is towards employing virtual methods, in particular within the aerospace and transportation industry, which pushes the boundaries of virtual Computer Aided Engineering (CAE) towards new modeling areas. One such area considered here is the prediction of manufacturing induced residual stresses and their evolution with time, where a definition of a cure state-dependent viscoelastic model may lead to improved results.

The development of residual stress in composites during manufacturing is caused by several factors. Thermally induced residual stresses in composite materials, for example, are caused by the mismatch between coefficients of thermal expansion (CTE) of the matrix and the reinforcement fibers.\(^2\)\(^4\)

The magnitude of these residual stresses depends on the difference of CTE between the matrix and the reinforcements multiplied by the change in temperature \(\Delta T\). Because of the fact that the CTE for the polymer is higher than the CTE for the fibers, cooling down from the manufacturing temperature generate thermal residual stresses that are tensile in the matrix and compressive in the fibers. Another source of residual stress is the result of chemical shrinkage which is related to reduction of free volume of the matrix during curing.\(^5\) This happens when the polymer molecules undergo end linking reactions at elevated temperatures during curing, sometimes

Abstract

It is shown, using thermodynamically consistent linear viscoelastic material model that accounts for properties dependence on test temperature and cure state parameters, that for rheologically simple materials the cure and temperature related reduced times and shift factors are the same for all viscoelastic compliances, relaxation modulus, and Poisson’s ratio as well as for the storage and loss modulus. A necessary condition for that is that the cure and temperature parameters are affecting the reduced time only. This means that the Poisson’s ratio of polymeric materials, which for simplicity is often assumed constant, in fact exhibits a small dependence on time which is affected by temperature and state of cure.

In this work, the evolution of the viscoelastic Poisson’s ratio of the commercial LY5052 epoxy resin is studied in relaxation test subjecting the specimen to constant axial strain. Specimens at several cure states are studied and Poisson’s ratio, defined as the lateral and axial strain ratio, is shown to evolve from 0.32 to 0.44 over time. Moreover, the data confirm that the cure state-dependent reduced time controlling the Poisson’s ratio development leads to the same shift functions as those identified in DMTA tests for storage modulus. The latter measurements also confirmed that the total shift can be considered as a sum of two shifts in the frequency domain, which means that function for reduced time calculation can be written as a product of two functions: one dependent on the test temperature and another one dependent on the cure state.

Keywords

Poisson’s ratio, Viscoelasticity, Cure dependence, Time dependence, Stress relaxation

Cite this article

Sibin Saseendran, Maciej Wysocki and Janis Varna. Adv. Manuf.: Polym. Compos. Sci., doi: 10.1080/20550340.2017.1348002

© 2017 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Received 24 April 2017 Accepted 23 June 2017

DOI 10.1080/20550340.2017.1348002

Advanced Manufacturing: Polymer & Composites Science

2017 VOL. 3 NO. 3
in the presence of hardening agents or accelerators to form long and interconnected chains in three dimensions. This pulls together the molecules inward tightly as the polymer matrix goes from a liquid state into a solid. As a consequence of this process, the free volume of the matrix is reduced and this leads to shrinkage distributed across the entire volume of the part. While thermally and chemically induced strains constitute the bulk of the residual stresses in the composite, some studies also indicate tool-part interaction, moisture absorption and aging of the matrix as contributing factors after curing.

A commonly used approach in the determination of residual stresses is based on the Cure Hardening Instantaneous Linear Elastic (CHILE) model. Though the model is simple to characterize and implement, it is not clear how valid the assumption of its linear elastic behavior is and how large the introduced errors are. This is of concern especially when a majority of the composites do not behave in a linear elastic manner. Many investigations into the subject show that the material actually behaves in a viscoelastic manner. The question that arises from this is whether the material properties during curing are linearly or nonlinearly viscoelastic with respect to stress or strain level. However, since the strains that are encountered during the manufacture of composites are small, it can be assumed that the behavior is linear viscoelastic. Nevertheless, it is expected that similar to temperature, parameters of the state of cure will affect the rate of viscoelastic processes and therefore this also needs to be included into the linear viscoelastic material model.

In a previous study, a methodology to analyze the influence of the curing history on the viscoelastic storage modulus was developed. It was determined that the storage modulus depends on time (equivalent to frequency in a DMTA test), temperature and the degree of cure. Functions called “shift factors” were introduced to characterize this dependence. While this dependence is generally agreed upon and supported by experimental evidence for several properties like moduli, compliances, and relaxation and creep functions, it is not clear whether all these properties are affected by the same function(s) of the cure state. For example, the Poisson's ratio is still often, mostly for simulation convenience, considered time independent and under this assumption the influence of the cure state is rendered meaningless. Results in this paper will show that during manufacturing the Poisson's ratio of the matrix evolves and therefore including this phenomenon in studies dealing with fiber–matrix interaction would prove beneficial; in particular to studies where stress develops during the manufacturing process of composites.

