Time and Temperature Effect on the Linear–Nonlinear Viscoelastic Transition Threshold of a Polymeric System

G. C. Papanicolaou, A. G. Xepapadaki, K. Karagounaki, S. P. Zaoutsos

Composite Materials Group, Department of Mechanical and Aeronautical Engineering, University of Patras, Patras 26500, Greece

ABSTRACT: In the present study, the transition of a polymeric material from the linear to the nonlinear viscoelastic behavior and the determination of the nonlinearity stress threshold variation with time and temperature are investigated. For this purpose a systematic experimental program consisted of thermal and mechanical characterization of certain polymeric material followed by isothermal creep tests at different stress levels and temperatures was conducted. Through isochronal curves that occurred from creep tests, the nonlinearity threshold dependence on both time and temperature is presented. The reported results provide information that is critical for the design and development of polymer structures and components. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 640–649, 2008

Key words: creep; composites; resin; transition

INTRODUCTION

Linear viscoelastic behavior of materials has been the subject of extensive studies for over a century, but it is only in the last few decades that researchers have started to pay special attention to the more complex subject of nonlinear viscoelasticity.

A certain number of nonlinear theories of viscoelasticity have been proposed and applied to a certain class of polymers and polymeric composites.[1–9] Most of them admit the existence of a threshold that depends on the applied stress level.[7–9] Beyond this stress dependent limit, viscoelastic behavior becomes nonlinear. However, existing models for the description of this behavior either determine the transition region from linearity to non linearity through experimental observations or assume linear response at a low stress level and then define the threshold as the limit of this response. However, from the experimental point of view the beginning of nonlinearity may appear either at low or high stress levels according to time and temperature conditions.

It is critical for engineers to take into account the limitations that occur beyond the linear–nonlinear viscoelastic stress threshold, in the design criteria of proportionality and superposition.

Few researchers have studied this threshold that is important for the overall time dependent behavior of any material.

In the present investigation, a systematic experimental study for the determination of the linear–nonlinear threshold transition of a polymeric material and its time and temperature dependence is conducted.

THEORETICAL BACKGROUND

At low stress levels, the creep strain is related to the applied stress by the so-called *creep compliance*, which is defined as:

$$D(t) = \frac{\varepsilon(t)}{\sigma_0} \qquad (1)$$

If a stress input $\sigma(t)$ is arbitrary (variable with time) instead of a constant, this arbitrary stress input can be approximated by the sum of a series of constant stress inputs.

The Boltzmann superposition principle,[10] applied in the case of linear viscoelastic behavior, states that the sum of the strain outputs resulting from each component of stress input is the same as the strain output resulting from the combined stress input and if the number of steps tends to infinity, the total strain can be expressed by an integral representation as:

$$\varepsilon(t) = D_0\sigma_0 + \int_0^t \Delta D(t - \tau)\frac{d\sigma}{d\tau}d\tau \qquad (2)$$

where the creep compliance $D(t)$ is separated into a time independent (elastic) compliance D_0, which is

Correspondence to: G. C. Papanicolaou (gpapan@mech.upatras.gr).

the *instantaneous compliance* value at $t = 0^+$ and a time dependent creep function $\Delta D(t)$ called the *transient compliance* component.

At every moment, t, both the instantaneous compliance and the transient compliance component are independent of the applied stress.

In general, the Boltzmann's superposition principle provides adequate representation of the material time dependent response in the linear region, i.e., at low stress levels.

For the case of a constant applied stress, i.e., the case described in eq. (1), the Boltzmann's superposition principle can be formulated as:

$$\varepsilon(t) = D_0\sigma_0 + \Delta D(t)\sigma_0 \qquad (3)$$

Most materials are nearly linear over certain ranges of the variables, stress, strain, time, and temperature and nonlinear over larger ranges of some of the variables. Any demarcation of the boundary between linear and nonlinear is arbitrary. The maximum permissible deviation from linear behavior of a material which allows a linear theory to be employed with acceptable accuracy depends on the stress distribution, the type of application, and the background of experience. For example, under very short duration of loading many plastics behave linearly even at stresses for which considerable nonlinearity is found if the duration of loading is much longer. In fact, the strain during creep of many plastics can be separated into a time-independent linear part and a time-dependent nonlinear part.

Consider another situation. The deflection of a member containing a steep stress gradient, such as a bar in tension containing a hole, may be essentially linear even under forces that cause highly nonlinear behavior in the very localized region of highest stress around the hole.

After all factors are taken into account, a designer must decide on an acceptable range of the variables over which linear theory may be employed. When the requirements of the design exceed these limits the use of linear constitutive equations will yield only a poor approximation of the actual behavior of the material. This limit constitutes of a critical value of stress, which is named as *stress threshold from linear to nonlinear viscoelastic behavior*.

