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Julie DIANI, Pierre GILORMINI, Juan Sebastain ARRIETA - Direct experimental evidence of time-temperature superposition at finite strain for an amorphous polymer network - Polymer - Vol. 58, p.107-112 - 2015

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## Direct experimental evidence of time-temperature superposition at finite strain for an amorphous polymer network

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### Abstract

The time-temperature superposition property of an amorphous polymer acrylate network is characterized at infinitesimal strain by standard dynamic mechanical analysis tests. Comparison of the shift factors determined in uniaxial tension and in torsion shows that both tests provide equivalent time-temperature superposition properties. More interestingly, finite strain uniaxial tension tests run until break at constant strain rate show that the acrylate network exhibits the same time-temperature superposition property at finite strain as at infinitesimal strain. Such original experimental evidence provides new insight for finite strain constitutive modelling of polymer amorphous networks.

Keywords: amorphous network; time-temperature superposition; finite strain

### 1. Introduction

The mechanical behaviour of amorphous polymers at finite strain is very sensitive to temperature and strain rate, especially in the glass transition temperature range, where a change of temperature affects greatly the molecular mobility. Various studies have reported experimental evidences supporting this fact ([1-7] among others), and several viscohyperelastic models with an account of temperature have been proposed for the representation of the mechanical behaviour of amorphous polymers at finite strain ([1,4-5,8-11] for instance). Despite interesting features, the models of the literature show difficulties to represent accurately the mechanical behaviour of amorphous polymers over a wide range of temperature and strain rate, let alone to predict it. In order to better model the time and temperature dependent behaviour of amorphous polymer networks, useful for shape memory applications for instance, it is proposed to explore the time-temperature superposition property at finite strain. Time-temperature superposition at infinitesimal strain in amorphous polymers is well known [12]. Such a property formulates the idea that time and temperature are dependent parameters. In other words, exposing the material to a high temperature and a short duration is the same as exposing it to a lower temperature over a longer span of time. When looking at the change of the stress-strain responses of amorphous polymers when the temperature or the strain rate varies, such a property seems also true at finite strain. Some authors showed that master curves could be built for finite strain behaviour quantities such as reduced yield stress [2-3,6] or stretch at break [13]. Nonetheless, finite strain time-temperature equivalence remains to be tested on the entire stress-strain response and its quantitative estimate to be compared to the time-

temperature superposition property measured at infinitesimal strain in order to rationalize its introduction in general constitutive equations. For this purpose, an amorphous acrylate network has been synthesized and tested in dynamic mechanical analysis and in conventional uniaxial tension until break. Several finite strain uniaxial tension tests were run at various constant temperatures and constant strain rates in order to show that stress-strain curve superposition exists also at finite strain and to calculate the time-temperature shift factors. The strain rates applied are moderate in order to avoid possible self-heating of the samples.

## 2. Material and experiments

### 2.1. Material

An acrylate network was prepared by copolymerization of benzyl methacrylate (BMA) with poly(ethylene glycol) dimethacrylate (PEGDMA) of molar weight 550 g/mol, which was used as crosslinker. 90% molar mass of BMA was mixed at room temperature with 10% molar mass of PEGDMA and 0.5% of 2,2-Dimethoxy-2-phenylacetone (DMPA) used as photoinitiator. Products received from Sigma Aldrich were used without transformation. The mix was cured between glass frames in a UVP ultraviolet chamber CL-1000 for 50 minutes in order to obtain plates of constant thicknesses as required for mechanical testing.

### 2.2. Experiments

The material was submitted to dynamic mechanical analysis (DMA) in torsion and in uniaxial tension. Dynamic torsion tests were run on a MCR502 rheometer from Anton Paar while dynamic uniaxial tension tests were performed on a DMA Q800 from TA instruments. Rectangular samples of length x width x thickness equal to 40 x 12 x 1.3 mm<sup>3</sup> were submitted to dynamic torsion and rectangular samples of 30 x 5 x 1.3 mm<sup>3</sup> were used for dynamic tension. In order to build the material storage modulus master curve and to calculate the shift factors characterizing the time-temperature superposition at infinitesimal strain, isothermal frequency sweeps at 0.1% strain from 0.01 to 10 Hz were applied from 37 °C to 64 °C every 3 °C in torsion and from 30 to 65 °C every 5 °C in tension.