Thus it can be safe to assume that Poisson's ratio for viscoelastic materials such as polymers and polymer matrix composites may be influenced by various factors like time, temperature, degree of cure and also the strain level. In comparison to other material properties, the viscoelastic behavior of Poisson's ratio is very complex and experimentally difficult to investigate. This is mainly due to the difficulty in measuring small transverse strains by common testing apparatus within a narrow strain range, selected to insure linear viscoelastic behavior with negligible irreversible strains. Several methods exist, direct and indirect, to measure the dependence of the Poisson's ratio on time, temperature, and strain. Direct measurements of the transverse and axial strains to get the Poisson's ratio can be performed by optical methods, using strain gages and/or contact extensometers. Limited accuracy is a common problem, for example, strain gauges record data from a rather local region comparing with the region covered by the axial extensometer. Glauling the strain gauge on partially cured resin specimen can also affect properties of the resin. The use of contact extensometers to measure the transverse strain is not recommended, due to the direct contact with the specimen and the possible introduction of localized plastic effects. In multiple studies, the stress relaxation test has been used to determine the time-dependent properties of polymers. Indirect methods involve measurement of two different independent viscoelastic parameters to determine the Poisson's ratio, for example by measuring the elastic modulus and shear modulus independently to obtain the Poisson's ratio. General trends from available data and the presented work indicate that the Poisson's ratio increases with time, temperature, and strain. However, contradicting data have also been presented; a decrease of Poisson's ratio with frequency in DMTA testing was found by Caracciolo and Giovagnoni and Arzoumanidis and Liechti.

Conclusive experimental and theoretical information that describe the influence of the cure state of the resin on the Poisson's ratio is not widely available. In one study, O'Brien et al. used Moire interferometry to study the cure dependence of the Poisson's ratio of EPON 862 bisphenol F epoxy and EPON 828 bisphenol-A epoxy resins. Using creep testing, they concluded that the viscoelastic Poisson's ratio obeys time–temperature superposition principles with the same horizontal shifting functions as for the creep compliance. However, they did not observe any influence of the cure state on the Poisson's ratio.

Dependence of the storage modulus on the cure state along with time and temperature was reported in Saseendran et al. using Dynamic Mechanical and Thermal Analysis (DMTA) on Araldite LY5052 bisphenol-A epoxy resin. Adolf and Martin argued that the cure state dependence of the storage modulus should also apply to the Poisson's ratio and the same cure state related shift functions should be valid for a thermo-rheologically simple material. This is, however, in direct contradiction to the observations by O'Brien et al.

We hope that the present work will help in understanding the differences between viscoelastic models accounting for the state of cure. In Section 2, a systematic presentation of simplifying assumptions for a thermodynamically consistent linear viscoelastic material model leading to a rheologically simple material with respect to temperature and to the cure state (i.e. the state variables) is made. It is shown that for a rheologically simple material the cure state-related reduced time is the same not only for all possible viscoelastic parameters (creep compliances, elastic relaxation modulus and Poisson's ratio) but also for storage modulus and loss modulus. These conclusions are confirmed with experimental results in Section 3 where the cure state-related shift factors deduced from lateral strain measurements in relaxation test for Poisson's ratio are compared with the shift factors obtained analyzing storage modulus by means of DMTA, showing that the same cure state related shift factors are indeed obtained in both cases. This supports the assumption that the analyzed material can be considered as thermo-rheologically simple.
Theoretical background

Material model

A good starting point developing viscoelastic material model which depends on temperature, $T$ and the set of internal variables characterizing the state of cure, $\eta$, is the Gibbs free energy expression and the procedure described by Schapery. In this way, the thermodynamic consistency of the obtained relationships is ensured. In a particular case, assuming linear viscoelastic behavior the strain ($\varepsilon$)–stress ($\sigma$) relationships obtained following the simple procedure in Schapery are

$$\varepsilon_i = \sum_{j=1}^{6} \int_{0}^{t} S_{ij}(\psi - \psi') \frac{d}{d\tau} (g_j(\eta, T) \sigma_j) d\tau; \quad i = 1, 2, 3$$

(1)

where $\tau$ is the instantaneous time, $S_{ij}$ is the viscoelastic compliance, $\eta$ is the Gibbs free energy expression, $\psi$ and $\psi'$ are reduced times, $g_j$ is a temperature and cure-dependent function and $i, j$ are vector indices. Expression (1) is written here for normal stress–strain components assuming orthotropic material behavior. For sake of clarity, the temperature $T$ is assumed constant during the test and the free thermal expansion terms are not shown.