From experimental point of view, the threshold of viscoelastic nonlinearity can be determined with the use of the isochronous stress–strain curves.[11] Such a curve can be drawn by taking a constant time section through the creep curves and plotting stress versus strain as shown in Figure 1. If isochronous stress–strain curve at a given time, is a straight line, then the material it is said to behave in a linear viscoelastic mode at that time. The divergence of
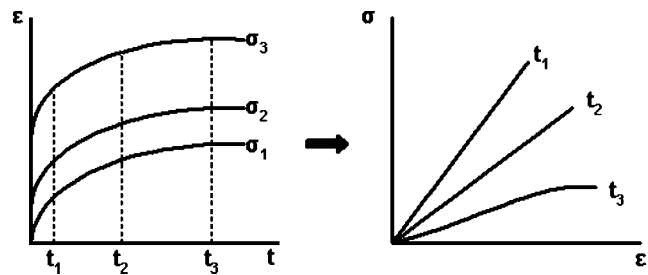

Figure 1 Construction of isochronous curves from creep curves.

points from the straight line, expresses the event of nonlinearity.

Assuming two points of the isochronous curve (ε_1, σ_1) and (ε_2, σ_2) for stress levels 1 and 2, respectively, then:

$$\varepsilon_1 = D_1\sigma_1 \qquad (4)$$

$$\varepsilon_2 = D_2\sigma_2 \qquad (5)$$

where D_1 and D_2 are the compliances for applied stress levels 1 and 2, respectively. If the two stress levels are found within the linear region, then the two compliances will be equal to each other.

Then, the slope α of the isochronous curve in logarithmic scale can be calculated as:

$$\alpha = \frac{\log \varepsilon_2 - \log \varepsilon_1}{\log \sigma_2 - \log \sigma_1} = \frac{\log(\varepsilon_2/\varepsilon_1)}{\log(\sigma_2/\sigma_1)}$$
$$= \frac{\log[(D_2/D_1)\sigma_2/\sigma_1]}{\log(\sigma_2/\sigma_1)} \qquad (6)$$

Then, if:

$$D_1 = D_2 \quad \Rightarrow \quad \alpha = 1 \qquad (7)$$

If isochronous stress–strain curves are drawn on a log–log scale, will usually give a straight line graph, the slope of which is an indication of the linearity of the material. If the material viscoelastic behavior is perfectly linear, the isochronous curve slope will be 45°. If the material viscoelastic behavior is nonlinear, the slope will be less than this.[12,13]

EXPERIMENTAL PROCEDURE

Materials

An epoxy resin propolymer with the commercial name Araldite CY 219 of CIBA-GEIGY (UK) and an isophorone diamine hardener HY 5161 of the same company with a mixture ratio 2 : 1 was used for the manufacturing of the polymer under investigation. Benzyl alcohol was used as an additive during manufacturing process for obtaining an optimum curing.

TABLE I
Characteristic Properties of the Resin Investigated

Property (after curing)	
Density	1.1–1.2 g/cm^3
Compressive strength (ISO 604)	40–50 MPa
Flexural strength (ISO 178)	95–100 Mpa
Impact strength (ISO 178)	20–25 kJ/m^2
T_g (TMA)	50–55°C

The characteristics of the particular resin are dimensional stability, high strength, and compatibility with usual reinforcing materials. Resin properties, as given from the manufacturer, are shown in Table I.

The reasons for selecting the particular resin for investigation is that it is a commercial resin with numerous applications in shipbuilding, as adhesive, even as matrix in several types of polymer-matrix composites because of its low viscosity in comparison to other resins. Moreover, CY219 is sensitive to temperature variations and because of its low T_g-value (50–55°C) extensive creep deformation is expected to happen at temperatures close to room temperature.

Molding

Special molds were designed for the manufacturing of the specimens from St37 steel plates with a nominal thickness of 2 and 4 mm in a laser CNC digital machine. The preparation of the mold included a treatment with a cohesive Mold Release QV 5110 of CIBA GEIGY specialty chemicals.

Manufacturing procedure

The procedure for specimens' preparation was the same for all types of specimens. The prepolymer and the proper amount of the hardener were stirred thoroughly and put in a vacuum chamber for about 10 min for degassing. Subsequently, the material was put in the proper metallic mold and the molding was subjected to thermal processing in an oven for complete curing. The recommended curing process demands exposure in 60°C for 16 h.

Tensile testing

The testing in tension was carried out using dumbbell-shaped samples according to ASTM D638 standards.[14] Each specimen (Fig. 2) was held into a preheated oven mounted on a tension-compression Housfield H25KM machine with a 20KN load cell, for 1 h before loading at a crosshead speed of 2 mm/min. Isothermal tensile tests were executed at 25, 35, 40, 45, and 50°C. The distance between the grippers was 120 mm. At least five samples were

used for each measurement and the average results were reported here. The nominal stress and nominal strain are defined as the ratio of the draw force to the initial cross-section of samples and the ratio of the crosshead displacement to the initial gauge length of samples, respectively. The nominal strain rate is the ratio of the crosshead speed to the initial gauge length of the sample.

The results were taken in the form of stress–strain curves by means of a proper data acquisition system. After data processing, all mechanical characteristics of the material tested, such as tensile modulus and strength, are calculated.

Differential scanning calorimetry tests

Thermal properties were measured with a TA Instruments® (UK) Q1000 Modulated differential scanning calorimetry (DSC). Samples crimped in aluminum pans. Spectra were recorded from room temperature to 120°C under a 50 mL/min N$_2$ flow, at five different heating rates: 5, 10, 20, 30, and 40°C/min. Sample sizes were 5–10 mg. The results presented herein represent average values from three tests at each condition.

