

Dynamics of Mechanical, Acoustical, and Electrical Properties of Epoxy-Amine Compositions During Cure

Vladimir I. Rimlyand, Vera N. Starikova, Alexander V. Bakhantsov

Department of Physics, Pacific National University, Khabarovsk 680035, Russian Federation

Received 20 October 2008; accepted 23 November 2009

DOI 10.1002/app.31870

Published online 2 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Dynamics of mechanical, acoustical, and electric properties is studied in the cure of three samples of polymeric compositions produced on the basis of epoxy oligomer with different content of the curing agent. The measurements were made in a parallel mode with an automated measuring complex. Variations in elastic modules, sound speed, attenuation coefficient, relaxation of the

shear stress, electric resistance of the samples during the complete cure in the transition from a liquid into a glass state are considered. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 143–147, 2010

Key words: curing of polymers; crosslinking; mechanical properties; resins

INTRODUCTION

Thermoset resins, among them epoxy resins, have found wide applications in industry. The conditions at which these are cured heavily influence the properties of the produced materials.^{1,2} Therefore, the problem of control of physico-mechanistic properties immediately during the formation of the hard structure of the composite material continues to be urgent. A great deal of data obtained in studying a long cure process requires the measurement techniques, which may be implemented in an automatic mode.

In the cure, a liquid oligomer with relatively small molecular weight undergoes transition into a highly crosslinked polymer. In the course of the process the composition goes through a number of physical states, namely, viscoflow, high-viscoelastic, and solid glass state.^{1,3} Such a transition can be studied with mechanical, acoustical, dielectrical, dynamic mechanical analyzer (DMA), differential scanning calorimetry (DSC), and other techniques.^{3–11} Nevertheless, to date there is a small number of experimental works which study dynamics of different physical features in the cure comprehensively. In this case of great complexity is the continuous study of rheological properties, since the variations in physico-mechanical parameters may be of several orders of magnitude and require, for determination thereof, application of various procedures to study

samples in different conditions (before and after gel formation).^{6,11}

The aim of the this work was a continuous study of the behavior of physical properties for a polymer composition with different curing agent content in the coarse of the whole curing process (at the transition from a liquid into a glass state).

EXPERIMENT

Epoxy oligomer ED-20 with different content of the curing agent polyethylene polyamine (the samples 1, 2, 3–10, 12, 15% in mass fraction respectively) was used. Formulas of the components are given in Figure 1.

The cure of all samples was at a constant temperature of 25°C, which controlled by a thermocouple. To study mechanical, acoustic, electric parameters a specially designed automated measuring complex was used, which had relevant measuring systems.¹² The measurements for samples with identical compositions were made in a parallel mode.

Dynamics of mechanical properties

To study mechanical characteristics (shear modulus and loss modulus) in the cure of samples an automated measuring system was used, which was made on the basis of free torsional vibration procedure we had modified.¹³ The free torsional vibration procedure is one of the most efficacious and commonly used dynamic procedures in studying mechanical properties of hard materials up to their softening stage.^{14,15} The given modified procedure makes it possible to study visco-elastic properties of

Correspondence to: V. I. Rimlyand (riml@fizika.khstu.ru).

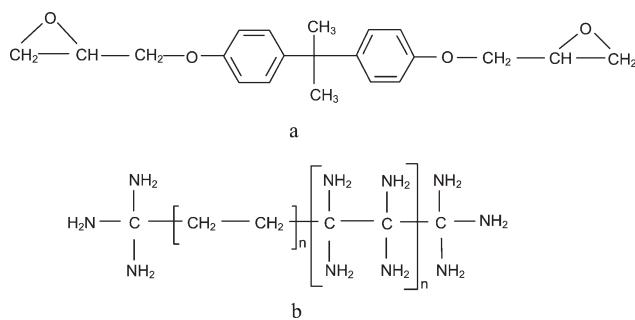


Figure 1 Epoxy resin ED-20 (a) and the curing agent polyethylene polyamine (b).

materials both in different physical states and in the transition from one state into the other if the conditions of the investigation are invariable throughout the experiment.