In (1), the viscoelastic compliances $S_{ij}$ are defined as follows

$$S_{ij}(t - \tau) = g_{ij}^0(\eta, T) + g_i(\eta, T) \sum_{m} S_{m} \exp \left( \frac{t - \tau}{\tau_m} \right)$$

(2)

Functions $g_{ij}^0 (i, j = 1, 2, 3)$, $g_i$ and $S_m$ depend on temperature and parameters of the material in uniaxial loading; $S_m$ are constants. The reduced time $\psi$ is defined as

$$\psi(t) = \int_{0}^{t} \frac{d\xi}{a(\eta, T)}$$

(3)

where $d\xi$ is the discretized total time. If we further assume that:

- The degree of cure and the temperature do not change during the mechanical test
- The shift factor $a(\eta, T)$ can be represented as a product of two shifts $a_1 a_2$; one for temperature $a_1$ and one for cure $a_2$, i.e.

$$a(\eta, T) = a_1 a_2$$

(4)

the above expressions simplify to

$$\varepsilon_i = \sum_{j=1}^{6} \int_{0}^{t} S_{ij}(t - \tau) \frac{d\sigma_j}{d\tau} d\tau$$

(5)

$$S_{ij}(t - \tau) = g_{ij}^0(\eta, T) + g_i(\eta, T) \sum_{m} S_{m} \exp \left( \frac{t - \tau}{\tau_m a_1 a_2} \right)$$

(6)

The next simplifying assumption which is not necessary valid for all materials is “rheological simplicity” which is often understood as the condition that only the shift parameter depends on temperature and on the cure state. Then (6) can be written as

$$S_{ij}(t - \tau) = g_{ij}^0 + \sum_{m} S_{m} \exp \left( \frac{t - \tau}{\tau_m a_1 a_2} \right)$$

(7)

The most important conclusion from (7) is that if the material is rheologically simple; all viscoelastic compliance matrix elements have the same shift factors.

Finally, sometimes it is assumed that instead of different coefficients $S_{m}$ for different compliance elements, a single, time-dependent function is sufficient to characterize approximately all elements of the compliance. This rather voluntary assumption is justified in Schapery by the usually weak time-dependence of the resin’s Poisson’s ratio. In this instance (which is not considered as applicable in this paper):

$$S_{ij}(t - \tau) = g_{ij}^0 + k_p S(t - \tau); \quad S(t - \tau) = \sum_{n} S^{\nu} \exp \left( \frac{t - \tau}{\tau_n a_1 a_2} \right)$$

(8)

Relaxation test

In this paper, uni-axial relaxation tests were performed on isotropic epoxy specimens to measure the axial stress relaxation and, most importantly, the lateral strain changes with time, in order to obtain viscoelastic function referred to as the viscoelastic Poisson’s ratio. It is of theoretical and practical interest to investigate whether the relaxation modulus $E(t)$ and the Poisson’s ratio $\nu(t)$ are also

- as for rheologically simple materials;
- the shift factors are the same as for compliances;
- the shift factors are the same for both viscoelastic functions.

The best method for this task is the integral Laplace transformation. In Laplace domain Equation (5), written for isotropic material in uniaxial loading ($\sigma_2 = a_1 = 0$) are

$$\bar{\varepsilon}_1 = \bar{S}_{11} \bar{p}; \quad \bar{\varepsilon}_2 = \bar{S}_{13} \bar{p}$$

(9)

Over-bar is used to denote Laplace transforms of various functions; $p$ is the variable in the Laplace domain. Now, we define new functions

$$\bar{E}(p) = \frac{1}{p^2 \bar{S}_{11}}; \quad \bar{\nu}(p) = \frac{\bar{S}_{12}}{p \bar{S}_{11}}$$

(10)

That allows (9) to be rewritten as

$$\bar{\sigma}_1 = \bar{E}(p) \bar{p} \bar{\varepsilon}_1; \quad \bar{\varepsilon}_2 = -\bar{\nu}(p) \bar{p} \bar{\varepsilon}_1$$

(11)

Since the inverse transformation of (11) leads to

$$\sigma_1 = \int_{0}^{t} \bar{E}(t - \tau) \frac{d\bar{\varepsilon}_1}{d\tau} d\tau; \quad \varepsilon_2 = -\int_{0}^{t} \bar{\nu}(t - \tau) \frac{d\bar{\varepsilon}_1}{d\tau} d\tau$$

(12)

we conclude that (10) are Laplace transforms of the relaxation modulus $E(t)$ and the Poisson’s ratio $\nu(t)$. Laplace transform of (7) is

$$\bar{S}_{11} = \frac{g_{11}^0}{p} + \sum_{n} \frac{S_{11}^{\nu}}{p + \frac{1}{\tau_n a_1 a_2}}; \quad \bar{S}_{12} = \frac{g_{12}^0}{p} + \sum_{n} \frac{S_{12}^{\nu}}{p + \frac{1}{\tau_n a_1 a_2}}$$

(13)

Introducing a new variable

$$s = pa_1 a_2$$

(14)

