Viscoelastic Characterisation of an Epoxy based Shape Memory Polymer(SMEP)

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ABSTRACT
Epoxy based shape memory polymer was developed by curing the epoxy resin, Diglycidyl Ether of Bisphenol A (DGEBA) with 4,7,10 trioxa-1,13-tridecanediamine (TTD). The viscoelastic behavior of the SMEP was evaluated using an Advanced Rheometric Expansion System (ARES). The well known Time Temperature Superposition (TTS) principle was applied to generate the master curve by selecting loss modulus peak as glass transition temperature (T_g). The two constants, C_1 and C_2 of the Williams Landel Ferry (WLF) equation were determined and they have been compared with the universal constant values for amorphous polymer. The results obtained from these studies have been reported in this paper which is useful inputs for predicting the shape memory behavior of the SMEP.

Keywords: Epoxy, Shape memory polymer, WLF equation, TTS curve.

1. INTRODUCTION

Shape memory polymers (SMPs) represent an important recent addition to the smart materials family [1-3]. Among the large variety of SMPs reported till date, chemically cross-linked thermosetting epoxy based shape memory polymers (SMEPs) [4-6] seem to possess unique thermomechanical properties with excellent shape memory behavior. They have immense potential for morphing futuristic aerospace structures [7]. At the molecular level, an SMEP network is composed of rigid hard segments such as high molecular weight bulky aromatic groups and flexible soft segments such as low molecular weight, linear, aliphatic long chains. Hard segments are responsible for setting the permanent shape while the soft segments enable the fixing of the temporary shape and recovery of the permanent shape. A typical shape memory cycle involves four important steps, deformation of the sample at high temperature (i.e at or above its T_g), cooling the deformed sample to room temperature under constraint, removal of the constraint and reheating the sample to study the shape recovery behavior. In each shape memory cycle, an SMEP experiences different temperature regimes ranging from glassy to rubbery phase. In order to understand the shape memory behavior of SMEPs in depth, it is very essential to study their viscoelastic properties in the glassy to rubbery regimes.

Time Temperature Superposition (TTS) is a valuable tool for describing the viscoelastic behavior of amorphou polymers over a broad range of time/frequency by shifting data obtained at several temperatures to a common reference temperature [8]. Generally the Tg of a polymer is taken as reference temperature. Mathematically this can be expressed by:

$$E(T_1, t) = E\left[T_2, \frac{t}{a_T}\right] \quad (1)$$

Where E = Modulus, T= Temperature, t = Time,
a_T = Horizontal shift factor

The degree of horizontal shift (a_T) required to shift a given set of data up on a reference temperature can be described by WLF equation (equation 2) or by simplified Doolittle equation (equation 3). Both equations are derived from the free volume theory of polymers [8].

$$\log a_T = \frac{-C_1(T-T_g)}{C_2+(T-T_g)} \quad (2)$$

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$$\log a_T = -\left(\frac{B}{2.303 f_g}\right)\left[\frac{T - T_g}{(f_g/\alpha_f) + T - T_g}\right] \qquad (3)$$

Equation 3 is a form identical to WLF equation where C_1 and C_2 are related to fractional free volumes as follows.

$$C_1 = \left(\frac{B}{2.303 f_g}\right) \qquad (4)$$

$$C_2 = \left(\frac{f_g}{\alpha_f}\right) \qquad (5)$$

where f_g is fractional free volume and α_f is the thermal coefficient of expansion of the free volume.

The free volume theory is important to understand the behavior of SMEPs. The constants C_1 and C_2 were originally taken to be universal for all amorphous polymers with C_1=17.44 and C_2 =51.6[8]. It was later found that these values vary with polymers and it is important to determine these constants for all polymers in order to evaluate their viscoelastic behavior.

TTS principle has been applied to a wide variety of polymers including elastomers, thermoplastics, partially crystalline polymers, and filled polymers [9-11]. It finds application in long-term structural durability design with short-term accelerating tests at elevated temperatures [12]. However, from the literature survey, very few have reported the use of this principle for predicting the shape recovery time–temperature dependence of the SMPs [13-15]. In most of the studies, they have used automated software to generate master curve [9-15].

