# Effect of Degree of Cure and Time on Viscoelastic Poisson's ratio

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## ABSTRACT

The Poisson's ratio of a solid under deformation is classically defined as the negative of the ratio between the lateral or transverse strain and the axial strain. Ideally for an elastic material, the Poisson's ratio is assumed to be a constant. However, for viscoelastic materials like polymers and polymer matrix composites this is also likely influenced by various factors like time [1], temperature, degree of cure and also on the strain. In this work, the evolution of the viscoelastic Poisson's ratio of the commercial LY5052 epoxy resin is studied under uniaxial tension subject to constant deformation stress relaxation testing. Measurements of the Poisson ratios are performed using contact extensometers and strain gages. Samples at five different cure states are manufactured and investigated. The relaxation testing is performed by loading the samples to 0.5% longitudinal strain and monitoring the relaxation behavior over a period of 24 hours per cure state. Poisson's ratio is observed to evolve from 0.32 to 0.44 over time depending on the cure state. Moreover the data indicates that the individual Poisson's ratio curves can be shifted horizontally following time-cure superposition. The shift functions used for this horizontal shifting are similar to those identified for DMTA tests for storage modulus under identical conditions. Following horizontal shifting, master curves that show the evolution of Poisson's ratio over time can be created for a particular reference cure state. This similarity of the shift functions in both micro-scale DMTA testing and macro-scale relaxation testing is an indicator of the validity of the shift factors. The observation is used to further develop a viscoelastic model which identifies the total shift function as the product of the temperature and cure shift functions.

## 1 INTRODUCTION

The development of residual stress in composites is caused by different factors. Thermally induced residual stresses in composite materials are caused by the mismatch between coefficients of thermal expansion (CTE) of the matrix and the reinforcements [2-4]. The magnitude of these residual stresses depends on the difference of CTE between the matrix and the reinforcements multiplied by the temperature change $\Delta T$ and other elastic or viscoelastic factors. 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 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, studies [2] and [4] also indicate tool-part interaction, moisture absorption and ageing 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 [2]. Though the model is simple to characterise and implement, it is not clear how valid the used assumption of its linear elastic behaviour is and how large are the introduced errors. This is of concern especially when realized that a majority of the composites

do not behave in a linear elastic manner. Many investigations show viscoelastic behaviour, see for example [6-10]. The question that arises is as to whether the material properties during curing are linearly or non-linearly 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 behaviour is linear viscoelastic. Nevertheless, it is expected that similarly to the temperature, parameters of the state of cure will affect the rate of viscoelastic processes and therefore it needs to be included into the linear viscoelastic material model.

In a previous study [11], 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 (frequency in 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 [12], 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 a time independent and under this assumption the question of the cure-state effect is 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 study where stress develops during the manufacturing process of composites [13].

Thus the Poisson's ratio for viscoelastic materials such as polymers and polymer matrix composites may be influenced by various factors like time [14], 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 [14, 15] and experimentally difficult to investigate. This is mainly due to the difficulty in measuring small transverse strains by common testing apparatus in a low applied strain region, selected to insure linear viscoelastic behavior with negligible irreversible strains. Several methods, direct and indirect, exist 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 [14, 16, 17], using strain gages [18-20] and/or contact extensometers [21, 22]. Limited accuracy is a common problem, for example, strain gauges give data from a rather local region comparing with the region covered by the axial extensometer. Gluing the strain gauge on partially cured resin specimen can 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 [19, 22, 23] 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 [22], for example by measuring the elastic modulus and shear modulus to find the Poisson's ratio. General trends from available data [7, 15, 19] and the presented work are 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[18] and Arzoumanidis and Liechti[21].