That allows (13) to be rewritten as
Table 1 Curing temperature and times

| Temperatures (°C) | Curing times (h) | Cure state (%) |
|-------------------|-----------------|----------------|
| 60                | 1.25            | 82.3           |
| 60                | 1.50            | 85.7           |
| 60                | 1.75            | 87.6           |
| 60                | 2.00            | 88.7           |
| Room Temp.        | 24 + 4          | 100; Fully cured |
| (21 °C) + 105 °C  | (FC)            |                |

\[
\tilde{S}_{11} = a_1 a_{11} \left( \sum_{\sigma}^n \frac{S_{11}^m}{\sigma + \frac{1}{\tau_m}} \right) = a_1 a_{11} R_{11}^m (s, \tau_m) ; \\
\tilde{S}_{12} = a_1 a_{12} \frac{R_{12}^m (s, \tau_m)}{\prod_m (\frac{1}{\sigma + \frac{1}{\tau_m}})} ; \\
(15)
\]

In (15) \( R_{11}^m \) and \( R_{12}^m \) are \( n \)-th degree polynomials \( (n) \) is the number of exponents in Prony series (7) with coefficients dependent on \( \tau_m \) (note that they do not depend on shift parameters). Substituting (15) in (10) we obtain

\[
\tilde{E} = \frac{a_1 a_{11}}{s} \prod_m \left( \frac{s + \frac{1}{\tau_m}}{\sigma + \frac{1}{\tau_m}} \right) ; \\
\tilde{\nu}(p) = \frac{a_1 a_{12}}{s} \prod_m \left( \frac{R_{11}^m (s, \tau_m)}{\tau_m} \right) ; \\
(16)
\]

Expressions for both viscoelastic functions have the same polynomial in denominator with roots \( \frac{1}{\sigma + \frac{1}{\tau_m}} \). Using these roots, the rational functions (16) can be presented in a form

\[
E = a_1 a_{11} \left( \frac{E_{11}}{s} + \sum_{\sigma}^n \frac{E_{11}^m}{s + \frac{1}{\tau_m}} \right) ; \\
\tilde{\nu} = a_1 a_{12} \left( \frac{\nu_{12}}{s} + \sum_{\sigma}^n \frac{\nu_{12}^m}{s + \frac{1}{\tau_m}} \right) . \\
(17)
\]

Returning to the old variable \( p \), see (14), we obtain

\[
\tilde{E} = \frac{E_{11}}{p} + \sum_{\sigma}^n \frac{E_{11}^m}{p + \frac{1}{\sigma + \frac{1}{\tau_m}}} ; \\
\tilde{\nu} = \frac{\nu_{12}}{p} + \sum_{\sigma}^n \frac{\nu_{12}^m}{p + \frac{1}{\sigma + \frac{1}{\tau_m}}} . \\
(18)
\]

Finally, inverse Laplace transformation gives

\[
E(t) = E_{11} \sum_{\sigma}^n E_{11}^m \exp \left( -\frac{t}{a_1 a_{11} \tau_m} \right) ; \\
\nu(t) = \frac{\nu_{12}}{p} \sum_{\sigma}^n \frac{\nu_{12}^m}{p + \frac{1}{\sigma + \frac{1}{\tau_m}}} . \\
(19)
\]

Conclusions following from (19) are:
- Both viscoelastic functions \( E(t) \) and \( \nu(t) \) have same shift factors
- These shift factors are the same as for viscoelastic compliances \( S_{ij} \)
- Both functions have the same relaxation times \( \tau_m \) (roots of polynomials \( R_{11}^m \) and \( R_{12}^m \)) that do not depend on shift factors
- These relaxation times, \( \tau_m \), are not the same as for compliance functions (\( \tau_m \)). However, they are unique functions of \( \tau_m \). Nevertheless, it is not important in practical applications because usually \( \tau_m \) have no physical meaning. They are selected to obtain the best fit with minimum number of terms in Prony series.

As one can see, these results obtained as a result of systematic analysis apply to both, to the temperature shift and to the cure state related shift.

Storage modulus

The stress–strain relationship in a viscoelastic material due to harmonic loading which is used in DMTA testing, is obtained assuming that the applied strain \( \varepsilon \) is a superposition of a constant pre-strain \( \varepsilon_{0} \) and a harmonic function of time

\[
\varepsilon(t) = \varepsilon_0 \exp(2\pi ft) \\
(20)
\]

In (20), \( i \) is the imaginary unit, \( f \) is the frequency in Hz. The material response change to the constant pre-strain is assumed much slower than the change with respect to the oscillatory part. Substituting (20) and (19) in (12) we obtain as the result of integration an expression for stress variation with time. After certain transition time the stress oscillations become stationary as the initial conditions for the loading decay. In this region, the expression for the stress oscillation resulting from (20)

\[
\sigma(t) = \frac{\varepsilon_0}{\rho_0} \sum_{\sigma}^n \frac{E_{11}^m}{1 + 2\pi \sigma a_1 a_{11} \tau_m f} + \frac{\varepsilon_0}{\rho_0} \sum_{\sigma}^n \frac{\nu_{12}^m}{1 + 2\pi \sigma a_1 a_{12} \tau_m f} . \\
(21)
\]

