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Torsion Pendulum for Monitoring Curing Behavior of an Epoxy Resin under Hydrostatic Pressure

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Abstract A newly designed torsion pendulum operating at high pressures and various temperatures has been constructed. The High Pressure Torsion Pendulum(HPTP) is capable of containing gaseous pressure to 690 MPa(100,000psi) and operating at temperatures from −100℃ to 300℃. A glass fiber braid is installed between two sample holders to accommodate liquid samples. The HPTP was fully automated and computerized using an IBM-AT personal computer to control initiation of oscillation, collect digitized data, and calculate the shear and loss moduli from damped curves. The curing process of an epoxy-amine(DGEBA-DDS) system under various pressures up to 124 MPa(18,000 psi) at 150℃ has been successfully carried out and some results are presented.

1. Introduction

A torsion pendulum operating at high pressures has previously been built by Parry and Tabor[1]. The high pressure torsion pendulum was applied to investigate the effect of pressure on secondary relaxations as well as glass transition temperatures of various polymers[1~3]. An inertia mass in this system was suspended to a silver steel wire(an inverted inertia mass system), and a specimen was clamped to sample holders and rotated mechanically by an activating piston. A rotated sample was then manually disengaged in order to let the inertia mass vibrate freely. Another application of a torsion pendulum is a torsional braided analysis(TBA) developed by Gillham and coworkers [4~7]. The TBA has been fully interfaced with a computer, and applied mainly to the curing behavior of thermosets at atmospheric pressure only.

A newly designed High Pressure Torsion Pendulum(HPTP) apparatus has been constructed to investigate the effect of pressure on curing behavior of thermosets. The HPTP was interfaced with an IBM-AT personal computer in order to control its motion, and collect and analyze the experimental data. For isothermal curing of an epoxy-amine system, a large number of damped oscillation curves are normally necessary in each test to monitor various phase changes, and therefore it is essential to utilize a computer for gathering and analyzing data.

In designing and operating an HPTP, we have taken into consideration the following important questions:

a. How do we activate an inertia mass repeatedly and automatically?

b. How do we measure the oscillation of the inertia mass or the sample without causing damping in the system?

A system which consists of a mechanical coupling, an electric motor and a solenoid can meet the first requirement. And for the second, a durable noncontacting sensor which will work under pressure environment is necessary for measuring the decaying of the rotational oscillation of the inertia mass. There were many difficulties to overcome in designing the HPTP, because of the limited space available in a pressure vessel. All devices must be miniaturized and function under high pressure and high temperature environment.

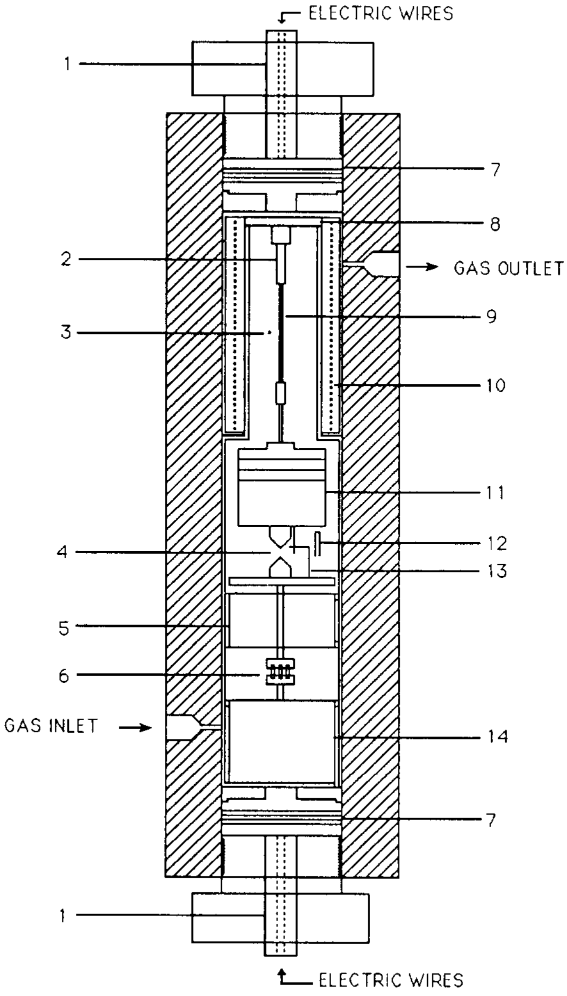


Fig. 1. Schematic diagram of High Pressure Torsion Pendulum.

