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DETERMINATION OF PHYSICAL AND STRUCTURAL PARAMETERS BY DMA AND DSC
Application to an epoxidic formulation

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Abstract

Mechanical behaviour play an important role in the election of an epoxidic formulation of well determined properties as it has a marked influence on both structural and external factors.

Temperature and time strongly act on polymers properties owing to their viscoelastic nature.

Knowledge of the dynamic moduli and properties of polymeric materials is indispensable for the design of this materials. At the same time, the influence of the temperature on polymers behaviour may be studied once the activation energy is known. In this paper the different dynamic moduli and activation energy are measured using a Perkin Elmer DMA 7.

The relationships between the dynamic mechanical properties and the molecular weight of the polymers make possible the calculation of the molecular weight.

Results reasonably agree with literature values.

Keywords: activation energy, DMA, DSC, loss modulus, polymers, storage modulus

Introduction

Epoxy resins derived materials play an important role when trying to find suitable materials for many different applications. Knowledge of some mechanical properties is indispensable for the design of these materials. Owing to their viscoelastic behaviour both temperature and time strongly influence on polymer properties. Their viscoelastic nature make them systems somewhere in the way between an elastic solid (following Hook's Law) and a Newton Law dependent viscous liquid. In the first case the relationship between applied forces and corresponding deformations is linear and so time independent while in the second case deformation depends on the time. In elastic systems the work done by the

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deforming force is stored as potential energy, and can be recovered. In viscous systems a part of the work is dissipated as heat or any other unrecovered energy. Owing to these behaviours it is very important the knowledge of the dynamic mechanical properties of this materials, that is, the mechanical properties of the materials as they are deformed under periodic forces. Among these mechanical properties we find both the storage and the loss moduli. Knowledge of this two moduli make possible to calculate the "molecular weight" of the polymers which gives information about the material structure.

The influence of the temperature on the polymer behaviour needs the knowledge of the activation energy.

In this paper storage modulus, loss modulus, molecular weight between crosslinks and activation energy are determined by using a Dynamic Mechanical Analyzer (DMA 7) and Differential Scanning Calorimeter (DSC 7) from Perkin Elmer.

Experimental

Materials

The resin used was diglycidyl ether or bisphenol A (Epikote 828 from S.P.E. Shell) and *m*-xylylenediamine (*m*-XDA), (Aldrich Chemical Co., 99% pure) as curing agent.

The election of this system was due to its easy handling both at low or high viscosity values in a wide range of frequencies and temperatures. This making it suitable in many fields.

Dynamic mechanical measurements

Dynamic mechanical properties were measured by using a DMA 7 built by Perkin Elmer. It was operated in the temperature scan mode in which temperature is programmed and the frequency and stress are held constant. Temperature dependent behaviour is characterized by changes in strain and phase. Elastic moduli may be readily quantitated as a function of temperature or time. DMA was calibrated following manual instructions. The results obtained for the molecular weight between crosslinks were checked calorimetrically using a DSC 7 from Perkin Elmer.

The DSC 7 was calibrated in the range of selected temperatures using high purity elements. The performance was as described in the DSC procedure manual. The system was continually under nitrogen and the baseline was adjusted daily. Also following manual instructions the DSC holder was frequently

cleaned. The weight of samples taking for DSC experiments was in the range between 10–14 mg.

Sample preparation

Resin and curing agents in a ratio 50/9 were homogeneously mixed. A ratio 100/18 is oftenly used. The mixture is introduced in a cylindric frame previously waxed to avoid adherence. After 24 h at room temperature frames are placed during 2 h in a stove at 120°C. Frames are taken off the stove and samples are cut to adequate dimensions using a wire saw [1].

Results and discussion

Activation energy, E_a, was calculated through an Arrhenius like equation

$$f = f_o \exp(-E_a/RT)$$

being f_o a previously fixed frequency value, of a so-called pre-exponential factor (a constant), R the gas constant and T the glass transition temperature. This value is taken as 40°C over the experimental value in order to assure crosslinks independence, that is, to assure them a certain degree of mobility. All the samples were twice scanned in order to assure crosslinking.