Introducing the complex modulus as stress–strain ratio

\[
E(f) = \frac{\sigma(t)}{\varepsilon(t)} = E_0 + \sum_{\sigma}^n \frac{E_{11}^m}{1 + 2\pi \sigma a_1 a_{11} \tau_m f} + \frac{\nu_{12}^m}{1 + 2\pi \sigma a_1 a_{12} \tau_m f} \\
(22)
\]

Where the complex modulus can be written as

\[
E(\omega) = E'(f) + iE''(f) \\
(23)
\]

Expressions for the storage modulus (the real part of the complex function) and the loss modulus (the imaginary part) are then identified as

\[
E'(f) = E_0 \sum_{\sigma}^n \frac{(2\pi \sigma a_1 a_{11} \tau_m f)^2}{1 + (2\pi \sigma a_1 a_{11} \tau_m f)^2} ; \\
E''(f) = \sum_{\sigma}^n \frac{2\pi \sigma a_1 a_{12} \tau_m f}{1 + (2\pi \sigma a_1 a_{12} \tau_m f)^2} . \\
(24)
\]

These expressions contain the frequency and the shift factors in a form of product \( a_1 a_{1f} \) and for a given value of this product the storage modulus is constant. This is the basis for the master curve construction which uses horizontal shifts in the frequency domain: for values of \( a_1 \) and \( a_{1f} \) different than in the reference state, the frequency corresponding to the given value of the storage modulus can be found by shifting in logarithmic axes using the property \( \log(a_1 a_{1f}) = \log a_1 + \log a_{1f} + \log f \).

The important information in this paper is that the shift factors for the complex storage modulus in the frequency domain are the same as in the relaxation test and in other mechanical tests on the macroscale.

Experimental

Materials

The resin system used was Araldite LY5052 epoxy resin with Aradur HY5052 hardener from Huntsman. LY5052 is a low viscosity resin commonly used in the composites industry with a long pot life and a maximum attainable glass transition temperature of 130 °C after post-cure. According to the manufacturer, LY5052 is a blend of butanedioildiglycidyl ether
where $\alpha$ is the degree of cure, $A (= 11e04 \text{ s}^{-1})$ is the pre-exponential rate constant, $T$ is the temperature in Kelvins, $B (= 52600 \text{ J/mol})$ is the reaction energy, $R$ is the ideal gas constant, $m$ and $n (=0.17$ and $1.83$ respectively) are constants independent of cure temperature that are obtained from fitting experimental data from the DSC using standard least-squares fit. Moreover, $\alpha$ is defined as

$$\alpha = 1 - \frac{H}{H_{tot}},$$  \hspace{1cm} (26)

where $H$ is the residual heat of reaction and $H_{tot}$ is the total heat of reaction which has been determined as $482 \text{ J/g}$ for the given resin system.\(^{2,11}\) $\alpha_{\text{max}}$ is defined as the maximum degree of cure attained at various curing temperatures. The values for $\alpha_{\text{max}}$ are obtained for each cure temperature ($T_c$) from the isothermal DSC experiments performed in Svanberg\(^{2}\) and fitted to obtain the relationship

$$\alpha_{\text{max}} = 0.002T_c + 78.2.$$  \hspace{1cm} (25)

After the predetermined cure times were attained, the specimens were immediately taken out of the oven and removed from the molds. The specimens were then cooled down rapidly using a coolant spray to prevent further curing and stored in the freezer until testing. Prior to testing the specimen edges were ground and polished to final dimension and to obtain flat parallel edges and brought back to room temperature.

### Relaxation testing

Before testing, strain gages manufactured by Kyowa for plastics and polymers (model KFP-5-120-C1-65 L1M2R) were glued onto the specimens using acrylate-based strain gage cement. The strain gages were glued on in the transverse direction to measure the transverse strains. A hydraulically actuated testing machine, Instron 8501 was employed to perform relaxation testing of the specimens. As specified earlier, the transverse strains were measured with the strain gages and the longitudinal strains were measured using an extensometer (Instron, model 2620). The specimens were mounted on to the grips with 25 mm of grip length on each side, leaving an effective gage length of 150 mm on the specimen. Grip pressure was of the order of 50 bars. All tests were performed at a controlled room temperature ($20 \pm 1 \text{ °C}$). After mounting the specimens, they were loaded to 0.5% strain in the axial direction and held so for 24 h ($\sim 10^5$ s) and then unloaded. The loading ramp from 0 to 0.5% in axial strain was completed in 15 s. The transverse strains and the stress were monitored throughout the tests.