Dynamic mechanical analysis tests

Dynamic mechanical analysis (DMA) was carried out in a nitrogen atmosphere with a DMA 983 DuPont Instruments (UK) device along with a Thermal Analyst 2000 software. Measurement of the storage modulus (E') and loss tangent (tan δ) of fully cured samples was carried out at a frequency of ω = 1 Hz and working in double cantilever with rectangular samples (60 mm × 13 mm × 2 mm) with a free length of 45 mm. The temperature was increased from 20 to 120°C at a constant rate of 5°C/min. T_g was taken as the maximum in the damping peak associated with α transition (maximum of the tan δ curve). The results presented herein represent average values from three tests.

Creep tests

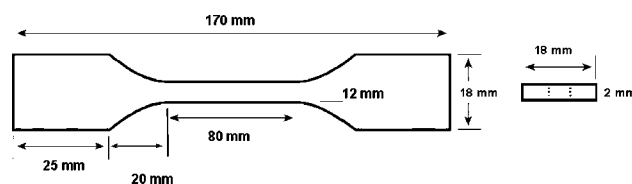Creep tests were performed in an arm lever creep test machine that has a ratio of load capacity ranging

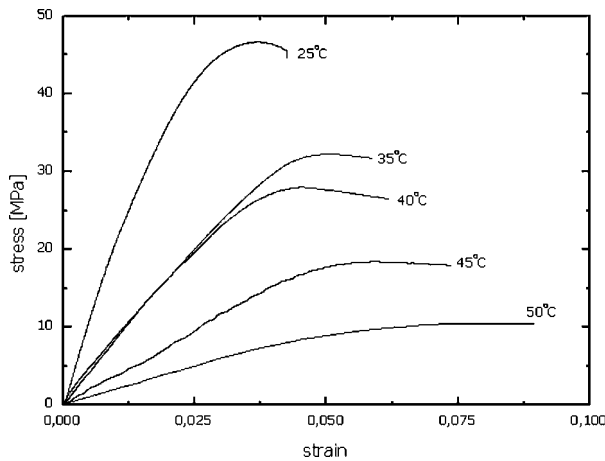**Figure 2** Schematic representation of tensile specimens in the present study.

Figure 3 Uniaxial stress–strain diagrams for the epoxy resin investigated at different testing temperatures.
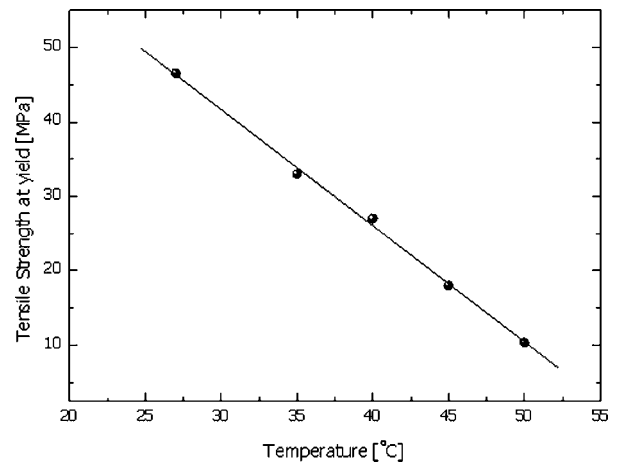

Figure 4 Variation of the tensile strength with temperature.

from 1 : 1 up to 5 : 1. Strain measurements were obtained using an LVDT displacement transducer of RDP Electronic. An A/D converter of National instruments Co was used to acquire the measurements while the treatment of signals was performed with LabView v.6.0 commercial software package.

Creep tests were performed at four different temperatures: 25, 35, 40, and 45°C and at nine different stress levels namely 10, 15, 20, 25, 30, 35, 40, 45, and 50% of the tensile strength.

Creep testing duration was 18 h for specimens conditioned at 25°C and 8 h for all the rest temperature levels. Specimen's dimensions were the same with respective dimensions of tensile specimens. The results presented herein represent average values from at least three tests at each condition.

EXPERIMENTAL RESULTS AND DISCUSSION

Mechanical characterization

Thermoset polymers are increasingly used in engineering applications. The relative ease of manufacturing light-weight components of complex shapes and the wide range of available physical properties makes these materials very attractive for industrial

use. Thermoset resins are often employed in neat form, but find their principle application as matrix materials for composites. A high degree of cross-linking provides thermosets with rigidity and causes them to behave in brittle manner. The brittle behavior remains at elevated temperatures, when the principle mechanism of deformation is microcracking.

Uniaxial stress–strain diagrams for the epoxy resin investigated at different testing temperatures are shown in Figure 3. Experimental values for both the tensile modulus and strength are tabulated in Table II.

As it can be seen from Figure 4, a dramatic linear decrease of the tensile strength with temperature is observed.