Conclusive experimental and theoretical information that describes the influence of the cure state of the resin on the Poisson's ratio is not available. In one study, O'Brien et al. [24] used Moire interferometry to study the cure dependence of the Poisson's ratio of EPON 862 bisphenol F epoxide and EPON 828 bisphenol-A epoxy resins. Using creep test, 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 development. Dependence of the storage modulus on the cure state along with time and temperature was reported in [11] using Dynamic Mechanical and Thermal Analysis (DMTA) on Araldite LY5052 bisphenol-A epoxy resin. Adolf and Martin [25] 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.

## 2 EXPERIMENTAL

### 2.1 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 butanedioldiglycidyl ether and epoxy phenol novolac resin and HY5052 is a mixture of cycloaliphatic polyamine, isophorone diamine, 2,4,6-tris(dimethylaminomethyl) phenol and salicylic acid. Prior to any experimental procedure, the resin and hardener were mixed in the ratio 100:38 by weight and stirred thoroughly, taking care not to introduce air bubbles.

### 2.2 Manufacturing Method

After mixing the resin and hardener, rectangular specimens were manufactured for relaxation testing. Specimen manufacture was performed by pouring the resin mix into a silicone mold that was clamped between Teflon coated aluminum plates used for the support of the mold and to help with heat transfer in the oven. The mold dimensions were 200x15x4mm. Prior to pouring the mold assembly was preheated in a convection oven. The resin was poured into the mold while in oven and cured at 60°C for various times to attain varying cure states. A similar procedure was used on a mold with different dimensions to manufacture specimens for DMTA testing. The mold dimensions were 17.5x2.8x3mm as specified by TA Instruments for a single cantilever mode specimen. The cure times are specified in Table 1.

Table 1: Curing temperature and times

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

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.

### 2.3 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 25mm of grip length on each side, leaving an effective gage length of 150mm on the specimen. Grip pressure was of the order of 50 bars. All tests were performed at a controlled room temperature (20±1°C). After mounting the specimens, they were loaded to 0.5% strain in the axial direction and held so for 24 hours (~$10^5$ seconds) and then unloaded. The loading ramp from 0 to 0.5% in axial strain was completed in 15 seconds. The transverse strains and the stress were monitored throughout the tests. Five specimens, each different cure states were tested in total. The post-curing at room temperature was found to be negligible and hence it is assumed that the degree of cure remains constant throughout the test.

## 3 RESULTS AND ANALYSIS

The stress relaxation test described in the previous section paper was used to determine the viscoelastic Poisson's ratio using

$$\nu_{rel}(t) = - \varepsilon_y(t)/\varepsilon_A \quad (1)$$

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, Eqn. 1 can be considered to be a definition of viscoelastic time dependent Poisson's ratio. The Poisson ratio values at selected time instants 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 used data points is reduced by extracting a sub-set of experimental data corresponding to time instants 50, 100, 1000, 10000 seconds and at the end of the test.