Figure 2 shows a schematic view of the setup. As a cuvette 1 for a sample under study a thin wall polymeric pipe is used with viscoelastic characteristics near zero with a length of 200 mm and a diameter of 5 mm. A liquid composition 2 is poured into the cuvette, and thus obtained compound sample is the heart of the vibrational subsystem of the torsion pendulum. Load 3 gives a constant tension of the cuvette. To add inertial features to the subsystem an inertial disk 4 is put to the cuvette bottom. An electromagnet 5 is needed to deflect the disk 4 in the horizontal plane by 5–8 degrees for the torsion pendulum to make vibrations in the course of the measurement. After the load is removed (the electromagnet is off) the vibrational subsystem undergoes free torsional vibrations, which are recorded by an angle rotation sensor 6 and fed into a PC. The direct result of one measurement is time dependence of the deflection angle $\varphi(t)$ of the pendulum [Fig. 2 (b)], with which the vibration frequency and the damping coefficient of the vibrational system are found needed for the calculation of the shear modulus and the loss modulus. At the initial stage of the cure, when elastic properties of the cured composition are not pronounced enough, an elastic component 7 is put into the vibrational subsystem, securing the number of vibrations needed for further calculations. The vibration parameters (frequency, damping constant, and vibration duration) are dictated by viscoelastic features of a sample under study and they change as it is cured. Before the start of the measurement the system vibrations with an empty cuvette are recorded and the setup parameters are calculated. Viscoelastic materials are characterized by a complex shear modulus $G = G' + iG''$, where G' is the dynamic shear modulus; G'' is the loss modulus. Values of G' and G'' are found from dynamic testing by using formulas¹⁴

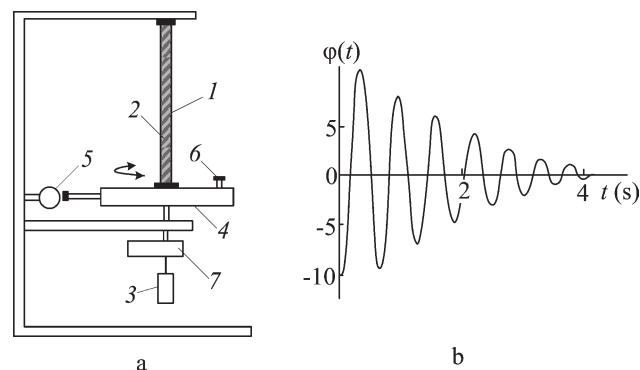


Figure 2 Measuring setup (a) and plot of vibration (b).

$$G' = \frac{I(\omega^2 - \omega_e^2 + \gamma^2 - \gamma_e^2)}{F}, \quad G'' = \frac{2I(\omega\gamma - \omega_e\gamma_e)}{F} \quad (1)$$

where ω_e , γ_e are the vibration frequency and the damping coefficient of the system with an empty cuvette, respectively; ω , γ are the same with the cuvette filled with a sample; I is the moment of inertia of the vibration system; F is the sample form-factor.

It is assumed, in making calculations that the chemical transformations occur on a much slower time scale than the cycle of one measurement (less than 10 s).

Mechanical stress relaxation

To study dynamics of the shear stress relaxation in the course of the cure an improved version of the above given setup was used. The inertial disk was substituted with a unit of the force measurement (Fig. 3). The unit had two special bars and a force sensor. The first bar 1 is firmly fixed to the bottom of a cuvette 2 filled with a sample, a second bar 3 is put to a hinge 4, which secures one degree of freedom, namely, in the direction of an electromagnet 5 (in the plane of the sample rotation). A force sensor 6 is clamped to the bar 1 (Honeywell FSS1500SSB) with a sensitivity of 0.12 V/N. The electromagnet 5 attracts the bar 3 turning the bottom end of a sample through the set angle φ , making the twisting strain. With elastic strain in the sample the torque is

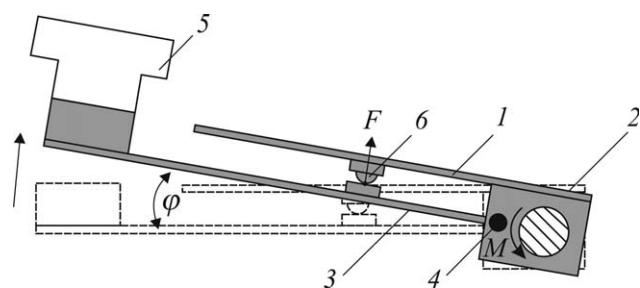


Figure 3 Unit of the force measurement.