At finite strain, dog-bone shape specimen of 1.3 mm thickness, 4 mm width and 20 mm gage length were submitted to isothermal uniaxial tension tests on an Instron 5881 testing machine equipped with a thermal chamber. Since crosshead displacements provide inaccurate measures of strain when dealing with finite strain, local strain was measured by video extensometry. The resulting force was recorded with a 1 kN cell. Some tests were run at constant crosshead speed of 1 mm/min. In order to run tests at constant strain rate, our experimental setup required to use constant piecewise displacement speed. The calculation of the strain rate afterward proved that it remained close to constant during these tests. The strain rate was estimated by taking the derivative with respect to time of the logarithmic strain,  $\varepsilon = \ln(l/l_0)$ , with  $l$  and  $l_0$  being the current and the initial distances between two markers painted on the free surface of the sample and followed by the video

extensometer. Therefore, the strain rate was calculated according to  $\dot{\varepsilon} = \frac{\dot{l}/l_0}{l/l_0} = \dot{l}/l$ . Note that

$\dot{l}/l_0$  is the engineering strain rate. It was observed that tests run at constant crosshead speed do not provide access to either constant engineering strain rate tests or constant strain rate tests due to

non-homogeneous strain within the sample resulting from the large strain applied. In order to satisfy to a commonly used representation of material behaviour in conventional uniaxial tension, the material response will be plotted in terms of the engineering stress ( $F/S_0$ ) with respect to the engineering strain  $\left(\frac{l-l_0}{l_0}\right)$ , with  $l$  and  $l_0$  being obtained from the video extensometer.

Each test was performed three times in order to validate the experimental reproducibility.

### 3. Time-temperature superposition at infinitesimal strain

The amorphous acrylate network was submitted to standard frequency sweeps in torsion at constant temperature. From the measured storage modulus  $G'$  and damping factor, master curves were built in order to verify the time-temperature superposition property (Fig. 1). The latter property is expressed mathematically by introducing a reduced time  $\tau$  defined at the reference temperature  $T_0$ , and writing the relationship between the reduced time and the actual time at temperature  $T(t)$  through the shift factor  $a_{T_0}$  according to:

$$d\tau = \frac{dt}{a_{T_0}(T(t))} \quad (1)$$

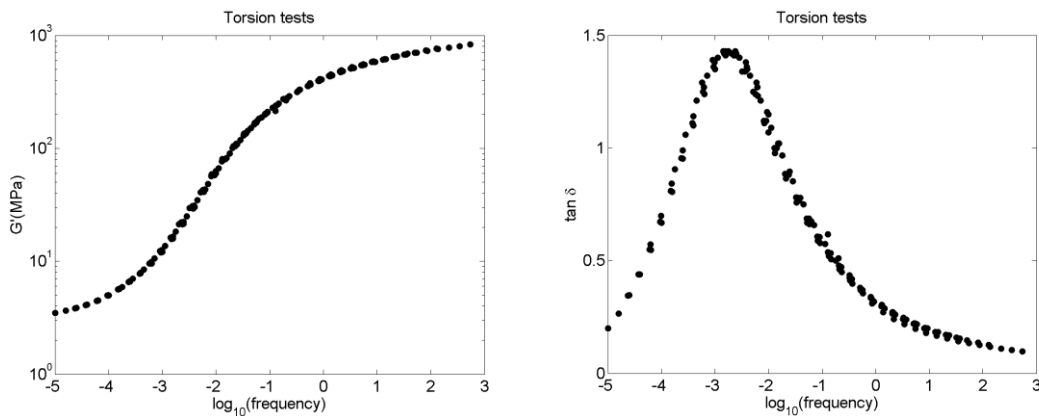


Figure 1. Master curves for the storage modulus and damping factor measured in torsion for a reference temperature of 45 °C.