1. Closure plug 2. Sample holder
3. Thermocouple 4. Magnetic stabilizer
5. Solenoid 6. Spring box 7. High pressure seal
8. Top screw 9. Sample 10. Furnace
11. Inertia mass
12. Noncontacting displacement sensor
13. Mechanical coupling 14. Miniature motor

2. High Pressure Torsion Pendulum Apparatus

The schematic diagram of the new HPTP is shown in Figure 1. The Pendulum was designed to be separated into two main chambers and a furnace as shown in Figure 2. The chambers made of stainless steel were to contain, respectively, the sample to be tested (chamber 1), and the controlling and sensing devices(chamber 2). The hollow cylindrical sample chamber is 1.588 cm in the internal diameter and 20.32 cm in length and is attached to the top of the device chamber which is 2.856 cm in the internal diameter and 21.27 cm long with 0.254 cm in the wall thickness for both. The device chamber contains a noncontacting displacement sensor(12), mechanical coupling (13), a solenoid(5), a spring box(6), and an

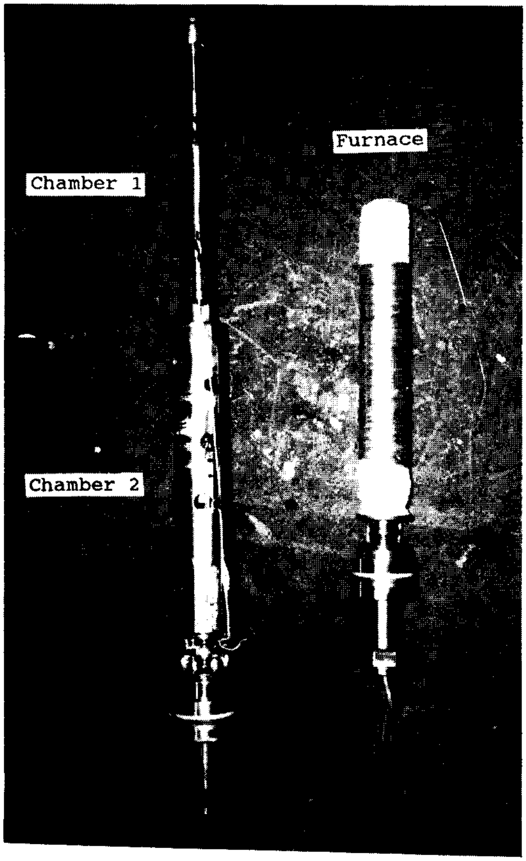


Fig. 2. Photograph of the furnace and chambers.

electrical motor(14). Temperature of the sample was measured by means of K-type thermocouple(3) placed at the center of the sample.

The furnace(10) was made of a brass tube which was wrapped around by a nichrome foil. Mica sheets were used to electrically insulate it from the foil and the pressure vessel. Glass fiber strands were then wound around the mica sheets again to hold them in place.

Three windows(2.856×17.78 cm) separated by an equidistance were inserted on the sample chamber for handling and viewing the sample. The ends of the sample holders were connected to an inertia mass(11) and a screw(8) at the top by extension rods. The role of the top screw will be explained later. Four circular windows(1.91 cm in diameter) were put in on the device chamber for easy observation of devices and electrical wiring.

The inertia mass, of which the weight can be varied, was 2.92 cm in diameter. Two pointed magnets(4) as shown in Figure 1 were employed to stabilize the rotational oscillation of the inertia mass without touching the vessel wall. The concentrated magnetic force at the tips stabilized the swing while rotating.