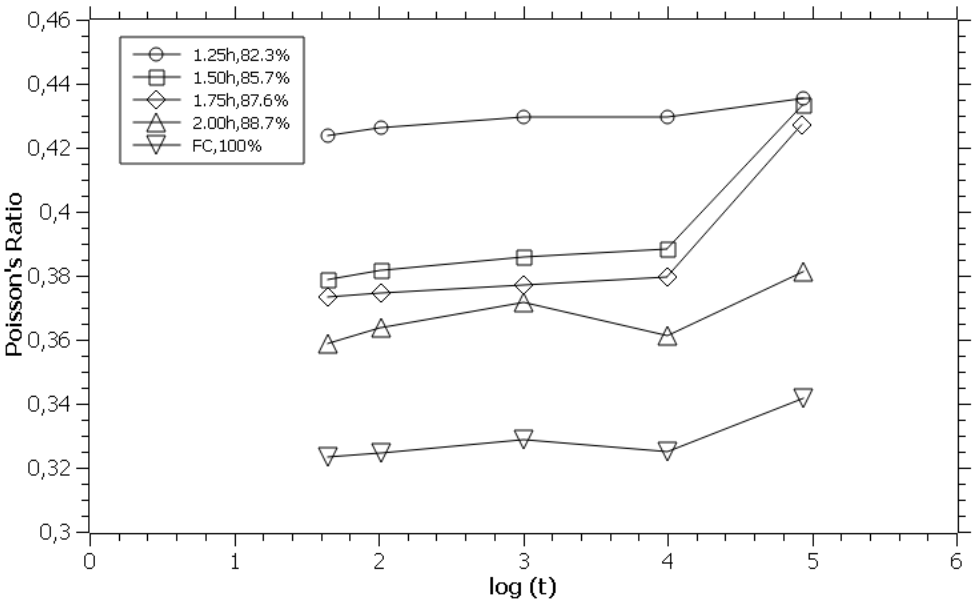


Figure 1: Poisson's ratio from stress relaxation testing of different specimens. Time *t* is in seconds.

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 [29] and Havriliak-Negami method of interconversions [30], some of the simplest analytical methods of interconversions are provided by Park and Schapery [31] and Christensen [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

$$f \rightarrow 2/\pi t \quad (2)$$

Using Eqn. 2, the time domain data in Fig. 1 was then converted to the frequency domain as shown in Fig. 2.

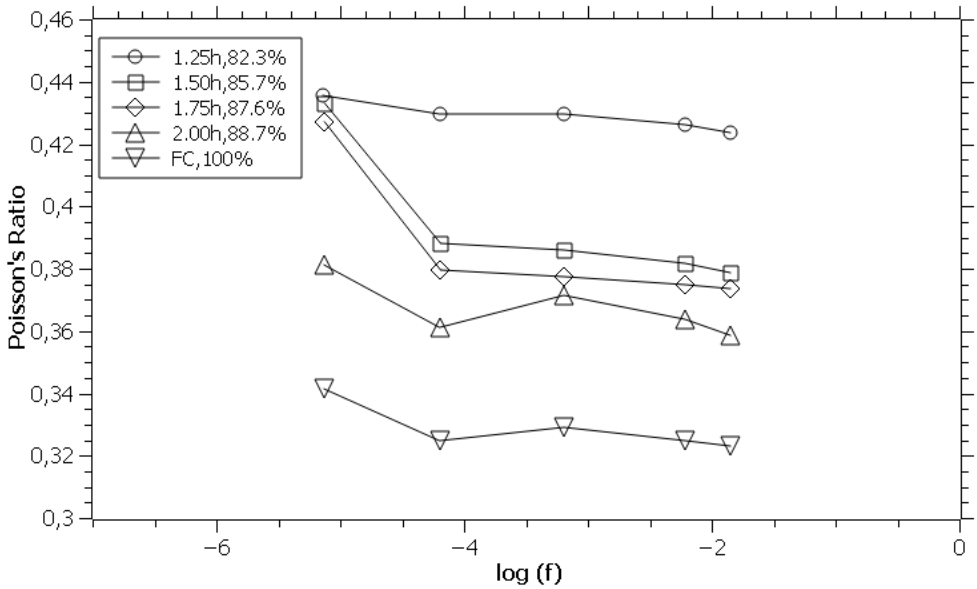


Figure 3: Poisson's ratio from Fig. 1 after transformation into frequency domain

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 different state of cure. A reference has to be specified and for the aforementioned shifting procedure this reference was chosen to be at 80% degree of cure. The resulting master curve is shown in Fig. 3. It is observed that the data do not overlap perfectly. One reason maybe 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. 4. Another reason is inaccuracy due to scatter in the experimental results for different specimens. Finally, it may be so that the material is not rheologically simple. 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 behaviour is more fluid-like, the curve apparently approaches 0.5 which corresponds to the Poisson's ratio of a rubbery material.