The material linear viscoelasticity was also characterized in uniaxial tension. Isothermal frequency sweep tests were carried out in order to determine the storage modulus  $E'$  and its associated damping factor. The master curves characterizing the material frequency dependence in tension are shown in Fig. 2.

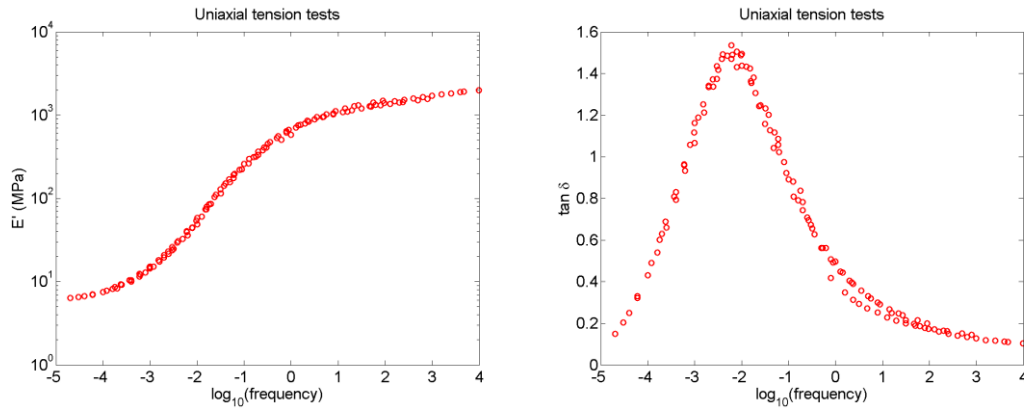


Figure 2. Master curves for the storage modulus and damping factor measured in uniaxial tension for a reference temperature of 45 °C.

The comparison of the shift factors directly obtained from the master curve building procedure is shown in Fig. 3. The material presents similar shift factor values in uniaxial tension and in torsion.

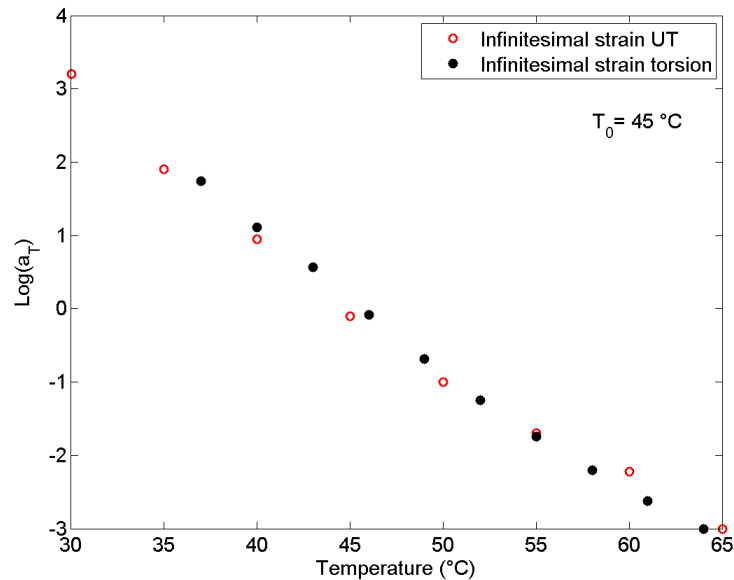


Figure 3. Comparison of the time-temperature superposition shift factors obtained at infinitesimal strain in torsion (MCR502) and in tension (DMA Q800).