It is essential for the proper functioning of the HPTP to come up with a sensor that meets the requirements described in the introduction. The detector must be a noncontacting electronic device, so that it would not cause additional drag on the rotating mechanism, and it converts the oscillations to electrical analog signals. The selections are very limited by space restriction and hydrostatic pressure environment of the HPTP. An EMDT(Electro-Mike Displacement Transducer) convertor-sensor system(Electro Inc.) was found to meet the above requirements. The device consists of a sensor(Model No. 4937) and an electronics module(PA115-37). This system has a high speed and noncontacting sensing capabilities with high accuracy and good linearity. The device has considerably greater sensitivity to ferrous metal than to common nonferrous materials.

A thin disc with a linear, circularly inclined slope shown in Figure 3 was attached to the bottom of the inertia mass. When the mass rotates, the distance between the sensor and the disc varies. Since the disc has a nonuniform weight distribution which can cause the inertia mass to swing, a light aluminum was selected as a material to minimize the swing. A ferrous circular shim was then epoxied to the bottom of the disc to enhance the sensitivity of the sensor. The maximum distance that the transducer can detect is 0.127 cm. All experiments must be performed in the linear range of 0.03-0.102 cm in the gap distance. Output voltages from the EMDT system in the linear gap range were around 2-8 volts. The output voltage from the sensor did not change during increasing pressure and temperature levels.

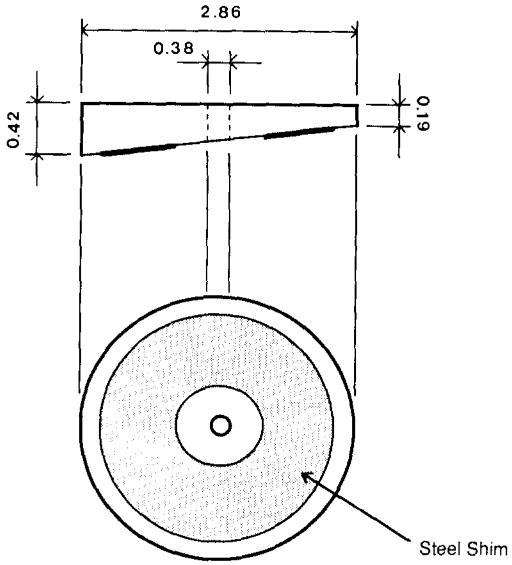


Fig. 3. Schematic diagram of the disc. (unit: cm)

A screw at the very top of the device chamber was used to adjust the air gap between the inertia mass and the sensor. The location of the linear range of the sensor can also be found by means of the screw at the top. A linear push/pull solenoid (Model No. 123421-031, Ledex Inc.) was connected to the inertia mass by a mechanical coupling(13). The solenoid has a stroke range of 0.61 cm. A 9-volt DC transformer was used to supply power to the solenoid. The engagement and disengagement of the coupling were achieved through the core shaft of the solenoid by moving it up and down. A shaft was extended from the core shaft of the solenoid to a spring box. The core shaft moves up for the engagement by a spring in the spring box located below the solenoid and moves down for the disengagement when the solenoid is on. During the disengagement, the spring is under compression.

Another shaft from the lower end of the spring box was extended to a miniature motor (Model No. 33639, Haydon Co.) at the bottom of the chamber. The unidirectional synchronous motor has an enough torque to initiate an angular displacement of the inertia mass. The motor rotates 2 π radians a minute at 115 volts, 60 Hz input, and does reverse direction if the input power is switched through a 0.35 mfd. capacitor from one coil to another. The reverse rotation may be useful to reset the position of the inertia mass when it is not at right position after tightening closure plugs and/or pressurizing.

As shown in Figure 1, the furnace and the device chamber are fixed to the closure plugs. Eight 0.159 cm diameter linear holes were machined through the bottom plug and two holes of the same size were machined through the top plug. Conical cavities were then machined on the top of each of the ten holes to hold hollow polyimide(PI) cones that served as the pressure seals. The holes are the conduits of electric wires and thermocouples. Stainless steel sheathed thermocouple and electrical leads were silver-soldered to steel cones which were in turn epoxied to the hollow PI cones. This assembly was then epoxied to the conical cavities on the plugs.

The seal assembly consisted of a combination of Teflon and Babbit metal washers, and a Viton rubber gaskets which were machined to slide along the stem of the end-plug. For the low pressure(less than 69.0 MPa(10,000 psi)), only the Teflon washers and the rubber gaskets were needed to seal.