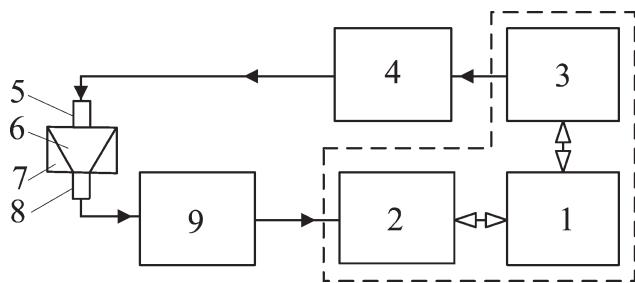


Figure 4 Block diagram of an automated system for studying acoustic features of composition cured.

produced, which tends to return the sample to the initial position. The force F produced by the bar 3 due to the torque is recorded by the force sensor. During measurements φ continues to be constant, and the force sensor records the time dependence of F .

For the given geometry the tangential stress on a cylindrical sample with a radius R and the force F are subject to the relationship

$$\sigma = \frac{2d}{\pi R^3} F \quad (2)$$

where d is the distance from the rotation axis of the sample to the sensor sensitive component, that is the arm of force.

Acoustic properties

To investigate acoustic properties (the sound speed and the attenuation coefficient of the acoustic pulse) an automated system whose block diagram is given in Figure 4 was used. The heart of the system is a PC 1 with build-in boards of a digital oscilloscope 2 and a digital generator 3. Signal from the generator lands to the input of a pulse generator 4 and further goes as a rectangular pulse with duration of 4 μ s and an amplitude of 70 V to an ultrasound emitter 5. The ultrasound signal goes through a polymer composition 6 poured into a special cuvette 7 and is transformed into an electric signal by a receiving transducer 8 put to the input of an amplifier 9. The signal lands further to the oscilloscope where is digitized with a given clock frequency (100 MHz) and is recorded in the PC. Both the emitter and the receiver are in contact with the cured composition. Using the signal oscillograms recorded in the given time periods throughout the cure the signal travel time through the sample and its amplitude are found. With these data the sound speed and the attenuation coefficient are determined.

Electric resistance

The electric resistance was measured by using the volt-ammeter method.¹⁶ A DC source, which pro-

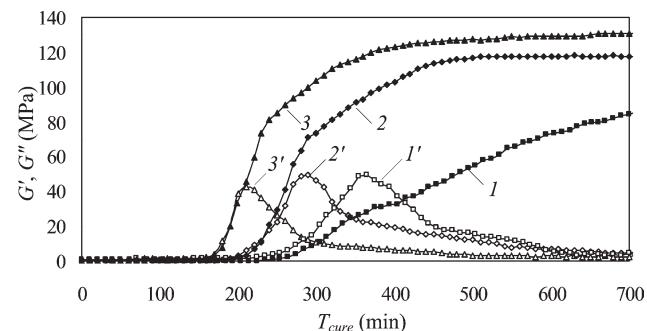


Figure 5 Dependence of the shear modulus G' (1, 2, 3) and the loss modulus G'' (1', 2', 3') as a function of the cure time for 1, 2, 3 samples, respectively.

vided 1500 V, was used. To measure current and voltage a digital high-precision electrometric voltmeter compatible with a PC was applied. The composition was poured into a measuring cell made from fluoroplastic. It had two measuring cylindrical electrodes and one grounded as a ring. The sample was 4 mm in thickness with a diameter of 100 mm.

RESULTS AND DISCUSSION

The calculation results for the shear modulus and the loss modulus as a function of the cure time for all the samples are shown in Figure 5.