Comparing the storage modulus and the damping factor obtained in uniaxial tension to those measured in shearing is possible but demands to make some assumptions. For linear viscoelastic isotropic materials, the complex moduli satisfy to the same relationship as the elastic moduli for elastic isotropic materials [14]. Therefore, denoting  $G^* = G' + iG''$  and  $E^* = E' + iE''$  the complex shear modulus and the complex Young modulus respectively, one may write:

$$G^* = \frac{3K^* E^*}{9K^* - E^*} \quad (2)$$

with  $K^*$  the complex bulk modulus. It is very difficult to reach  $K^*$  experimentally. Moreover, the storage bulk modulus is expected to drop by a factor of 2 to 3 only when temperature rises above the

glass transition [15]. Therefore, a first assumption consists in assuming the bulk modulus as elastic ( $K^* = K$ ) and constant. Doing so and choosing a value of 1150 MPa to reach a Poisson ratio of 0.41 in the glassy state and 0.499 in the rubbery state, complex shear storage modulus values may be calculated from the values of  $E^*$  measured by uniaxial dynamic mechanical analysis, using Eq. (2). It is also known that the DMA apparatus compliance may introduce some measure inaccuracies [16], especially at high frequencies when the material stiffness is high. During our experiments, it was noted that the DMA Q800 measures obtained at low frequencies compare well with standard uniaxial tension at low strain rates. To the contrary, at high frequencies, the storage modulus was observed to be significantly overestimated. In torsion, the MCR502 rheometer was shown to provide inaccurate measures at both low and high frequencies. As a consequence, adjustments of the storage modulus  $G'$  estimated with Eq. (2) from the measures of  $E^*$  and the assumption  $K^* = K$ , are necessary at both rubbery and glassy plateaus to compare it to the values of  $G'$  that has been measured with the Anton Paar rheometer. This adjustment is made according to equation:

$$\tilde{G}' = a + b.(G' - \min(G')) \quad (3)$$

with  $a$  and  $b$  two constants. Constant  $a$  corrects the storage modulus at low frequencies and  $b$  corrects it at high frequencies. Values of  $a=2$  MPa and  $b=1.18$  have been used. Acknowledging both assumptions, one may compare the storage modulus and the damping factor provided by both sets of measurements (Figs. 1 and 2). Figure 4 shows the comparison between the measured storage modulus  $G'$  and the storage modulus  $\tilde{G}'$  deduced from Eq. (2) and Eq. (3). One notices a very satisfactory matching between the data, which leads to several remarks. First, assuming the bulk modulus as elastic is a satisfactory assumption when studying the material viscoelasticity in tension and in shearing. Note that measures of  $E^*$  and  $G^*$  are not accurate enough to reach the dynamic values of  $K^*$  with the relationship,

$$K^* = \frac{G^* E^*}{3(3G^* - E^*)}. \quad (4)$$

Second, the linear viscoelasticity and time-temperature superposition property of an isotropic amorphous polymer network may be well estimated by either uniaxial tension or shearing dynamic tests since both lab tests provide with similar results.

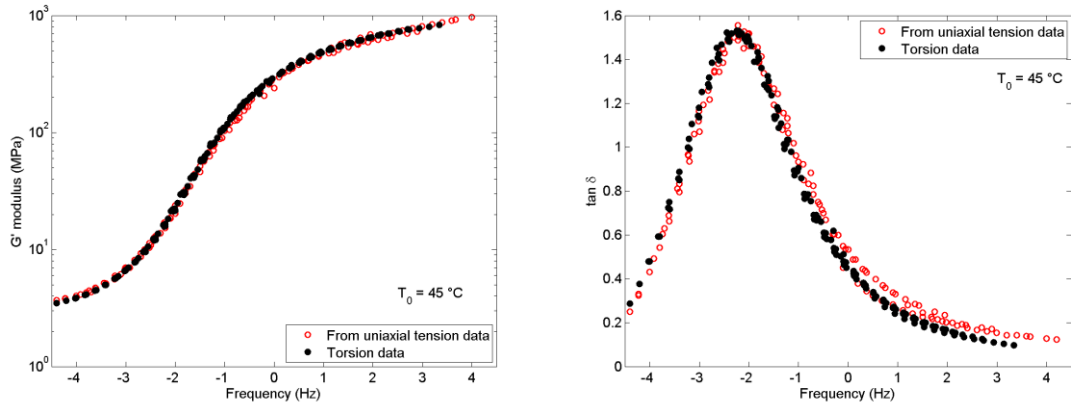


Figure 4. Comparison of the master curves for the storage moduli  $G'$  and damping factors  $G''/G'$  measured by torsion DMA tests and calculated from uniaxial tension DMA data, assuming the bulk modulus elastic.