3. Operating System of HPTP

A block diagram of an HPTP operating system is schematically shown in Figure 4. The entire system consists of a thick-walled cylindrical vessel, a programmable temperature controller(Eurotherm Inc.), a pressure generating system, and a control unit.

The vessel was made of Vasco Max 300 VM (Teledyne Vasco) having the ultimate tensile strength of 2,027 MPa(294,000psi). Because of its excellent mechanical properties-strength, ductility, toughness, hardness-the alloy steel is widely adopted for high pressure vessels. In addition to the mechanical properties, a major benefit arises from a hardening reaction of the nickel maraging steel. It is supplied in very tough but relatively soft[Rockwell hardness(R_c) $=32$]. Therefore, it is easily machinable. After machining, a precipitation hardening process gives the vessel to achieve the hardness level sufficient to reach $R_c=55$. The vessel has an outer diameter of 9.525 cm, an inner diameter of 3.81 cm and is 60.96 cm long. The maximum internal pressure that can be contained by the cylindrical vessel is about 690 MPa (100,000 psi).

3.1 Pressure generating system

The pressure generating system is made up of a gas booster, a dry nitrogen gas tank, two decompression valves, a check valve, and a dial pressure gage. The tubing configuration is represented at the lefthand side of the pressure vessel in Figure 4. The vessel, the gas booster, and tubings were encased in a 0.635 cm thick steel closet for safety.

The gas booster(14AGT-125/135, Haskel

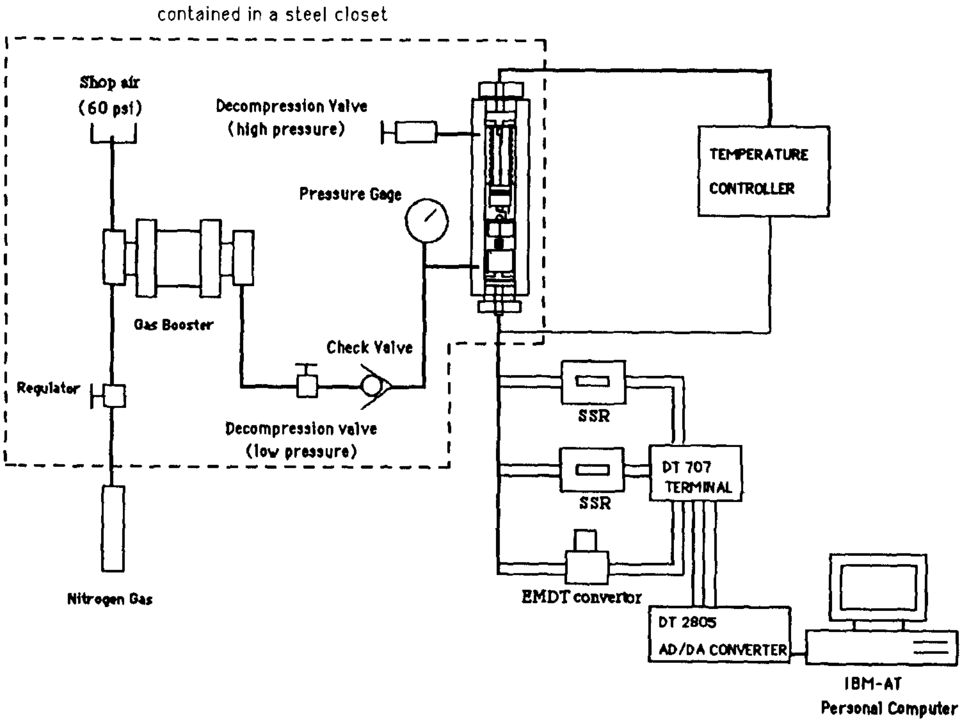


Fig. 4. Control system of High Pressure Torsion Pendulum.

Inc.) driven by air or inert gas is capable of pressurizing up to 241 MPa(35,000 psi) without an intensifier. The maximum air or gas pressure to drive the booster is 0.86 MPa(125 psi). The pressure in the high pressure vessel was measured by a dial pressure gage(Heise Inc.) capable of measuring up to 690 MPa (100,000 psi).