In the present work, an SMEP of 33 % soft segment content was prepared and viscoleastic characterization has been performed. Temperature sweep experiments were carried out at frequencies ranging from 0.1Hz to 70Hz. Using simple MS Excel tool, the horizontal shift factors were evaluated and the master curve was generated for the SMEP. WLF equation constants C_1 and C_2 were determined and compared with the universal constants reported in literature [8].

2. EXPERIMENTAL
2.1 Material Details
An aromatic epoxy resin, Diglycidyl Ether of Bisphenol A (LY556), procured from M/s. Huntsman advanced materials (India) Pvt. Ltd., Mumbai, was cured with a long chain aliphatic diamine, 4,7,10 – Trioxa -1, 13-Tridecanediamine (TTD), procured from M/s. Sigma Aldrich, USA.

2.2 Preparation of Castings
Measured quantities of LY 556 resin was heated at 80°C for 1h to reduce its viscosity. After heating, the resin was degassed under vacuum for 1h in order to remove the entrapped air bubbles. It was then cooled to room temperature and stoichiometric amount of TTD hardener was added to it. The resin and hardener mixture was stirred thoroughly and degassed once again for 20 minutes. The mixture was then poured into a metallic cavity mould of dimensions 200mm X 200 mm X 2 mm and cured for 24h at room temperature. Then, the casting was released from the mould and ARES test specimens of dimensions 45mm X 10mm X 2 mm were prepared by using water jet machining. These specimens were post cured in steps (50°C-½ h, 70°C-1h, 85°C-2h). Before subjecting to ARES test, the specimens were thermally cycled 3 times between 25°C and 100°C so as to remove the thermal strains that could be accumulated during fabrication.

2.3 Viscoelastic Characterization
An Advanced Rheometric Expansion System (ARES - M/s. Waters Inc., USA make) was used to determine viscoelastic properties of TTD SMEP. The samples were tested using torsion rectangular geometry. They were heated from 25°C to 150°C at a heating rate of 5°C/min and a strain of 0.1% with frequencies ranging from 0.1Hz to 70 Hz.

3. RESULTS AND DISCUSSION
3.1 Viscoelastic Characterization
Storage modulus (G'), loss modulus (G") and tan δ as a function of temperature at 1Hz have been represented in Figure 1. From this figure, it can be noticed that the loss modulus peaks at 60°C and tan δ peaks at 68°C. To generate the master curve, loss modulus peak (60°C) was selected as T_g.
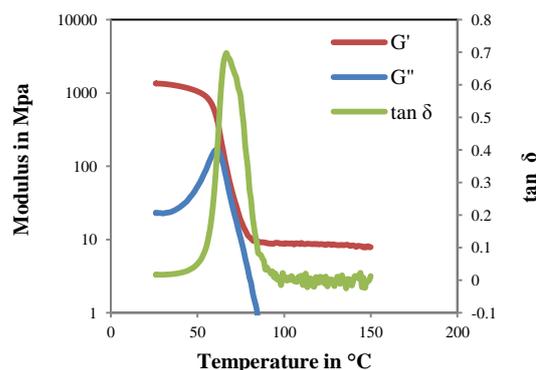

Figure 1: ARES data of the TTD SMEP at 1Hz.

Figure.2 shows the storage modulus (G') vs temperature curves at various frequencies (i.e 0.1Hz to 70Hz) and it has been used to generate master curve. It can be observed from the figure that curves shift from left to right with increasing

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frequencies. At lower frequencies, G' is found to be low and G' increases with the increase in frequency and this phenomenon has been well explained by the theory of viscoelasticity [8]. At lower frequencies the samples have sufficient time to relax and the viscous component of the polymer dominates where as at higher frequencies the experimental time scale becomes too short, hence elastic component dominates and the polymer behaves like a rigid elastic rod. By transposing the data obtained from Figure 2, G' as a function of log (f) has been plotted (Figure 3). The master curve (Figure 4) was generated by horizontally shifting the G' of various temperatures on a reference temperature i.e T_g of the SMEP (60°C). The WLF equation (equation 2) is rearranged as follows
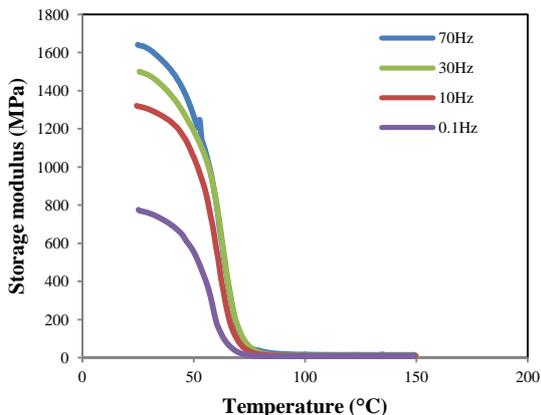