Table 1 shows experimental values in the temperature range 30–250°C for different given frequency value.

From this data and after a linear fitting the value of the activation energy is calculated

$$E_a = 483.21 \text{ kJ/mol}$$

Molecular weight between crosslinks was determined from the experimental values shown in Table 2, using rubber kinetic theory [2, 3]

$$M = \frac{3 \cdot \Phi \cdot d \cdot R \cdot T}{E'}$$

where Φ is a form factor taken as 1, d the polymer density and E' the storage modulus. In this case the glass transition temperature was taken as above, but we used first scanning values to assure a bigger mobility of crosslinks. Density was measured as 1.185 g/cm^3. Molecular weight determined from the above equation is shown in Table 3.

The molecular weight was also determined by stoichiometry

$$M = \frac{\sum n_i \cdot M_i}{\sum n_i}$$

A value $M=271$ g/mol is obtained. This value is in good agreement with those in Table 3.

Finally molecular weight was obtained using Nielssen equation [4]

Table 1 Experimental values of glass transition temperature

f/Hz	Inf	T (40°C + t_{exp}) / K	$1000 \cdot T^{-1}$
First scanning			
1	0	421.42	2.62
5	1.61	423.73	2.61
10	2.30	427.36	2.58
15	2.71	427.71	2.58
20	3.00	428.16	2.58
25	3.22	428.52	2.57
Second scanning			
1	0	431.52	2.55
5	1.61	434.76	2.53
10	2.30	436.68	2.52
15	2.71	438.24	2.51
20	3.00	439.40	2.50
25	3.22	440.13	2.40

Table 2 Experimental values of activation energy

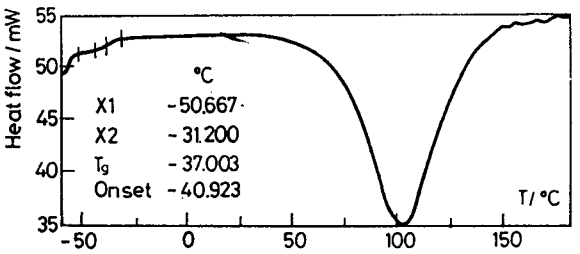
f/Hz	T / K	E' /J·cm^{-3}
First scanning		
1	414.20	46.20
5	414.70	49.87
10	420.97	48.87
15	427.39	48.87
20	435.82	50.88
25	437.23	51.88
Second scanning		
1	431.52	56.86
5	434.76	64.85
10	436.68	61.84
15	438.24	56.86
20	439.40	54.85
25	440.13	61.84

Table 3 Experimental values of molecular weight

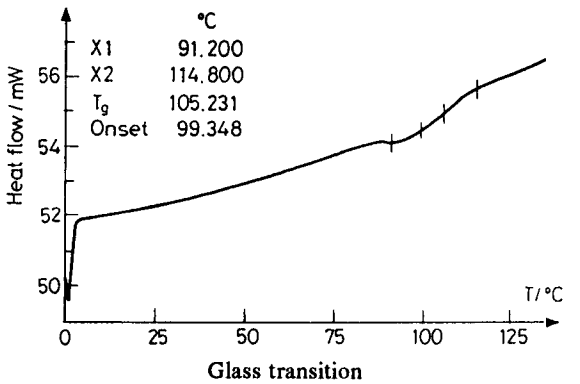
f /Hz	T / K	E' /J·cm^{-3}	M /g·mol^{-1}
1	414.20	46.90	265.50
5	414.70	49.87	250.94
10	420.97	48.87	258.25
15	427.39	48.87	258.46
20	435.82	50.88	253.56
25	437.23	51.88	248.80

$$M = \frac{3.9 \cdot 10^4}{T_g - T_{go}}$$

The glass transition temperature T_g and the glass transition temperature for thermoset with degree of conversion $\alpha = 0$, T_{go} [5] were measured by a DSC 7 of Perkin Elmer, $T_{go} = -37.087$°C and $T_g = 105.231$°C. From the equation $M = 274.03$ g/mol. Figure 1 shows T_g and T_{go} measured by DSC 7.
Figure 2 shows storage moduli in the first scanning for several frequencies.