Now that the time-temperature superposition property has been estimated at infinitesimal strain, let us return to our primary focus that is exploring the possible time-temperature superposition property at finite strain and its quantitative comparison with the time-temperature property characterized above.

#### 4. Time-temperature superposition at finite strain

##### 4.1. Dependence of the material stress-strain behaviour to temperature and strain rate

The effect of strain rate or temperature on the mechanical behaviour of amorphous polymers at finite strain in uniaxial tension has been illustrated in various contributions. Nonetheless, one may note that experimental focus has been emphasized on thermoplastics rather than on thermosets. An illustration of the impact of the temperature on the acrylate network stress-strain responses, when uniaxially stretched until break at a constant displacement rate, is presented in Fig. 5. The effect of a change of strain rate at constant temperature is also shown in Fig. 5. The material stress-strain responses obtained at constant strain rates are less smooth due to the fact that constant strain rates were applied thanks to piecewise constant crosshead displacement speed as explained in section 2.2. When presented as such, the stress-strain responses plotted in Figure 5 suggest that time-temperature superposition exist at finite strain but without providing access to its quantitative estimate.

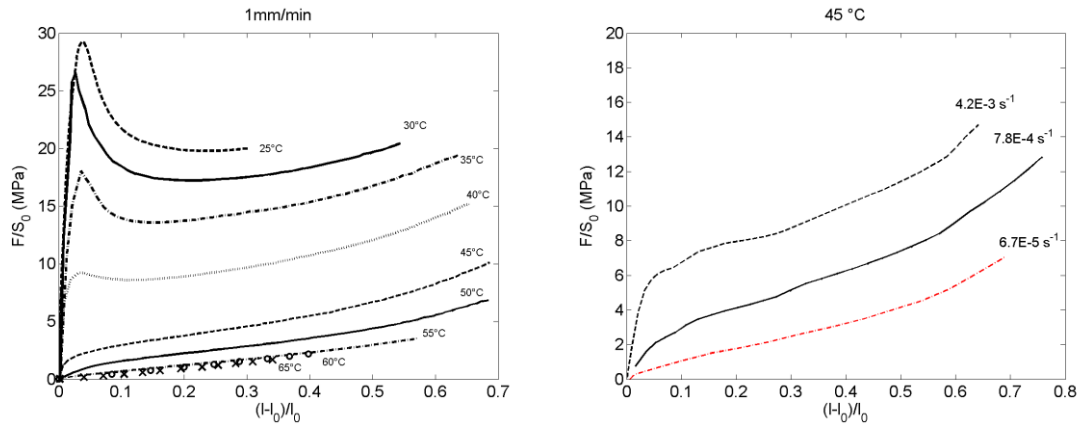


Figure 5. Temperature and strain rate dependences of the acrylate network stress-strain response to uniaxial tension tests. Left: Tests run at various temperatures and at a constant displacement speed of 1 mm/min. Right: Tests run at various constant strain rates at 45 °C.