In addition, as it is shown in Figure 5, an exponential decrease in modulus with temperature is observed.
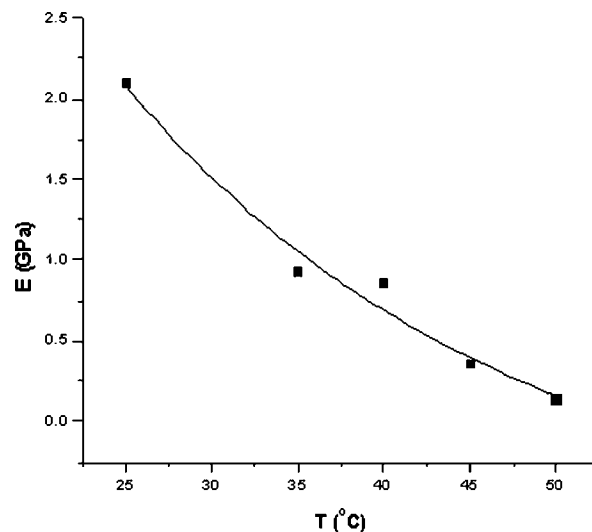
TABLE II
Values for the Strength and Modulus at Different Temperatures

Temperature (°C)	Strength (MPa)	E (GPa)
25	46.50	2.10
35	33.15	0.93
40	28.20	0.86
45	18.13	0.36
50	10.11	0.14

Figure 5 Variation of the tensile modulus with temperature.

Heating rate (°C/min)	Transition region (°C)	T_g (°C)
5	48.77–62.35, $\Delta T = 13$	59.25
10	49.97–71.19, $\Delta T = 22$	56.10
20	50.57–73.71, $\Delta T = 22$	58.82
30	42.60–75.71, $\Delta T = 32$	59.04
40	59.42–98.12, $\Delta T = 39$	67.91

Glass transition temperature (T_g) measurements

Amorphous polymers are viscous liquids when they are held at temperatures above their glass transition temperature, T_g. Below T_g, the material is solid, yet has no long-range molecular order and so is non-crystalline. In other words, the material is an amorphous solid, or a glass.

The glass transition of a polymer is related to the thermal energy required to allow changes in the conformation of the molecules at a microscopic level, and above T_g there is sufficient thermal energy for these changes to occur. However, the transition is not a sharp one, nor is it thermodynamically well defined.

Under elastic tension or compression conditions, a polymer tries to move apart or together its molecular chain-ends. For a simple polymer chain to change its conformation, individual C—C bonds must twist from the trans to gauche position or vice versa, i.e., the torsion angles must change. This is a thermally activated process. At low temperatures, there is not enough thermal energy available to allow torsion angle changes, so the conformation becomes frozen in. The temperature above which the torsion angles can change is called the glass transition temperature. The changes in conformation also depend on timescale, so the apparent value of T_g depends on the

time-scale over which the behavior is being monitored.

The strain in a polymer is accommodated by the change in shape of the individual molecules, but it should be noted that the response of the bulk polymer is influenced by the interactions between the molecules. This affects the ability of the bonds to rotate, and also the viscosity of the bulk polymer.

The T_g of a polymer is affected by many factors, which are classified into two main categories. The first one includes factors related to the polymer structure and these are: chain length, chain flexibility, side groups, branching, cross-linking, and the presence of plasticizers. The second category includes factors related to: (a) the method applied (i.e., TMA, DMA, DSC, etc.), (b) mode and rate of mechanical loading, and (c) rate of heating or cooling.

Especially with rate effects, at very short loading times the polymer can still be glassy because there is no time for the chains to move. At intermediate times the polymer may be rubbery, i.e., chains can uncoil and recoil between entanglements, which remain stable. Finally, at very long times, the chains can move past each other permanently, and so the polymer behaves as a viscous liquid.

Since the value of the glass transition temperature depends on the strain rate and cooling or heating rate, there cannot be an exact value for T_g.

DSC measurements

The enthalpy of a polymer decreases as the temperature decreases, but with a change in slope in the graph at T_g. Taking the derivative of this graph with respect to temperature, the specific heat capacity can be plotted. The specific heat capacity, C_p, can be
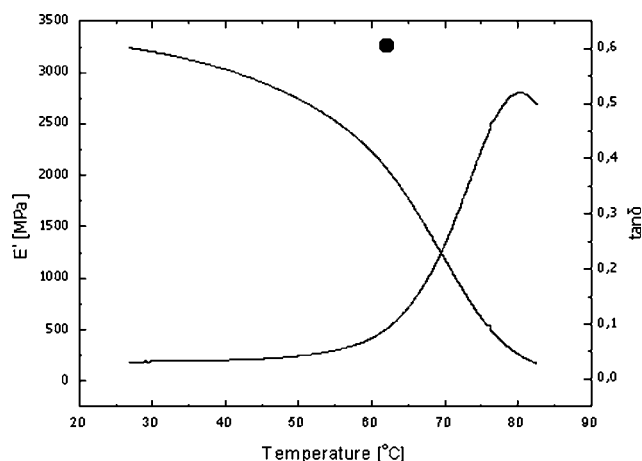

Figure 6   Variation of T_g with heating rate.

