

## 硬化中の 에폭시레진에 대한 구성방정식

### Constitutive Equations for Curing Epoxy Resins

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#### 초 록

에폭시 레진이 경화될 때 이들의 기계적 성질의 변화는 지금까지 주로 실험과 실험식에 의하여 구하여졌다.

근간에 이들의 변화를 이론적으로 구하기 위한 구성방정식이 본 발표자에 의하여 발표되었으나 실험데이터와 구성방정식 상호간의 정량적 관계가 정립되지는 못하였다.

본 연구에서는 세 종류의 시료, 즉 Epon 815/V140, Epon 820/Z와 DER 332가 경화될 때 이들의 기계적 성질을 구성방정식을 사용하여 구하여 초음파 방법으로 측정된 실험 결과와 비교 검토함으로써 에폭시 레진의 경화에 따른 기계적 성질들의 대부분을 제안된 구성 방정식으로 구할 수 있음을 보였다.

### Constitutive Equations for Curing Epoxy Resins

#### I. Introduction

In recent years, the processing of thermosetting polymeric resins has received increasing attention from industry, especially from the automotive and aerospace industries.

When mixed with an appropriate kind and amount of curing agent and subjected to a prescribed temperature history, these resins change in physical character from viscous liquid to viscoelastic rubber, and finally to a glass stage.

The knowledge of property changes during cure is essential to the establishment of an optimum process cure.

Many techniques were developed for monitoring cure. All these techniques are based on the change of properties of one type or another. Some of the properties frequently used are electric resistance, dielectric loss tangent (1,2), wave absorbancy, complex modulus (3, 4, 5) and heat generation (6, 7).

Since the design of a process cycle depends mostly on the thermo-mechanical properties, the last two methods are of prime interest.

The cure of most epoxies is exothermic and generates heat. The time rate of heat generation is measured in Differential Scanning Calorimeter. The completion of cure is the indicated by the lack of heat generation. However, this method does not provide any information in mechanical behavior.

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The mechanical properties frequently measured are the complex moduli in shear and the viscosity (3, 4). Both the storage modulus and the shear viscosity increase with cure. The loss modulus initially increases to peak and then decreases.

The measurements of the complex moduli are taken by ultrasonic wave propagation through a curing resins (4, 5, 7, 8, 9) and by dynamic mechanical method (3).

In the ultrasonic cure method, wave speed and attenuation are monitored, but in dynamic mechanical method, complex moduli and viscosity are monitored.

There was an attempt to find a constitutive equations for a material undergoing solidification for hardening as the result of a chemical reaction (10). These equations take the form of stress rate/strain rate relations.

At the present time, few constitutive model exist, which relate the cure cycle to the mechanical processes occurring in epoxy resins during cure, which would be used to establish the most appropriate cure cycle in any given application.

Fortunately a simple constitutive model was developed to explain the experimental data on the wave speed and attenuation (7). However, no quantitative correlation between the proposed constitutive model and the experimental data is made.

Most of the test data which can be used to validate the developed constitutive model were obtained from Lindrose (4), Hahn (7) and some of them were obtained from this experiment.

The purpose of this paper is to show how the developed constitutive model can be used to quantitatively correlate the mechanical property parameters and the experimental data, and to show how the model can be used to

monitor the cure cycle.

## 2. Constitutive Model

A thermosetting polymeric system is a viscoelastic material throughout cure in both shear and bulk deformation. Introducing a complex longitudinal stiffness  $C_{11}^*$ ;

$$C_{11}^* = C_{11}' + iC_{11}'' \quad (1)$$

where  $C_{11}'$  is storage stiffness and  $C_{11}''$  loss stiffness.

We obtain the wave speed  $C$  as (11)

$$\rho C^2 = 2C_{11}' \frac{1 + \tan^2 \delta}{1 + (1 + \tan^2 \delta)^{1/2}} \quad (2)$$

$$\tan \delta = \frac{C_{11}''}{C_{11}'} \quad (3)$$

where  $\delta$  is phase angle.

The attenuation coefficient  $\alpha$  is related to the complex stiffness by

$$\alpha = \frac{\omega}{C} \tan \frac{\delta}{2} \quad (4)$$

where  $\omega$  is frequency.

If the loss stiffness is much smaller than the storage stiffness, i.e.,  $\tan \delta \ll 1$ , Eqs. (2) and (4) reduce respectively to

$$C = (C_{11}'/\rho)^{1/2} \quad (5)$$

$$\alpha = \frac{\omega}{2C} \tan \delta = \frac{1}{2} \omega \rho^{1/2} C_{11}''/C_{11}'^{3/2} \quad (6)$$

Eqs. (5) and (6) indicate that the changes in  $C_{11}'$  and  $C_{11}''$  will be similar to those in  $C$  and  $\alpha$ , respectively.