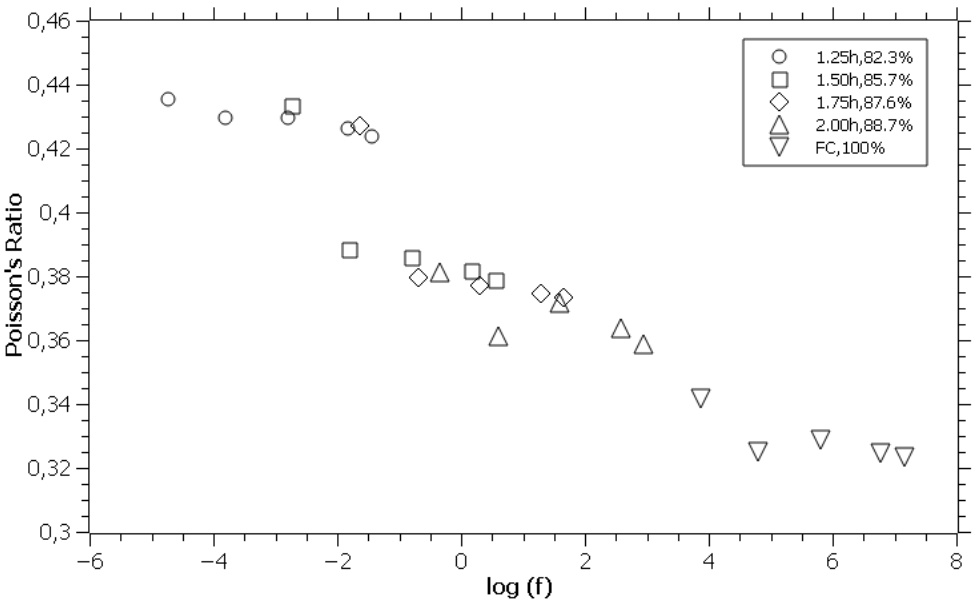


Figure 3: Master curve for Poisson's ratio obtained by horizontally shifting data in Fig. 3.

The cure state related shift factor obtained in relaxation test for Poisson's ratio and the DMTA based shift factor for storage modulus as obtained in [11] 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.

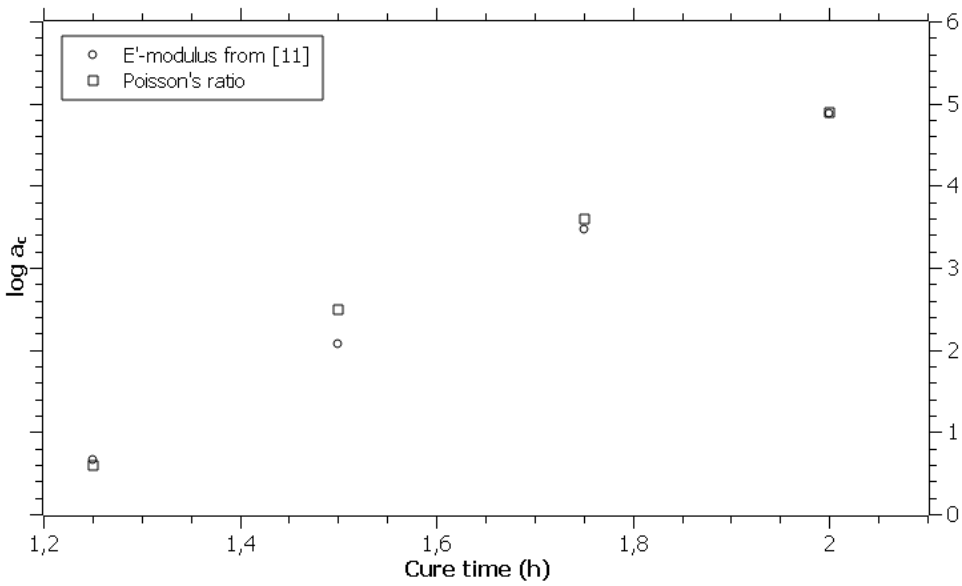


Figure 4: Shift factors for cure state from Poisson's ratio test and from DMTA experiments for the storage modulus [11].

## 5 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.

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 constructing 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 the cure state.

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