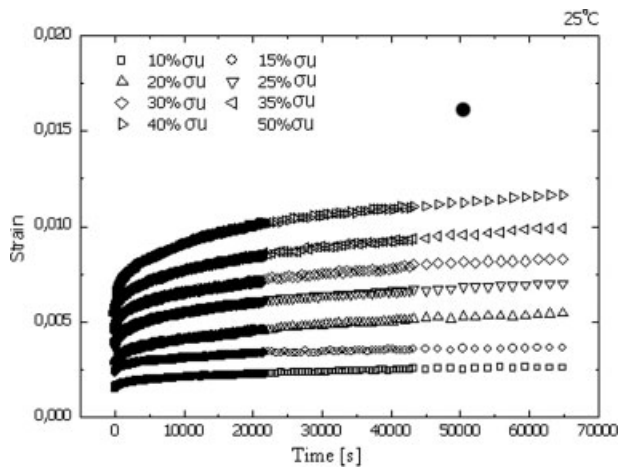**Figure 7**   Variation of storage modulus, E' and tan δ with temperature at 5 °C/min.

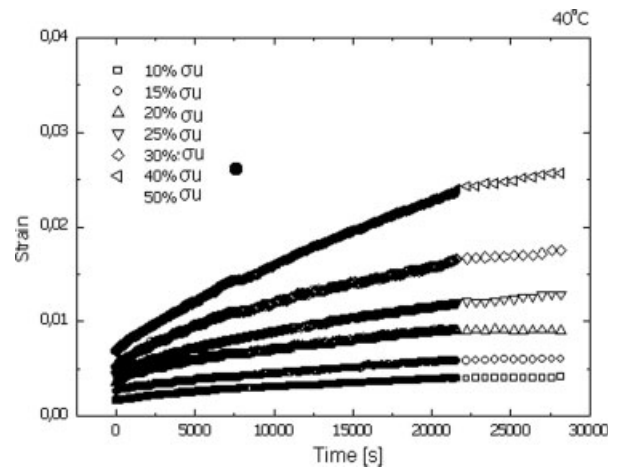**Figure 8** Creep curves at $T = 25°C$ and different stress levels.

Figure 10 Creep curves at $T = 40°C$ and different stress levels.

measured using calorimetry, e.g., DSC. The value of T_g depends on the heating or cooling rate.

In the present investigation, a series of DSC and DMA tests were executed in order to thermally characterize the polymeric material under investigation. T_g values derived from DSC tests at five different heating rates are shown in Table III.

As expected, an increase in T_g values with heating rate is observed (Fig. 6).

Dynamic mechanical thermal analysis measurements

A more common method is dynamic mechanical thermal analysis (DMTA), which measures the energy absorbed when a specimen is deformed cyclically as a function of the temperature, and a plot of energy loss per cycle as a function of temperature shows a maximum at T_g.

Figure 7 shows the storage modulus, E', and tan δ variation as a function of temperature. It is important to notice that T_g value derived from DSC tests and for 5°C/min heating rate is 59.25°C while respective value as derived from DMTA experiments for the T_g and for the same heating rate taken as the maximum in the damping peak associated with α transition (maximum of the tan δ curve) is 82°C. Such an increase is expected since T_g depends on the time allowed for chain segment rotation.

Creep tests

Creep curves occurring from the respective applied stress levels at different temperature conditions are illustrated in Figures 8–11.

To better show the effect of temperature on the creep behavior of the resin, families of strain-time creep curves are displayed in a single graph corre-
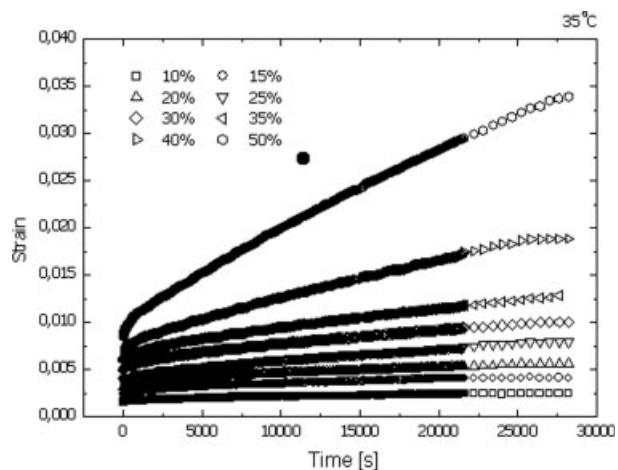
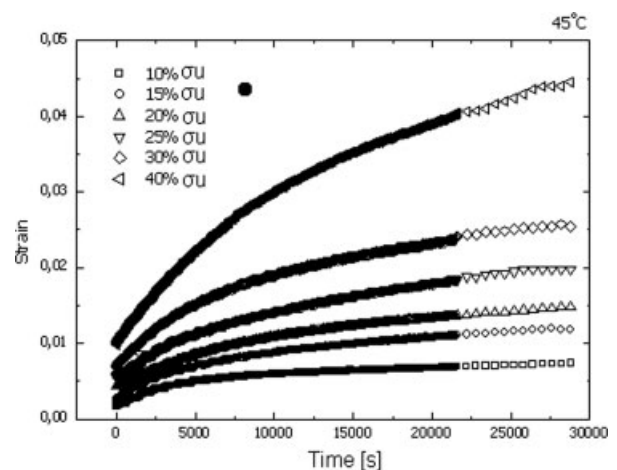**Figure 9** Creep curves at $T = 35°C$ and different stress levels.