The larger content of the curing agent the more intensive occurs the formation of crosslinking chemical bonds and the faster vary physical characteristics. In this case the shear modulus rises to a maximum corresponding to the hard glass state. The loss modulus curve goes through a maximum at the moment when the rate of increase of the shear modulus is maximal. The maximum in the curve G'' indicates the moment of "mechanical" vitrification, dictated by a frequency effect on a sample and begins earlier than structural vitrification.³ Therefore, one may say about the transition from a gel-like to a solid state.³

Figure 6 shows relaxation of the shear stress as a function of time for different T_{cure} for the sample 1.

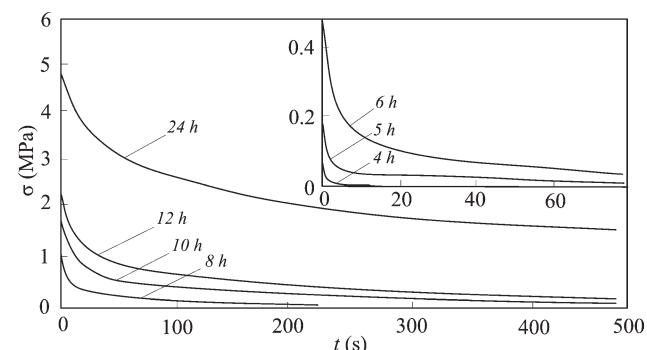


Figure 6 Relaxation of mechanical stress for the sample 1 for different cure times T_{cure} .

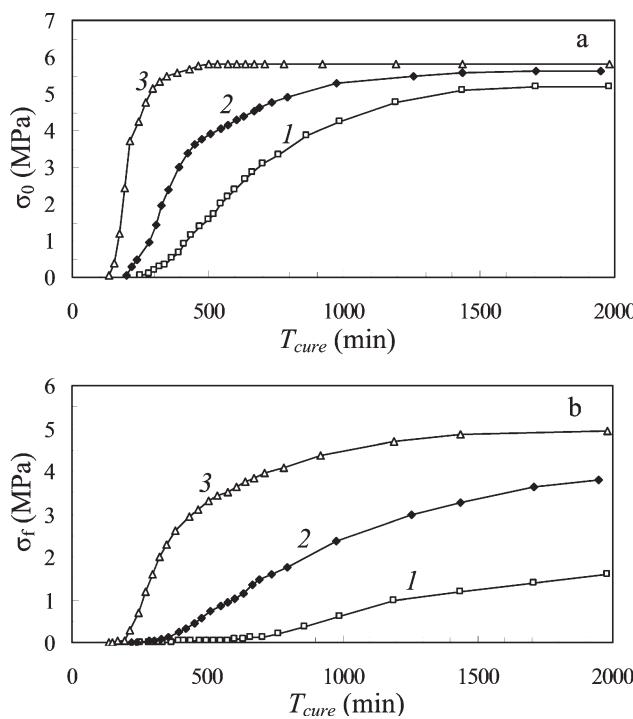


Figure 7 The initial stress σ_0 (a) and residual stress σ_r (b) as a function of the cure time T_{cure} for the samples 1, 2, 3.

Using the relaxation curves the initial σ_0 and residual σ_r mechanical stress are determined, whose time dependencies are given in Figure 7.

Initially the material presents a viscous liquid. In the course of cure particular structure units first increase (microgel formation) then these components are linked with each other by cross links (macrogel formation) and these links undergo further condensation. As is seen from Figure 6, the mechanical stress before the start of the transversal links formation is insignificant and rapidly drops virtually to zero due to a rapid rearrangement of loosely linked structure units; therefore, that deformation is irreversible. Figure 5 shows that essential variation in the mechanical modules begins a considerable period of time after the compound preparation (250, 200, and 150 min for the samples 1, 2, 3, respectively) and continuous for a long time. At that time the initial stress σ_0 starts to rise intensively [Fig. 7(a)]. Further increase in the polymerization time leads to an increase in the shear modulus and the relaxation time. At $T_{\text{cure}} = 350$ min in the sample 1 nonzero residual stress σ_r begins to manifest itself [Fig. 7(b)], indicating the formation of cross-linked structure throughout the sample (macrogel formation). Unlike noncross-linked polymer, in which only the fluctuation network occurs dictated by physical crosslinks, in the spatially cross-linked polymer, additionally, chemical bond network exists that are not broken at small deformations. The mechanical stress relaxation occurs because of the destruction of