To illustrate the change of  $C_{11}^*$  with cure, it is more convenient to introduce the complex bulk modulus  $K^*$  and the complex shear modulus  $G^*$  such that

$$C_{11}^* = K^* + \frac{4}{3}G^* \quad (7)$$

Hahn developed the constitutive models, where moduli can be expressed in terms of the elastic moduli and viscosities during the cure of epoxy, as follows (7):

$$K' = \frac{k_f + k_s w^2 \tau_k^2}{1 + w^2 \tau_k^2}, \quad K'' = \frac{(k_s - k_f) w \tau_k}{1 + w^2 \tau_k^2} \quad (8)$$

$$G' = g_s \frac{w^2 \tau_g^2}{1 + w^2 \tau_g^2}, \quad G'' = g_s \frac{w \tau_g}{1 + w^2 \tau_g^2} \quad (9)$$

where  $k_f$  is the liquid bulk modulus,  $k_s$  solid bulk modulus,  $g_s$  solid shear modulus,  $\tau_k$  bulk relaxation time and  $\tau_g$  shear relaxation time. The relaxation time  $\tau_k$  and  $\tau_g$  are defined by;

$$\tau_k = \frac{\eta_k}{k_s - k_f}, \quad \tau_g = \frac{\eta_g}{g_s} \quad (10)$$

Hahn developed the following constitutive equations for storage and loss stiffness with the assumption of  $\tau = \tau_k = \tau_g$ ;

$$C_{11}' = \frac{k_f + (k_s + 4g_s/3)w^2 \tau^2}{1 + w^2 \tau^2} \quad (11)$$

$$C_{11}'' = \frac{(k_s - k_f + 4g_s/3)w\tau}{1 + w^2 \tau^2} \quad (12)$$

The changes of  $C_{11}'$  and  $C_{11}''$  with  $\tau$  are thus similar to those of the wave speed and the relative attenuation, respectively, with time.

The change of the complex modulus with time can be determined if the reaction between the relaxation time and the real time is known.

### 3. Results and Discussion

Hahn measured the change of longitudinal wave speeds and their relative attenuations of two epoxy systems, i.e., Epon 828/Z

(80/20), Epon 815/V140 (60/40), with the cure time at room temperature (RT) by ultrasonic method (7), where the numbers inside the parentheses denote the weight ratio.

Lindrose and et. al. (4) measured the change of longitudinal wave speeds and their relative attenuation, shear wave speeds and their relative attenuation at RT by ultrasonic method for DER 332. And then calculated the changes of mechanical properties of DER 332 by the empirical equations with cure time.

To ascertain if the constitutive equations developed by Hahn can be used to calculate the mechanical property variation and to monitor the cure of epoxy resins during cure, above and author's experimental data are used and compared between them.

It can be obtained the change of exact wave speed denoted by  $C_e$  by the Eqs. (2), (11) and (12), and the variation of approximate wave speed (denoted by  $C_a$ ) by the Eq. (5).

The obtained results of longitudinal exact wave speed ( $C_e$ ) and longitudinal approximate wave speed ( $C_a$ ) by using the results of  $C_{11}'$  for DER 332 are expressed in Figure 1. Furthermore, Figures 2 and 3 show the calculated values of  $C_e$  and  $C_a$  during cure for Epon 828/Z and Epon 815/V140, respectively. To compare the calculated values and experimental data, the experimental variations of longitudinal wave speed are included in Figures 1, 2 and 3, respectively. As can be seen from the Figures, there are not much differences between the calculated and the experimental results. Especially a good agreement is existed between the experimental wave speed and the approximated wave speed variation.

To check the variation of shear wave speed, we calculated the variation of shear

wave speed by using the constitutive equations with cure time, and then compared with the experimental data. Figure 4 shows the above results for DER 332. The results calculated by the constitutive equations are in excellent agreement with the experimental data.

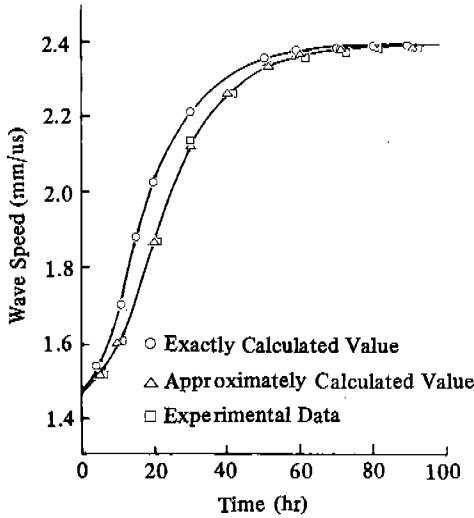


Fig. 1. Longitudinal Wave Speed During Cure, DER 332.