Figure 11 Creep curves at $T = 45°C$ and different stress levels.
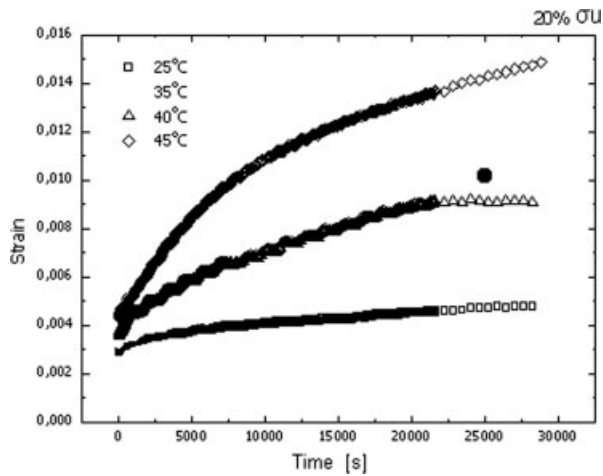
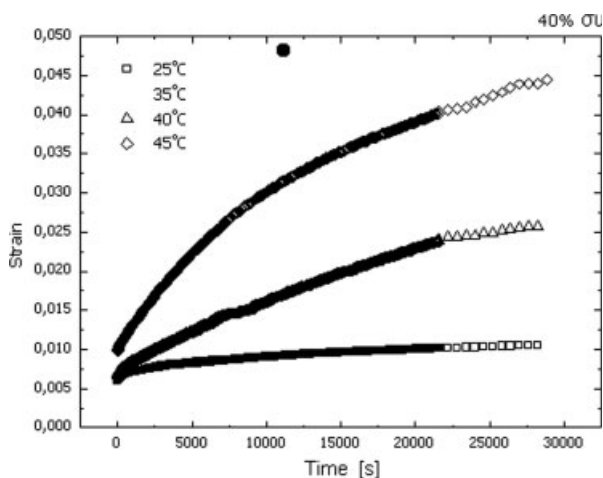**Figure 12** Creep curves at 0.2 fraction of UTS and four different temperatures.

Figure 14 Creep compliance vs. time curves at 25°C.

sponding to the same applied stress level (Figs. 12 and 13).

The creep compliance versus time curves for the above creep curves are shown in Figures 14–17. The nonlinear character of the response of the material under constant stress level is evident from the compliance curves, as compliance increases with stress increase under a certain stress level at every tested temperature.

Next, the characteristic surface in a compliance-time-temperature 3D diagram for applied stress level 0.4 fraction of ultimate tensile strength (UTS) is shown in Figure 18.

Next, the characteristic surface in a compliance-time-stress 3D diagram at $T = 45°C$ is shown in Figure 19.

The isochronous stress–strain curve is a, particularly, useful form of presentation that shows the relation between stress and strain at some fixed time t.

A family of such curves is often displayed on a single graph. In the present investigation, such families of isochronous stress–strain curves were derived from the creep curves and corresponding results are shown in Figures 20–23. The isochronous stress–strain curve for linear viscoelastic behavior is itself linear, and so the curvature of lines is a measure of the nonlinearity of the viscoelastic behavior of the material.

Next, the linear–nonlinear viscoelastic stress threshold (LNST) was determined as the stress corresponding to the point of deviation of the isochronous curve from linearity (Fig. 24).

A significant decrease of the LNST with both temperature and time was found and corresponding results are shown in Figures 25 and 26.

The simultaneous variation of the LNST with both time and temperature is shown in Figure 27. A characteristic surface for the above variation is generated in a stress threshold-temperature-time 3D diagram.
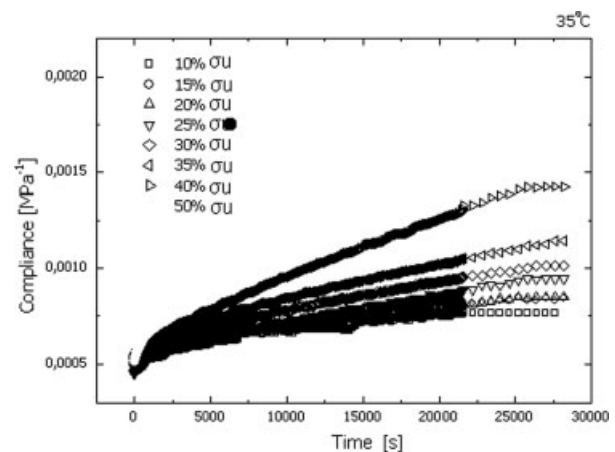