the fluctuation network. The origination of chemical bond network causes the appearance of the residual stress σ_r , which is greater the denser is the chemical bond network. With time the increase in both the initial and residual stress occurs; however, the rates of their variations are distinct. As is seen from Figure 7(a,b) at some point variations in the initial stress turn insufficient, whereas the residual stress continuous to increase, suggesting further formation of new links and condensation of macrogel. For that reason the relaxation curve flattens with a passage of the cure time and finally becomes a straight line ($\sigma_r \rightarrow \sigma_0$), indicating the termination in the linked structure formation. To that moment the elastic modules (Fig. 5) reach constant values. In this case one may believe that the relaxation occurs infinitely slowly and the mechanical behavior of the material is characterized by the classical Hooke law for a perfect elastic body.

Plotted in Figure 8 are the dependencies of the sound speed C and the attenuation coefficient α of longitudinal waves. It is seen that the acoustic parameters begin to vary earlier than the mechanical modulus. This is due to the great frequency of acoustic effect and the longitudinal type of the waves, which are sensitive to variations in the microstructure. Our data are in agreement with those of other workers.¹³ The nature in the variation of the sound speed and the attenuation coefficient with the cure time has common features with time dependencies of these parameters when the temperature of the polymer with invariable chemical properties drops.³

Volume resistivity ρ as a function of the cure time is plotted in Figure 9. The rise in ρ observed is due to a decrease in both the number and the mobility of ions in polymerization.¹⁷ At the initial stage of the cure the resistivity of the compound is greater the less is the curing agent content. Further the situation reverses. Such a behavior of resistivity is explained by the fact that, on the one hand, the curing agent addition raises the ion mobility and decreases ρ at the initial stage; on the other, raises the rate of

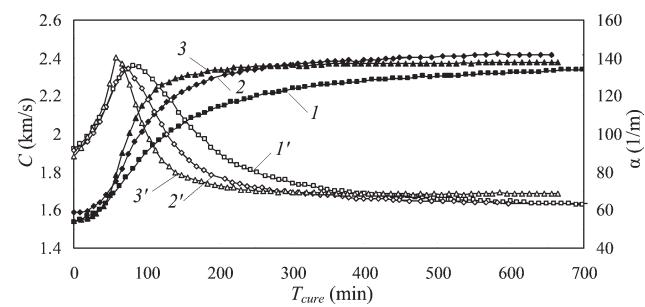


Figure 8 The sound speed C (1, 2, 3) and the attenuation coefficient α (1', 2', 3') as a function of the cure time for the samples 1, 2, 3.

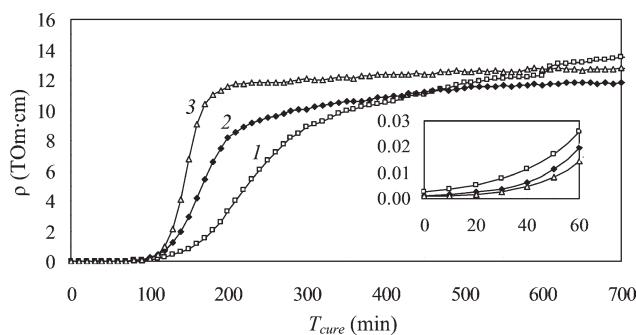


Figure 9 Volume resistivity ρ as a function of the cure time T_{cure} .

curing, leading to an increase in ρ . Therefore, the break in the resistivity curve begins virtually concurrently for the three samples (roughly at $T_{\text{cure}} = 100$ min).