3.2 Machine control and data acquisition

The torsion pendulum was interfaced with an IBM-AT personal computer in order to control the operation automatically. Analog signals from the EMDT sensor were converted to digitized data which were then stored to be analyzed by the computer. A single board analong and digital I/O system(DT-2805, Data Translation Inc.) was used for both the machine control and data collection. The DT-2805 board includes a low level, wide range 12-bit analog to digital(A/D) and digital to analog(D/A) converter system for 8 differential input channels. A pregrammable gain amplifier accommodates a 20 mV to 10 V full scale range of input signal levels by selecting gains in software. A convenient and reliable screw terminal connection(DT-707, Data Translation Inc.) for input and output signals was hooked up to the DT-2805 board for an easy connection.

Two solid state, relays(SSR-240 D10, Omega engineering Inc.) control the motor and the solenoid. The relays are a single-pole, solid state switching device with no moving parts. A control signal(input voltage) causes the relay to switch the AC load ON or OFF just as a conventional mechanical switch does. A 5-volt signal from a computer is generated to switch ON and zero-volt to be OFF.

The software used to control the pendulum and collect data was a PCTHERM software (Data Translation Inc.) written in BASIC language. The computer program has the following flow:

a. Turn off the solenoid for the mechanical coupling to be engaged.

b. Rotate the motor shaft for a predetermined angular displacement, and then stop it.

c. Disengage the coupling by means of the solenoid.

d. Read the digitized data coming from the sensor, and store them into a hard disc.

These steps are repeated automatically. The PCTHERM is a real-time software package designed to support the DT-2805 board, and is a collection of machine language routines which are accessed by a BASIC compiler or interpreter. IBM-BASIC or BASICA and MS-BASIC can be used for programming.

4. Data Analysis

It is necessary to obtain at least two periods of a damped oscillation curve to determine the elastic modulus and loss modulus. The shear modulus(G') is represented by[5]

$$G' = KI\left(\frac{2\pi}{P}\right)^2\left[1 + \left(\frac{\Delta}{2\pi}\right)^2\right]$$

or approximately

$$G' \cong 4\pi^2 KI\left(\frac{1}{P}\right)^2$$

were P is the period, Δ the logarithmic decrement, I the moment of inertia of inertial mass and K a geometric constant. When a composite sample is used like in a TBA experiment[4~7], the geometric constant(K) is not known. Therefore, only the relative shear rigidity value(G'_R) as $(1/P)^2$ can be determined.

The loss modulus(G″) and logarithmic decrement(Δ) are given by

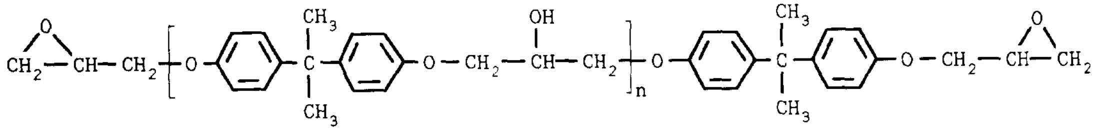
$$G'' = G'\frac{\Delta}{\pi}$$

$$\Delta = \ln\frac{A_i}{A_{i+1}}$$

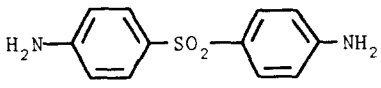
where the A_i and A_{i+1} are the amplitudes of two successive oscillations.

5. Results

Experiments have been preformed by the HPTP to examine effects of pressure on curing of diglycidyl ether of bisphenol A(DGEBA, Epon 828 from Shell) epoxy resin with 4,4'-diaminodiphenyl sulfone(DDS, from Aldrich Chemical Co.) hardener. The chemical formulae of the epoxy and the hardener are represented in Figure 5. Since the sample to be tested is initially in liquid state, an glass fiber braid is used to hold it in place in the pendulum. Figure 6(a) shows one of the original



Epoxy Resin : Epon 828 (n=0.15)
Diglycidyl ether of bisphenol-A



Hardener : 4,4'-Diaminodiphenyl sulfone

Fig. 5. Chemical formulae of an epoxy and a hardener.

damped oscillation curves obtained from the HPTP system during curing. The original wave form depends on the number of points taken. The number of the points for the best result depends on the shape of the wave. For 230 points, the wave looks like the one shown in Figure 6(a). Then, using a smoothing program written in FORTRAN, it becomes a smooth oscillation curve as shown in Figure 6 (b).