Figure 13 Creep curves at 0.4 fraction of UTS and four different temperatures.
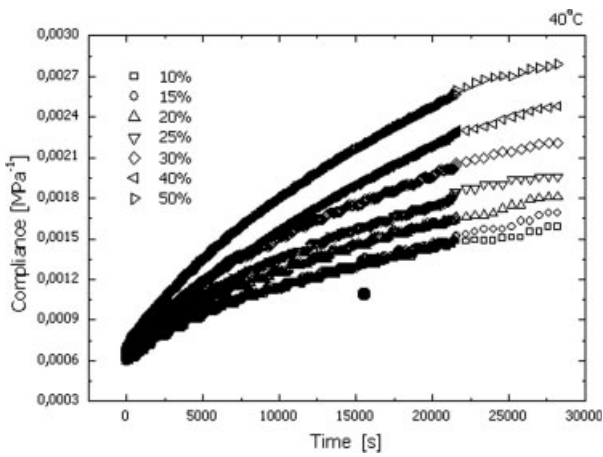

Figure 15 Creep compliance vs. time curves at 35°C.
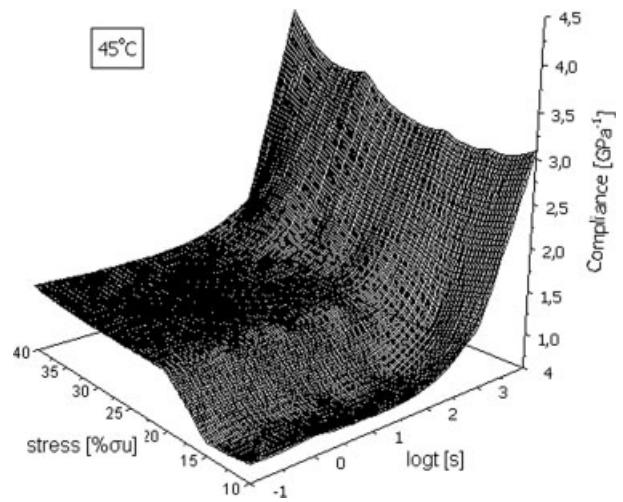
Figure 16 Creep compliance vs. time curves at 40°C.

Figure 17 Creep compliance vs. time curves at 45°C.

Figure 18 The characteristic surface in a compliance-time-temperature 3D diagram.

Figure 19 The characteristic surface in a compliance-time-stress 3D diagram at $T = 45°C$.

Figure 20 Isochronous stress–strain curves for $T = 25°C$.
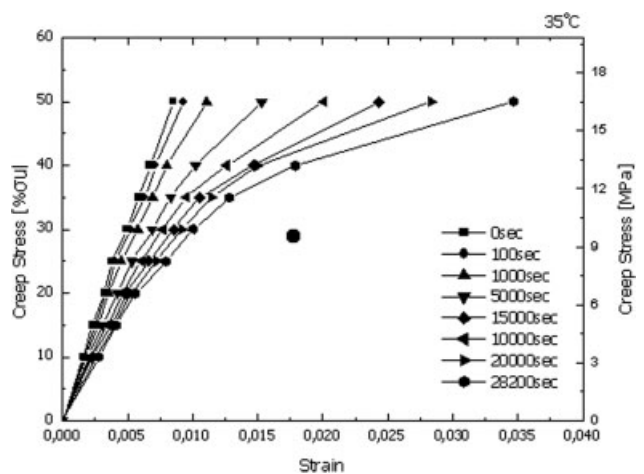
Figure 21 Isochronous stress–strain curves for $T = 35°C$.

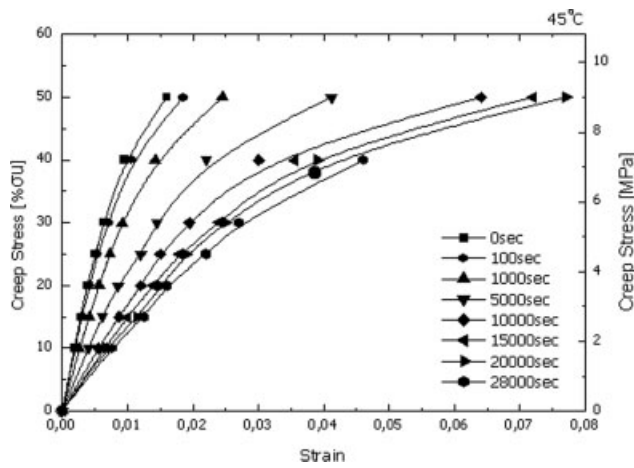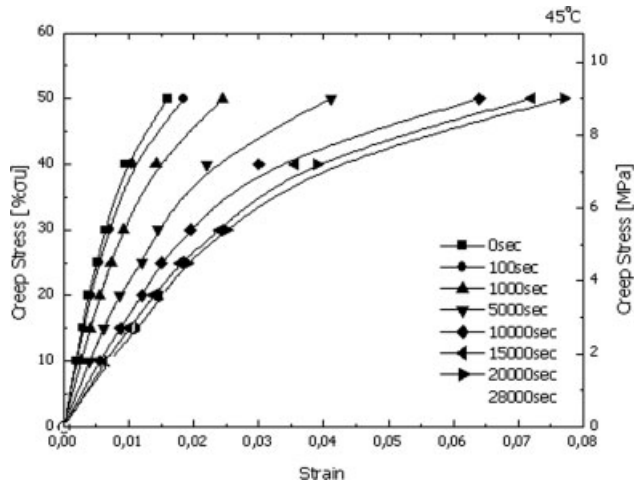**Figure 22** Isochronous stress–strain curves for $T = 40°C$.