![Figure 1](image1.png)  
**Figure 1** Poisson’s ratio from stress relaxation testing of different specimens. Time $t$ is in seconds

![Figure 2](image2.png)  
**Figure 2** Poisson’s ratio vs. degree of cure after (a) 100s and (b) 1000s of relaxation
Poisson’s ratio in relaxation test

The stress relaxation test described in Section 3 of this paper was used to determine the viscoelastic Poisson’s ratio using

\[
\nu_{\text{rel}}(t) = - \frac{\varepsilon_y(t)}{\varepsilon_A}
\]  

(27)

where \(\varepsilon_y\) is time-dependent lateral strain and \(\varepsilon_A\) is the applied axial strain. Since the axial strain is constant and only one stress component is applied, Equation (27) can be considered to be a definition of viscoelastic time-dependent Poisson’s ratio. The Poisson ratio values at selected times for a representative specimen for each cure state thus obtained are shown in Fig. 1.

In spite of the large scatter between specimens and environmental perturbations (temperature and moisture variations) it is evident from Fig. 1 that there is a dependence of the Poisson’s ratio on the degree of cure. An increase of the Poisson’s ratio is observed with decreasing cure state. The fully cured specimen displays a Poisson’s ratio of about 0.32 at the beginning. According to the resin manufacturer’s specifications, the Poisson’s ratio of a fully cured resin is between 0.33-0.35. For the sake of simplicity, in Fig. 1 and in the analysis demonstrated below the number of data points used is reduced by extracting a sub-set of experimental data corresponding to time instants 50, 100, 1000, 10000 s, and at the end of the test.

The data at a given time instant for all cure states is used to illustrate the dependence of the Poisson’s ratio vs. degree of cure. In Fig. 2, this is done by extracting values of the Poisson’s ratio for each test at 100 and 1000 s and plotting against the degree of cure. Therefore, some additional data points for low degree of cure are “introduced” based on Saseendran et al.²⁸ were it was found that the gelation point for LY5052 resin is at a cure state of 64%. It is reasonable assuming the Poisson’s ratio 0.5 at this cure state and lower, since below the gel point the resin is effectively in the liquid state. From Fig. 2, it can be

Figure 3  Poisson’s ratio from Fig. 1 after transformation into frequency domain

Figure 4 Master curve for Poisson’s ratio obtained by horizontally shifting data in Fig. 3

Results and analysis

According to the theoretical analysis in Section 2 the cure state-related shift factors are the same for all viscoelastic material functions if the material is rheologically simple. Since the rheological simplicity of the used epoxy this is a-priori not known, we will perform relaxation tests and DMTA testing to investigate cure state related shift factors.
observed that the Poisson ratio varies with degree of cure in a manner that conforms to a sigmoid curve.

Curves in Fig. 1 can be shifted horizontally in log $t$ to obtain the so-called master curve. Instead, in order to compare the results shown in Fig. 1 to the experimental DMTA results presented in Section 4.2 and to identify shift factors, transformation of data from the time domain to the frequency domain was performed. While multiple approximate methods exist to perform this task, including Schwarzl approximations\(^\text{29}\) and Havrilak-Negami method of interconversions\(^\text{30}\), some of the simplest analytical methods of interconversions are provided by Park and Schapery\(^\text{31}\) and Christensen\(^\text{32}\). Christensen’s method was found to be quite accurate when fitted to a simple Maxwell viscoelastic model. The interconversion according to Christensen is performed from the frequency ($f$) domain to time ($t$) by

$$f \rightarrow \frac{2}{\alpha T}$$

Using Equation (28), the time domain data in Fig. 1 was then converted to the frequency domain as shown in Fig. 3.

The next step after transformation is to shift the individual curves horizontally to generate a master curve. Since the curves correspond to Poisson’s ratios for various cure states, different shifting corresponds to a different state of cure. A reference has to be specified and for the aforementioned shifting procedure this reference was arbitrarily chosen to be at 80% degree of cure. The resulting master curve is shown in Fig. 4. It is observed that the data do not overlap perfectly. One reason may be the fact that the complete data-set from the experimental data was not included in the shifting. The shift factor dependence on curing time is presented in Fig. 8. Another reason is inaccuracy due to scatter in the experimental results for different specimens. Nevertheless, the obtained master curve is assumed to be sufficient to support the assumption the Poisson’s ratio is rheologically simple, depicting a typical shape. At the lower end of the frequency spectrum where the material behavior is more fluid-like, the curve apparently
approaches 0.5 which corresponds to the Poisson’s ratio of a rubbery material.

Storage modulus

As an example, DMTA results for specimens cured at 60 °C for 1.5 h are shown in Fig. 5(a). Master curve was subsequently generated from data corresponding to frequency scan at different temperatures, applying time–temperature superposition and using 23 °C as a reference temperature, see Fig. 5(b). A set of master curves corresponding to different cure states is shown in Fig. 6(a).

The shift factor dependence on temperature, see Fig. 6(b), was found to be fairly linear and in close agreement with the Williams-Landel-Ferry (WLF) equation

\[
\log a(T) = \frac{-c_1(T - T_{ref})}{c_2 + T - T_{ref}}
\]

where \(c_1\) and \(c_2\) are material-dependent constants, which for the epoxy system LY5052/HY5052 are 77.59 and 433.6 K respectively and \(T_{ref}\) (23 °C) is the reference temperature and \(T\) is the corresponding testing temperatures in the DMTA.