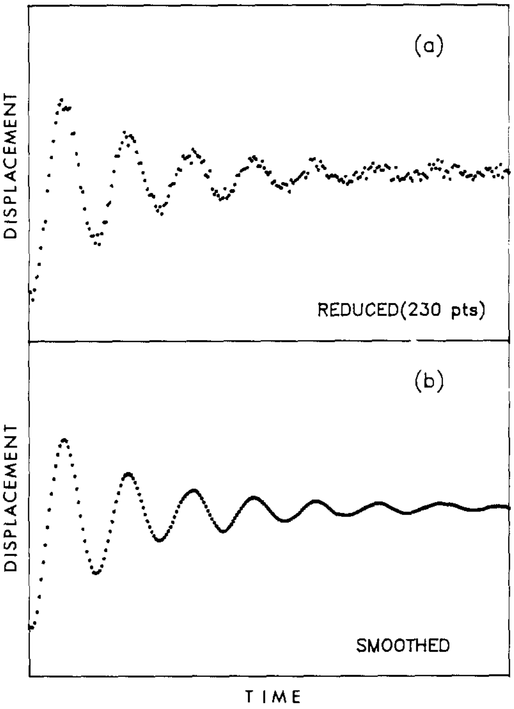


Fig. 6. Reduced(a) and smoothed(b) damped curves.

The location of the peaks is readily found by the following equation from the smoothed curves,

$$(P_{i+1} - P_i)(P_{i+3} - P_{i+2}) < 0$$

where P_i are the smoothed data points at times j. When above equation is satisfied, either P_{i+1} or P_{i+2} are then taken as the peak points of the damped curves.

In Figures 7, 8 and 9, the variations of the relative shear rigidity(G'_R) and log decrement (Δ) calculated from the periods and amplitudes are plotted against the isothermal cure time at atmospheric pressure, 66 MPa(9,500 psi), and 124 MPa(18,000 psi), respectively. The whole relative shear rigidity curve moves to a shorter time with inceasing pressure at 150℃. The initial slope of the curves increases with increasing pressure. The logarithmic curve shows two peaks at atmospheric pressure. It is known that the first peak is due to gelation and the second denotes vitrification[5]. The two peaks merge together with increasing pressure and appear to merge to become one, indicative of gelation and vitrification occurring simultaneously[8,9].

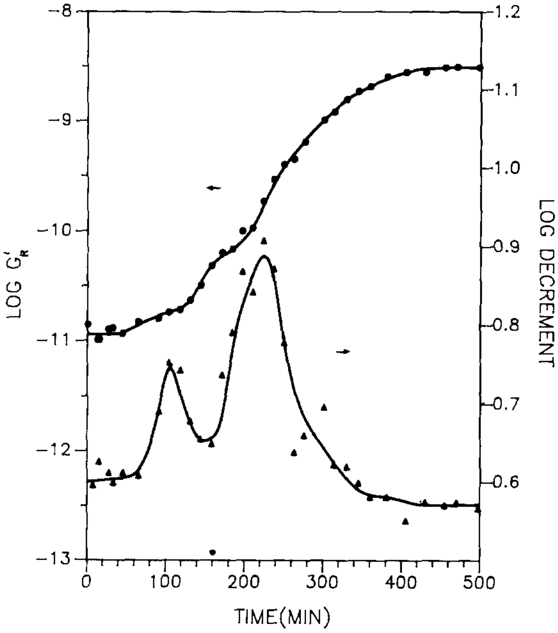


Fig. 7. Dynamic mechanical spectra during curing at atmospheric pressure and 150℃.