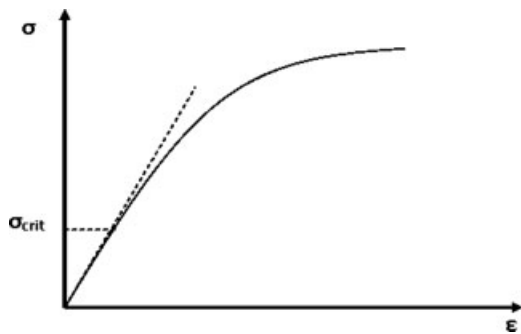**Figure 23** Isochronous stress–strain curves for $T = 45°C$.

Figure 24 Schematic representation of the LNST from an isochronous stress–strain curve.

CONCLUSIONS

A thermoset resin was thermally characterized by DSC at five different heating rates. The dynamic mechanical behavior of the material was investigated by DMA measurements. Next, tensile and short term (12 h) creep tests were performed on the cured resin,
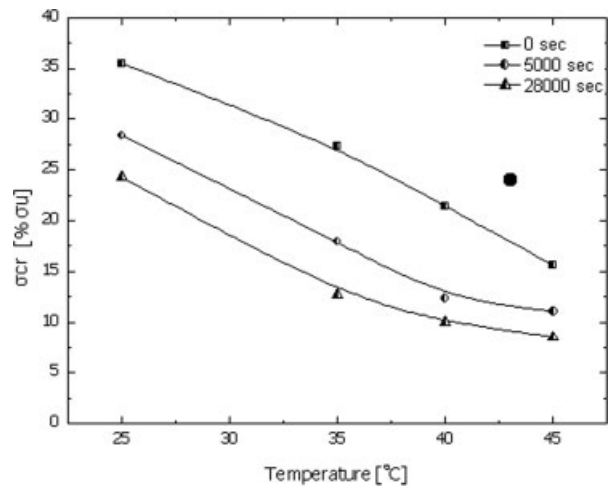

Figure 25 Variation of linear–nonlinear stress threshold with temperature at three fixed times.
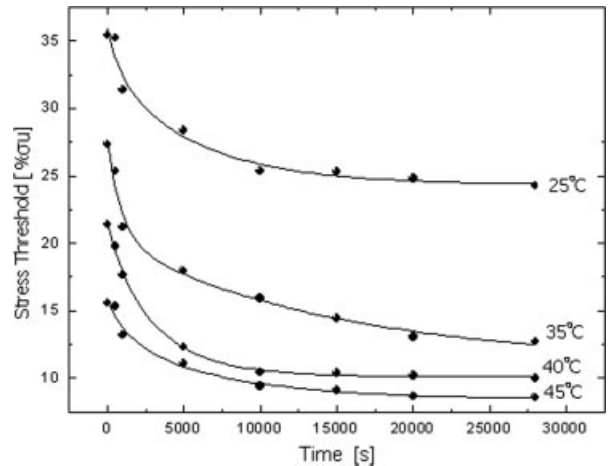

Figure 26 Variation of the linear–nonlinear stress threshold (LNST) with time at four different temperatures.
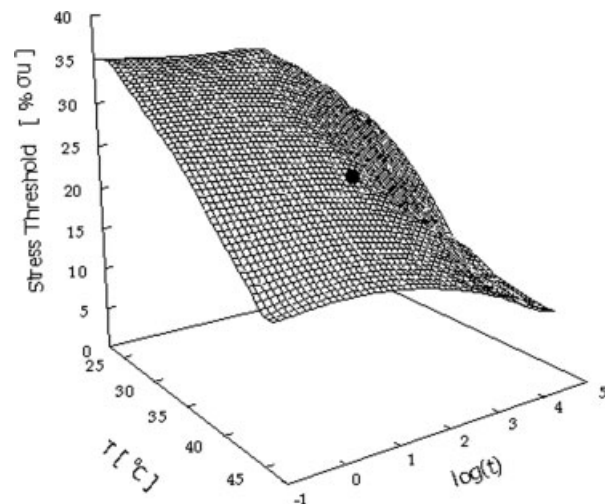

Figure 27 Characteristic surface showing the LNST dependence upon time and temperature.

at five different temperatures and nine different stress levels ranging from room temperature to 50°C and 0.1 fraction of the UTS to 0.5 fraction of UTS, respectively. Resulting conclusions can be summarized as follows:

- Temperature was found to have an effect on the short term tensile properties.
- The resulting strain vs. time creep curves showed the expected dependence of creep strain on temperature and stress level.
- Creep compliance and isochronous curves were derived from the creep curves from which the linear–nonlinear viscoelastic stress threshold (LNST) was determined.
- A significant reduction of the LNST value was observed at 50°C.
- The characteristic surface for the LNST of the polymer under investigation showing its simultaneous dependence on the time, temperature, and applied stress level was constructed and presented.
- The characteristic surface gives the limits of application of the laws of linear viscoelasticity and it is useful for design purposes.

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