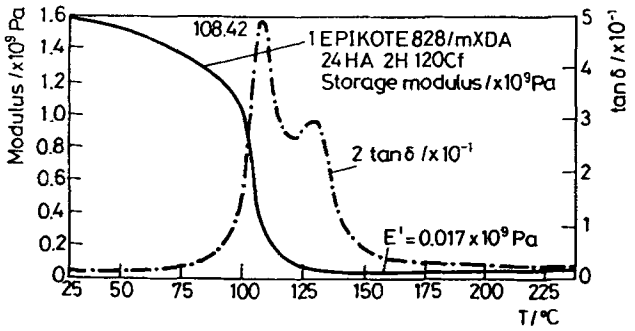


Glass transition for termoset with degree of conversion $\alpha = 0$

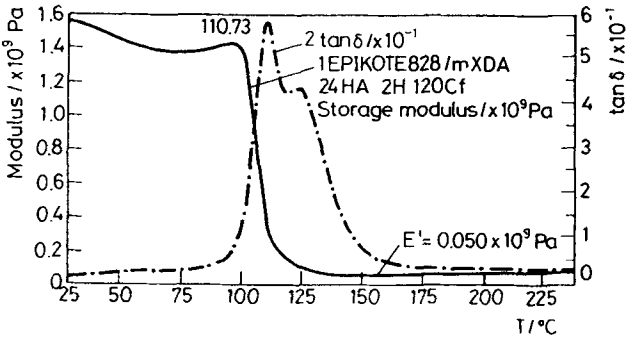


Glass transition

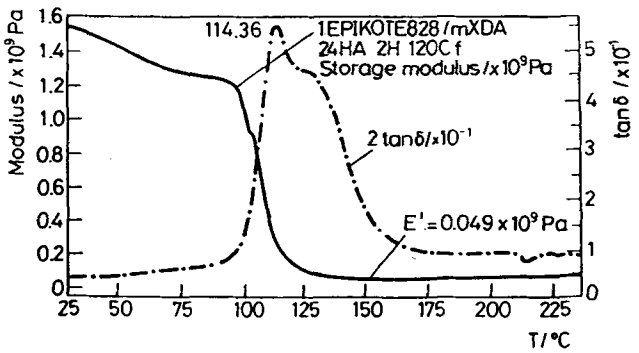
Fig. 1 DSC curves of EPIKOTE 828/mXDA. Sample mass: 10.4 mg; Heating rate: 10 deg·min^{-1}



Modulus and tan δ *vs.* temperature, showing the glass transition peak at frequency 1 Hz

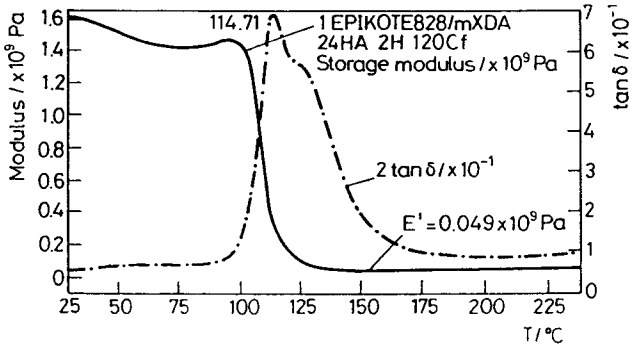


Modulus and tan δ *vs.* temperature, showing the glass transition peak at frequency 5 Hz