It is seen from the comparison of the results that while the sound speed C and the resistivity ρ reached their critical values and further vary weakly, the mechanical characteristics (both dynamic and static) continue to vary significantly. That is dictated by the fact that the formation of chemical bonds continues even after the "penetration" of the hard structure throughout the volume. After $t = 200\text{--}300$ min the hard structure is virtually formed; a sample keeps the shape and has mechanical parameters good enough to be removed from the mold. From the above follows that C and ρ may be good indicators for a compound transition to a solid state. In this case the measurement of the sound speed as a technological parameter is more favorable and found its application.^{18,19} C depends on the particular composition to a lesser degree and varies weakly against ρ , which is especially important in producing materials. Also, measuring technique for the sound speed is considerably simpler than that for resistivity whose values may reach teraohms.

CONCLUSIONS

This study has revealed that in the cure of a sample the values of the shear stress increase from undetected to tens of MPa. Variations in acoustic and electric features occur considerably earlier than those of mechanical features, which is due to their sensitivity to the microstructure. In this case acoustic characteristics vary relatively weakly, while the variation in the sensitivity is of several orders of magnitude. From that one may conclude that the most

effective way to control the degree of cure for polymerized compounds under industrial conditions is to conduct acoustic measurements. The hard structure forms when the acoustic parameters reach their constant values. The values of the sound speed and the attenuation coefficient depend on the sample composition to a lesser degree than the resistivity, which is particularly important in manufacturing composite materials. Measuring technique for the sound speed is considerably simpler than that for mechanical moduli or resistivity. Under industrial conditions ultrasound sensors may be built immediately in molds, and the control of the cure may be fully automated.

References

1. Lee, S. M., Ed. Reference Book for Composites Technology; CRC Press: Lancaster, Pennsylvania, 1989; Vol. 1, 208.
2. Joubert, C.; Michel, A.; Choplin, L.; Cassagnau, P. *J Polym Sci Part B: Polym Phys* 2003, 41, 1779.
3. Bartenev, G. M.; Frenkel, S. Y. Physics of Polymers; Leningrad: Chimiya, 1990; 432 (in Russian).
4. Guney, H. Y. *J Polym Sci Part B: Polym Phys* 2005, 43, 2862.
5. Simpson, J. O.; Bidstrup, S. A. *J Polym Sci Part B: Polym Phys* 1995, 33, 55.
6. Daniel, J. O.; Patrick, T. M.; Scott, R. W. *J Comp Mater* 2001, 35, 883.
7. Plazek, D. J.; Frund, Z. N. Jr., *J Polym Sci Part B: Polym Phys* 1990, 28, 431.
8. Kim, Y. K.; White, S. R. *Polym Eng Sci* 1996, 36, 2852.
9. White, S. R.; Mather, P. T.; Smith, M. J. *Polym Eng Sci* 2002, 42, 51.
10. Luo, Z. h.; Wei, L.; Li, F.; Liu, F.; Zhao, T. *J Appl Polym Sci* 2008, 109, 525.
11. Simon, S. L.; Mckenna, G. B.; Sindt, O. *J Appl Polym Sci* 2000, 76, 495.
12. Bakhantsov, A. V.; Rimlyand, V. I.; Starikova, V. N. *Automation Adv Technol* 2007, 8, 34 (In Russian).
13. Bakhantsov, A. V.; Starikova, V. N.; Rimlyand, V. I. R. F. Russian Federation, Pat. 2,307,337, 2005 (In Russian).
14. Malkin, A. Y.; Askadskiy, A. A.; Kovriga, V. V. Means of Measuring Mechanical Properties of Polymers; Chemistry: Moscow, 1976; 336 (In Russian).
15. Yudin, V. E.; Volodin, V. P.; Kenunen, I. V. *Mech Compos Mater* 1991, 3, 542 (In Russian).
16. Luscheikin, G. A. *Investigation Techniques of Polymer Electric Properties*; Chemistry: Moscow, 1988; 160 (In Russian).
17. Blythe, A. R.; Bloor, D. *Electrical Properties of Polymer*, 2nd ed.; Cambridge University Press: New York, 2001; 492.
18. During, J.; Bartusch, J.; Mchugh, J.; Stark, W. In *Proceedings of the 15th World Conference on Nondestructive Testing*; Roma, 15–21 October 2000.
19. During, J.; Stark, W. In *Proceedings of the 7th European Conference on Nondestructive Testing*; Copenhagen, 26–29 May 1998.