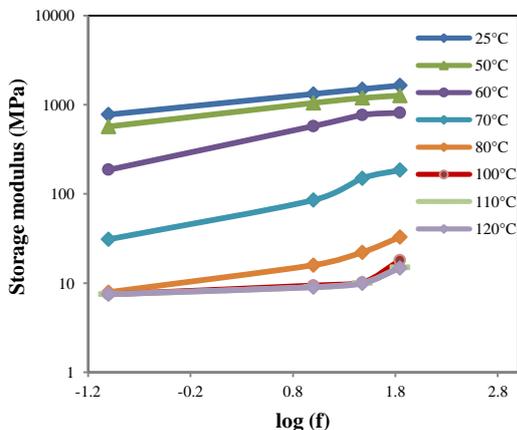**Figure 2:** Storage modulus as a function of temperature at different frequencies.

Figure 3: Storage modulus as a function of log (f) at various temperatures.

$$\frac{1}{\log a_T} = \frac{-1}{C_1} - \frac{C_2}{C_1}\frac{1}{(T-T_g)} \qquad -------(4)$$

and $1/\log (a_T)$ is plotted against $1/(T-T_g)$ [Figure 5] and constants C_1 and C_2 of the WLF equation were evaluated from the intercept and slope of the figure. For TTD SMEP, the values of the constants obtained are, $C_1= 12.2$ and $C_2= 50.08$. These data
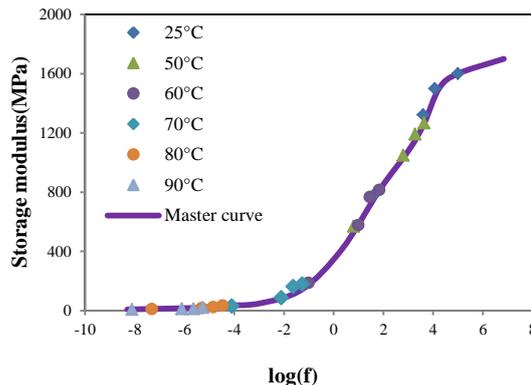

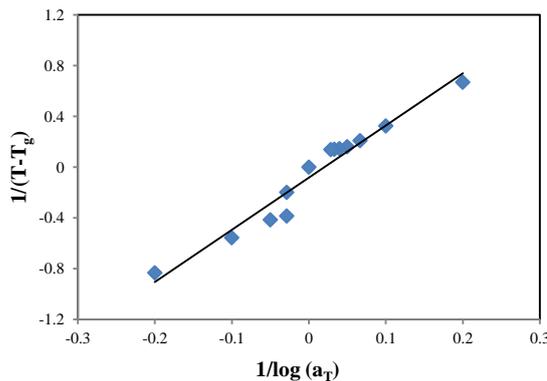**Figure 4:** Storage modulus master curve at 60°C.

Figure 5: WLF approximation of the horizontal shift factor.

are very useful for relating the viscoelastic properties of the SMEP at one temperature to that at another temperature by a change in frequency scale which in turn will be applicable in the prediction of shape recovery behavior of the SMEP.

It is worthwhile comparing the constants C_1 and C_2 for the present SMEP with the universal constants reported in literature [8]. The presence of soft segment content in the SMEP increases the fractional free volume. Since the C_1 is inversely proportional to the increase in f_g, it is found that the C_1 value for SMEP is lower than that of the universal constants.

4. CONCLUSION
In order to arrive at the viscoelastic behavior of SMEP over a wide range frequencies, a well known TTS principle has been used. The Temperature function (horizontal shift factor, a_T) has been determined. Further, the constants, C_1 and C_2 of WLF equation were evaluated and compared with those of universal constants for amorphous polymers. The presence of soft segment in the SMEP seems to influence the C_1 value. These studies on viscoelastic characterization of the TTD SMEP will be useful in understanding and

predicting the shape memory behavior over a wide range of service conditions.

Acknowledgements

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