Additional horizontal shifting of master curves in Fig. 6(a), representing different cure states, was performed using 80% cure as a reference state. The obtained super-master curve is shown in Fig. 7. Even if the degree of cure may be the best and unique characterization of the cure state, it was found that for specimens cured at the same temperature, the shift factor dependence of the cure time is much more reliable representation; the empirical relationship is rather linear.\(^{11}\) These shift factors (log \(a_c\)) are also shown in Fig. 7. The cure shift factor as a function of curing temperature \(T_c\) and curing time \(t_c\) was experimentally determined in Saseendran et al.\(^{11}\) for LY5052 epoxy resin as

\[
\log a_c(T_c, t_c) = C \cdot (t_c - t_{ref}),
\]

where

\[
C = 0.0026T_c^2 - 0.0903T_c + 1.39.
\]

Here, \(t_{ref}\) is the time of cure at which the reference cure state of 80% is attained. At 60 °C isothermal cure, this time was determined to be 68 minutes.

Comparison of cure-state related shift factors

The cure state-related shift factor obtained in relaxation test for Poisson’s ratio and the DMTA-based shift factor for storage modulus are shown in Fig. 8. It is observed that the shift factors are nearly identical in both cases and approximately linear when plotting the logarithm of the shift factors against cure time. The fact that the shift factors used for shifting the Poisson’s ratio curves is similar to the shift factors used for shifting the storage modulus in cure, points to the rheological simplicity of the material. As discussed earlier, thermo-rheological simplicity results in one set of shift factors in temperature for all material properties. This is also apparent when shifting between cases with different degree of cure.

Conclusions

Poisson’s ratio of polymeric materials, which for simplicity is often assumed constant, in fact exhibits a small dependence on time which is affected by temperature and state of cure. In this work, the evolution of the viscoelastic Poisson’s ratio of the commercial LY5052 epoxy resin is studied in relaxation test subjecting the specimen to constant axial strain. Poisson’s ratio of the resin during stress relaxation test was measured for various cure states to evaluate its dependence on the degree of cure and time, assuming that the degree of cure does not change during testing.

A marked influence of the degree of cure and time on the Poisson’s ratio was observed and the trend points to increasing Poisson’s ratio with decreasing degree of cure. It was also observed that the Poisson’s ratio increases with time...
under relaxation. The individual Poisson ratio curves from each experiment were transformed to frequency domain and horizontally shifted there to generate master curve. The cure state-related shift factors used to generate the master curve are nearly linear with respect to the cure time. It was also determined that the cure state related shift factors for Poisson’s ratio are nearly identical to the cure state shift factors obtained when constructing a master curve for storage modulus of the same material using DMTA data. This is an indication of the rheological simplicity of the material with respect to its cure state. The DMTA measurements also confirmed that the total shift can be considered as a sum of two shifts in the frequency domain, which means that function for reduced time calculation can be written as a product of two functions: one dependent on the test temperature and the other dependent on the cure state.

Acknowledgments

The authors would like to thank the SICOMP Foundation for providing financial support for this research.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the VINNOVA (Sweden) [grant number 2014-06041] is greatly acknowledged.

ORCID

Maciej Wysocki (http://orcid.org/0000-0002-2841-7188)