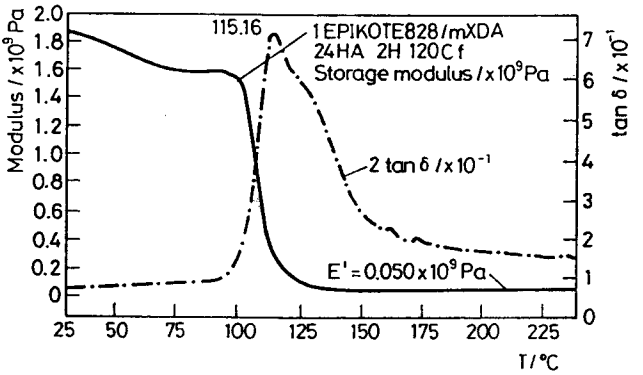


Modulus and tan δ *vs.* temperature, showing the glass transition peak at frequency 10 Hz

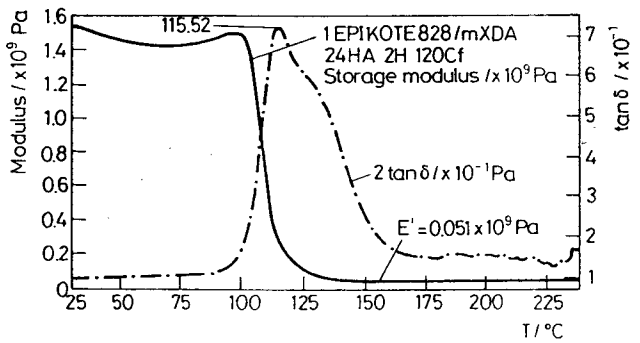
Fig. 2 DMA curves of EPIKOTE 828/mXDA at different frequencies; Dynamic stress: 700 mN; Heating rate: 10 deg·min^{-1}



Modulus and tan δ *vs.* temperature, showing the glass transition peak at frequency 15 Hz



Modulus and tan δ *vs.* temperature, showing the glass transition peak at frequency 20 Hz



Modulus and tan δ *vs.* temperature, showing the glass transition peak at frequency 25 Hz

Fig. 2 (Continued) Continued DMA curves of EPIKOTE 828/mXDA at different frequencies; Dynamic stress: 700 mN; Heating rate: 10 deg·min^{-1}

Conclusions

1. Values of storage modulus, loss modulus and tan δ measured by DMA are in good agreement with literature values.

2. Values of the activation energy obtained from experimental DMA experiments fairly agree with those in the literature, obtained mainly by calorimetric methods.

3. Three different methods: DMA, DSC and stoichiometry were used to estimate molecular weight between crosslinks. The results fairly agree. This means that DMA method can be reasonably accepted for this kind of measurements.

* * *

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Zusammenfassung — Mechanisches Verhalten spielt eine wichtige Rolle bei der Auswahl der Epoxidzubereitung gut definierter Eigenschaften, da es sowohl auf strukturelle als auch auf externe Faktoren einen eindeutigen Einfluß besitzt.
Temperatur und Zeit wirken stark auf die mit der viskoelastischen Natur verbundenen Eigenschaften von Polymeren ein.
Das Kennen der Elastizitätsmoduln und Elastizitätseigenschaften von Polymermaterialien ist für das Design dieser Materialien unentbehrlich. Ist die Aktivierungsenergie erst einmal bekannt, kann gleichzeitig der Einfluß der Temperatur auf das Verhalten der Polymere untersucht werden.
Vorliegend wurden mittels eines Perkin Elmer DMA 7 die verschiedenen Elastizitätsmoduln und die Aktivierungsenergie gemessen.
Die Beziehung zwischen dynamischen mechanischen Eigenschaften und dem Molekulargewicht der Polymere ermöglicht es, dieses Molekulargewicht zu berechnen.
Die Resultate stimmen recht gut mit den Literaturangaben überein.