#### 4.2. Direct experimental evidence of time-temperature superposition

In order to evidence and estimate the time-temperature superposition property of the acrylate at finite strain, uniaxial tension tests were run at various temperatures and various constant strain rates in order to study the superimposition of the stress-strain behaviours over the complete stretch range sustained by the material. Three different material stress-strain responses were measured at 45 °C according to various applied test strain rates  $\dot{\varepsilon}$  as presented in Fig. 5. For each of these stress-strain responses, different pairs  $(T, \dot{\varepsilon})$  are to be found in order to show that it is possible to find the same stress-strain response at other temperatures by setting the strain rate to the suitable values. For temperatures lower than 45 °C, the adequate strain rate is expected below the strain rate applied at 45 °C, while at temperatures higher than 45 °C, the applied strain rate should be above. It was decided to change the temperature within a 10 °C range in order to keep the strain rate variations within our equipment capacity. Once the temperature set, several tests at constant strain rates were run until reaching a good match of the material stress-strain response with one of the responses obtained at 45 °C and plotted in Fig. 5. Fig. 6 shows the material stress-strain responses obtained at 45 °C that were presented in Fig. 5 and similar stress-strain responses obtained with the same material at other temperatures and constant strain rates. Therefore, a time-temperature superposition does apply at finite strain, at least in the temperature and strain rate ranges considered. Moreover, this superposition requires a mere shift factor to be applied to the strain rate, which is in favour of thermorheologically simple (TRS) models [5,17,18], where the material free energy is written in terms of strain history using a reduced time that depends on temperature history through the shift factor.

Using the same definition as in Eq. (1), the experimental values of the shift factors at finite strain can be deduced from the strain rate values  $\dot{\varepsilon}$ ,



$$\dot{\varepsilon}(T) = \frac{\dot{\varepsilon}(T_0)}{a_{T_0}(T)}. \quad (5)$$

From Fig. 6 and using Eq. (5), one may estimate three sets of  $a_{T_0}(T)$  values at finite strain for the reference temperature of  $T_0=45$  °C. Fig. 7 presents a comparison of these shift factors and those obtained at infinitesimal strain (Fig. 3), and it can be observed that all shift factors are aligned. Therefore, the acrylate network shows the same time-temperature superposition property at infinitesimal strain as at finite strain. As a consequence, standard small-strain DMA tests may be enough to identify easily the time-temperature superposition that applies at finite strain, which was already used for shape memory modelling for instance [5,17] but without experimental evidences supporting it. Note that this conclusion was reached at moderate strain rates, further work would be necessary to investigate the case of high strain rate conditions, which has interested several authors [2-3,19-20]. The latter recent publications, dealing with amorphous or semi-crystalline polymers, have evidenced time-temperature superposition at finite strain on the peak stress value only and without direct comparisons with the time-temperature superposition property measured by DMA.