References

1. S. G. Advani and E. M. Sozer: ‘Process modeling in composites manufacturing,’ 2012, New York, CRC Press.
2. J. M. Svanberg: ‘Predictions of manufacturing induced shape distortions,’ Doctoral dissertation, Luleå University of Technology, Sweden, 2002.
3. I. Baran, K. Cinlar, N. Ersoy, R. Akkerman and J. H. Hallett: ‘A review on the mechanical modeling of composite manufacturing processes,’ Archives of computational methods in engineering, 2016, 1–31.
4. M. R. Wisnom, M. Gigliotti, N. Ersoy, M. Campbell and K. D. Potter: ‘Mechanisms generating residual stresses and distortion during manufacture of polymer–matrix composite structures,’ Compos. Part A: Appl. Sci. Manufac., 2006, 37, (4), 522–529.
5. D. B. Adolf, J. E. Martin, R. S. Chambers, S. N. Burchett and T. R. Guess: ‘Stresses during thermoset cure,’ J. Mater. Res., 1998, 13, (3), 530–550.
6. Y. Eom, L. Boogh, V. Michaud, P. Sunderland and J. A. Månsén: ‘Time-cure-temperature superposition for the prediction of instantaneous viscoelastic properties during cure,’ Polym. Eng. Sci., 2000, 40, (6), 1281–1292.
7. D. J. O’Brien, P. T. Mathier and S. R. White: ‘Viscoelastic properties of an epoxy resin during cure,’ J. Compos. Mater., 2001, 35, (10), 883–904.
8. R. Thorpe and A. Pursariti: ‘Experimentally determining the viscoelastic behavior of a curing thermoset epoxy,’ 19th International Conference on Composite Materials, Montreal, 2013, 1997–2002.
9. M. Sadeghinia, K. M. Jansen and L. J. Ernst: ‘Characterization of the viscoelastic properties of an epoxy molding compound during cure,’ Microelectron. Reliab., 2012, 52, (8), 1711–1718.
10. K. Suzuki, Y. Miyano and T. Kunio: ‘Change of viscoelastic properties of epoxy resin in the curing process,’ J. Appl. Polym. Sci., 1977, 21, (12), 3367–3379.
11. S. Saseendran, M. Wysocki and J. Varna: ‘Evolution of viscoelastic behavior of a curing LY5052 epoxy resin in the glassy state,’ Adv. Manufac. Polym. Compos. Sci., 2016, 2, (2), 74–82.
12. H. H. Hilton: ‘Implications and constraints of time-independent Poisson ratios in linear isotropic and anisotropic viscoelasticity,’ Journal of elasticity and the physical science of solids, 2001, 63, (3), 221–251.
13. A. H. Tsou, J. Greener and G. D. Smith: ‘Stress relaxation of polymer films in bending,’ Polymer, 1995, 36, (5), 949–954.
14. N. W. Tschoegel, W. G. Knauss and I. Emri: ‘Poisson’s ratio in linear viscoelasticity—a critical review,’ Mechanics of Time-Dependent Materials, 2002, 6, (1), 3–51.
15. R. S. Lakes: ‘The time-dependent Poisson’s ratio of viscoelastic materials can increase or decrease,’ Cell. Polym., 1992, 11, 466–469.
16. A. D. Drozdov: ‘A model for the viscoelastic behavior of polymers at finite strains,’ Arch. Appl. Mech., 1998, 68, (5), 308–322.
17. S. Jazouli, W. Luo, F. Brémand and T. Vu-Khanh: ‘Nonlinear creep behavior of viscoelastic polycarbonate,’ J. Mater. Sci., 2006, 41, (2), 531–536.
18. R. Caracciolo and M. Giovanoni: ‘Frequency dependence of Poisson’s ratio using the method of reduced variables,’ Mech. Mater., 1996, 24, (1), 75–85.
19. L. J. Ernst, G. Q. Zhang, K. M. Jansen and H. J. Bessers: ‘Time-and temperature-dependent thermo-mechanical modeling of a packaging molding compound and its effect on packaging process stresses,’ J. Electron. Packag., 2003, 125, (4), 539–548.
20. O. I. Okoli and G. F. Smith: ‘The effect of strain rate and fibre content on the Poisson’s ratio of glass/epoxy composites,’ Compos. Struct., 2000, 48, (1), 157–161.
21. G. A. Arzoumanidis and K. M. Liechti: ‘Linear viscoelastic property measurement and its significance for some nonlinear viscoelasticity models,’ Mechanics of Time-Dependent Materials, 2003, 7, (3–4), 209–250.
22. S. Pandini and A. Pegoretti: ‘Time, temperature, and strain effects on viscoelastic Poisson’s ratio of epoxy resins,’ Polym. Eng. Sci., 2008, 48, (7), 1434.
23. H. Lu, X. Zhang and W. G. Knauss: ‘Uniaxial, shear, and Poisson relaxation and their conversion to bulk relaxation: studies on poly (methyl methacrylate),’ Polym. Eng. Sci., 1997, 37, (6), 1053–1064.
24. D. J. O’Brien, N. R. Sottos and S. R. White: ‘Cure-dependent viscoelastic Poisson’s ratio of epoxy,’ Exp. Mech., 2007, 47, (2), 237–249.
25. D. Adolf and J. E. Martin: ‘Time-cure superposition during crosslinking,’ Macromolecules, 1990, 23, (15), 3700–3704.
26. R. A. Schapery: ‘Nonlinear viscoelastic and viscoplastic constitutive equations based on thermodynamics,’ Mech. Compos. Mater., 1997, 1, 209–240.
27. R. A. Schapery: ‘Viscoelastic behaviour and analysis of composite materials’ in ‘Mechanics of composite materials’, 85–168; 1974, New York, Academic Press.
28. S. Saseendran, M. Wysocki and J. Varna: ‘Evolution of viscoelastic behaviour of a curing LY5052 epoxy resin in the rubbery state,’ Adv. Compos. Mater., 2017, 1–15.
29. F. R. Schwarzl: ‘Encyclopedia of Polymer Science,’ 2003, 2, 250.
30. S. Havrilak and S. Negami: ‘A complex plane representation of dielectric and mechanical relaxation processes in some polymers,’ Polymer, 1967, 8, 161–210.
31. S. W. Park and R. A. Schapery: ‘Methods of interconversion between linear viscoelastic material functions. Part I-a numerical method based on Prony series,’ Int. J. Solids Struct., 1999, 36, 1653–1675.
32. R. Christensen: ‘Theory of viscoelasticity: an introduction,’ 2012, New York, Elsevier.