The HPTP was also employed to investigate dynamic mechanical properties during a temperature scan at atmospheric pressure after the sample had been subjected to isothermal curing under pressure. The heating rate for this test was 1.5℃/min. Dynamic mechanical spectra for a sample cured at 66 MPa(9,500 psi) and 150℃ for 650 minutes are shown in

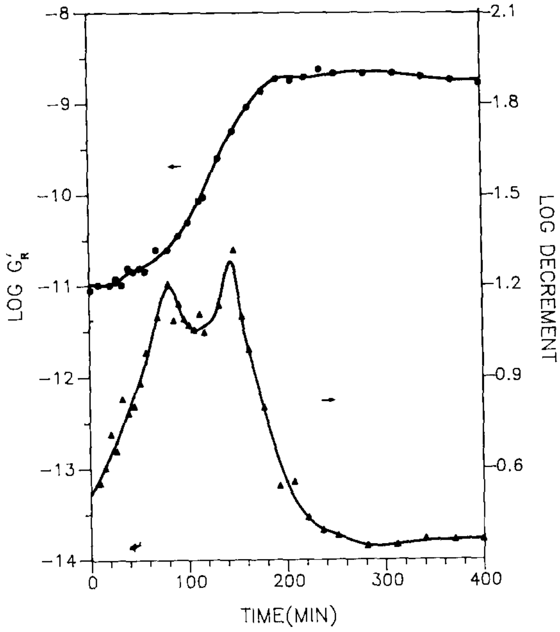


Fig. 8. Dynamic mechanical spectra during curing at 66 MPa(9,500 psi) and 150℃.

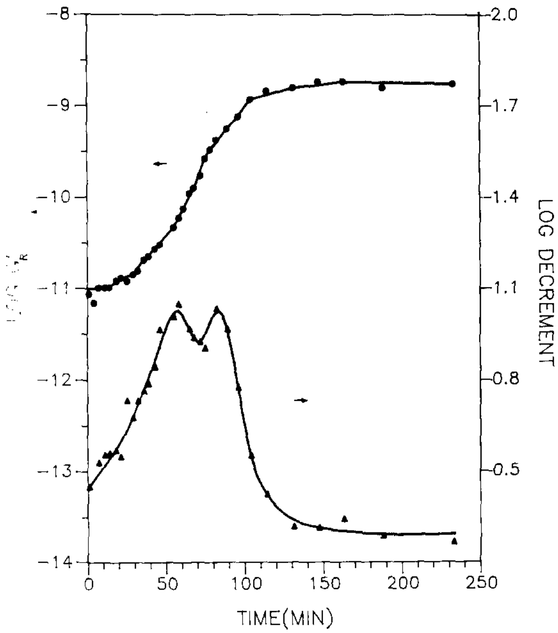


Fig. 9. Dynamic mechanical spectra during curing at 124 MPa(18,000 psi) and 150℃.

Figure 10. It shows a distinct transition which corresponds to glass transition. The glass transition temperature(T_g) determined from the peak on the log decrement curve is 195℃ in this study. It has been found that the T_g increases with curing pressure[8].

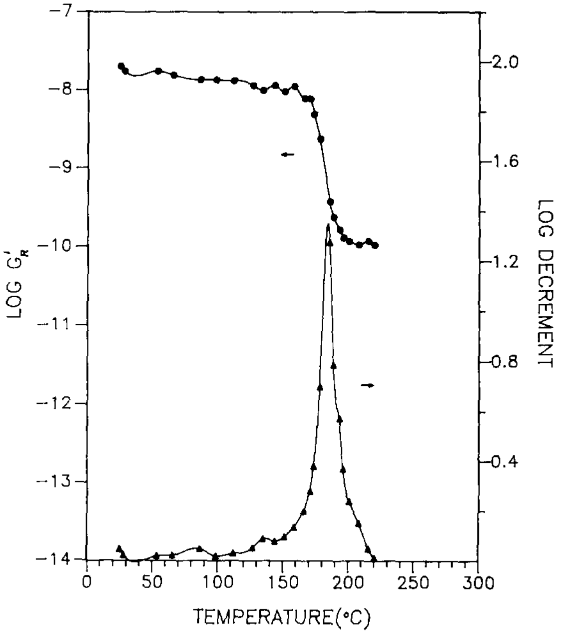


Fig. 10. Dynamic mechanical spectra for a sample cured at 66 MPa(9,500 psi), obtained at atmospheric pressure.

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