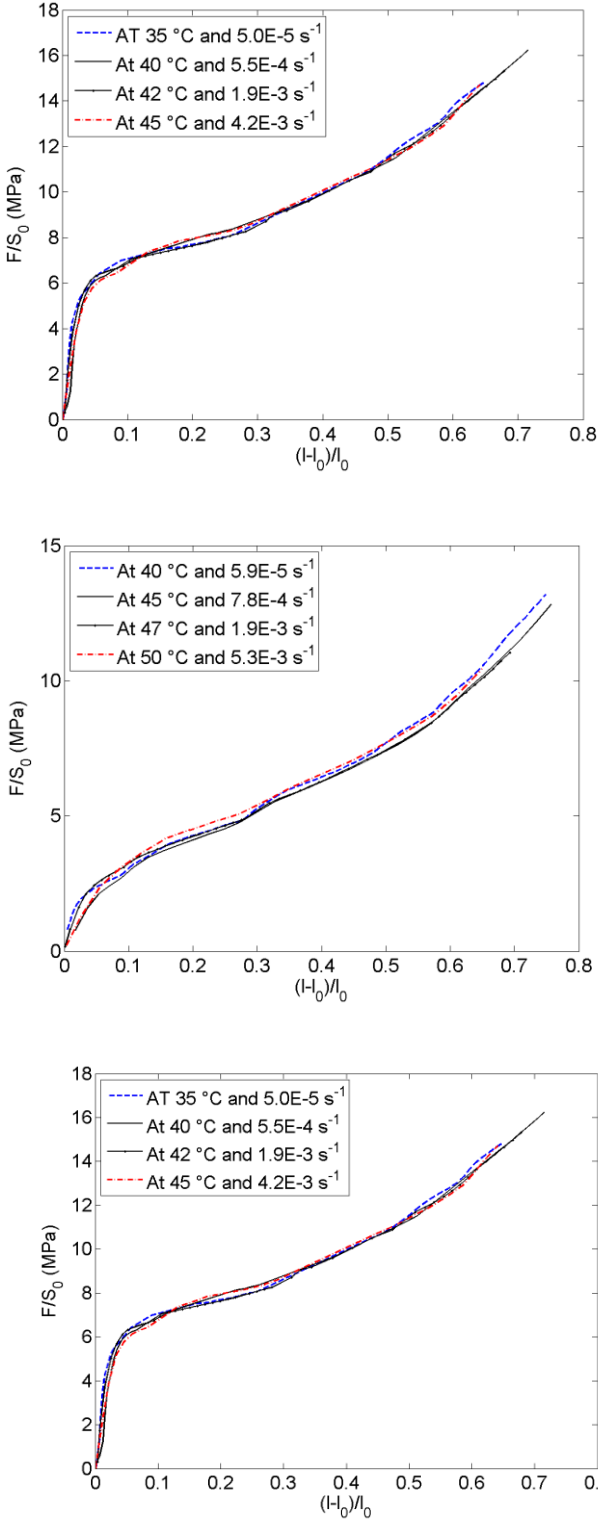


Figure 6. Experimental evidence of time-temperature equivalence at finite strain: Uniaxial tension stress-strain material behaviour for various temperatures and strain rates.

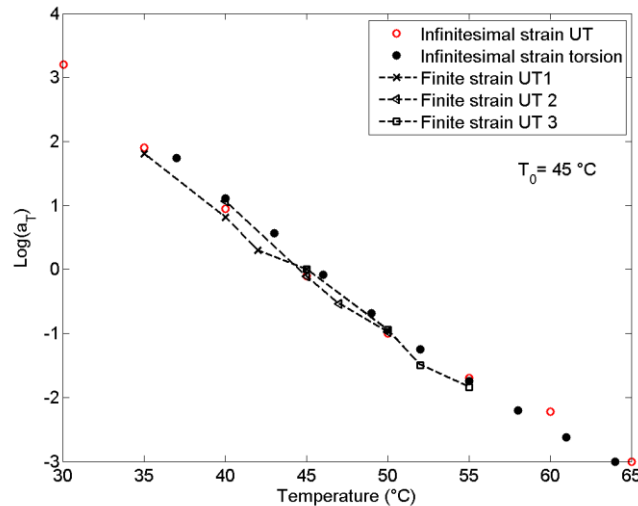


Figure 7. Comparison of the time-temperature superposition shift factors obtained at infinitesimal strain (Fig. 6) and at finite strain in uniaxial tension (UT).

## 5. Conclusion

An acrylate network was synthesized in lab and submitted to mechanical tests in order to better understand the temperature and strain rate dependences of the mechanical behaviour of amorphous networks when submitted to finite strain. The time-temperature superposition property of the acrylate amorphous network was studied at infinitesimal strain by classic dynamic mechanical analysis and at finite strain by applying uniaxial tension until break at various constant temperatures and constant strain rates. Experimental results obtained at finite strain confirmed results from the literature exhibiting a strong dependence of the material uniaxial tension stress-strain response to temperature and strain rate. More interestingly, it was observed that the same stress-strain response could be obtained for various temperature and strain rate conditions. From these experimental evidences, it was possible to determine the time-temperature shift factors measured at finite strain. When compared to the infinitesimal strain time-temperature shift factors, it was showed that the time-temperature superposition property exhibited by the material was the same at small strain and at finite strain. This original experimental result should help defining more relevant temperature and rate dependent constitutive models for amorphous networks at finite strain relevant for rubber or shape memory polymer applications for instance.

## Acknowledgement

This work was supported by the French Agence Nationale de la Recherche, through project REFORM 10-JCJC-0917.

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