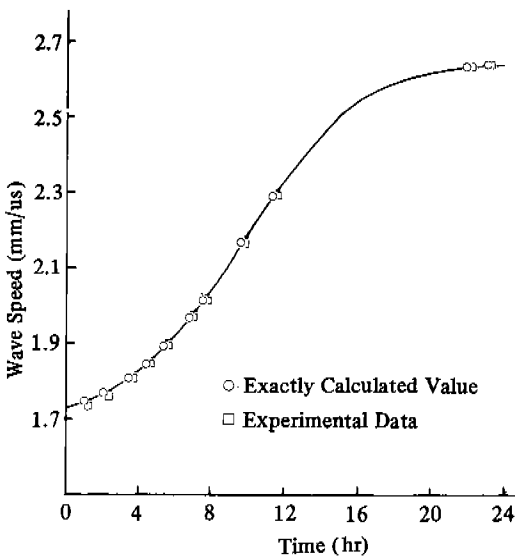


Fig. 2. Longitudinal Wave Speed During Cure, Epon 828/Z.

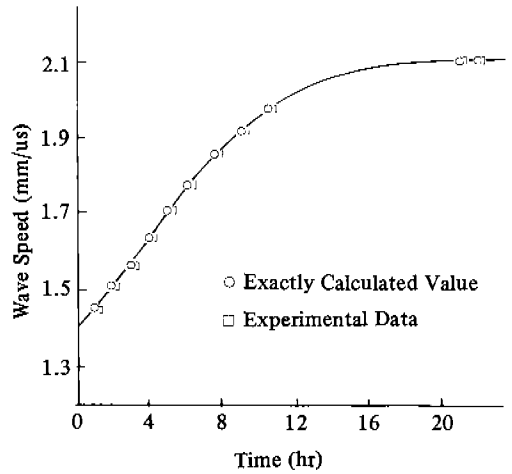


Fig. 3. Longitudinal Wave Speed During Cure, Epon 815/V140.

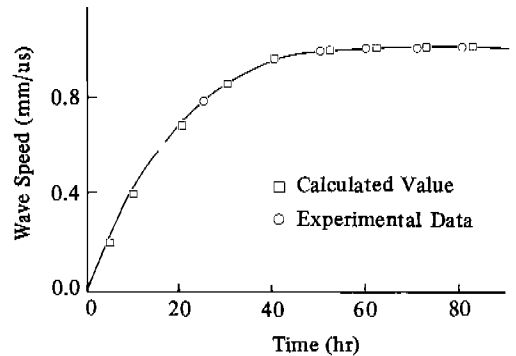


Fig. 4. Shear Wave Speed During Cure, DER 332.

The variation of the absolute wave attenuation can be calculated theoretically by the Eqs. (4) and (6). But the relative attenuation can be obtained by experiment. The definition of relative attenuation for DER 332 is  $\alpha_R = V_{REF}/V_1$ , where  $V_1$  and  $V_{REF}$  are the first-echo and reference voltages, respectively. Reference voltage is the voltage at the fully cured state. But the definition for Epon 828/Z and Epon 815/V140 is  $RA = 20 \log (A_L/A)$  (dB), where  $A$  and  $A_L$  are the first-echo and reference amplitude. The initial amplitude of the echo is chosen as reference amplitude.

The relationship between relative and absolute attenuation is as follows for DER 332 and Epon 828/Z respectively;

$$\alpha = \alpha_{REF} + \frac{1}{n} \ln (\alpha_R) \quad (13)$$

$$\alpha = \alpha_L + \frac{1}{20 \log e} \cdot \frac{RA}{h} \quad (14)$$

Where  $h$  is twice the depth of the specimen and  $e$  is the Napierian base.  $\alpha_{REF}$  is the absolute attenuation at fully cured state and  $\alpha_L$  is the absolute attenuation at the beginning of cure.

The variation of shear wave relative attenuation can be calculated as follows;  $\alpha$  can be calculated from Eq. (13), because  $\alpha_R$  is obtained by experiment. And then  $C_{11}''$  by Eq. (6). We can get the variation of  $w$  and  $k_s$  during cure from  $C_{11}'$  and  $C_{11}''$ . The shear storage ( $C_{11}'_s$ ) and loss stiffness ( $C_{11}''_s$ ) can be obtained by Eqs. (11) and (12). And so we can calculate  $\alpha_s$  and  $\alpha_{R_s}$ . Where  $\alpha_s$  is shear wave absolute attenuation and  $\alpha_{R_s}$  is shear wave relative attenuation. The calculated values of  $\alpha_{R_s}$  for DER 332 are expressed in Figure 5 and compared with the experimental results.

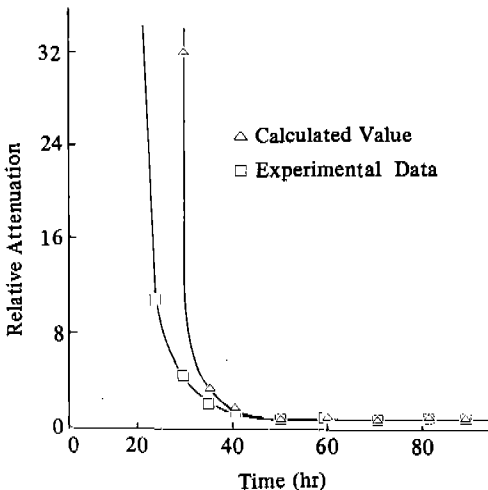


Fig. 5. Shear Wave Attenuation During Cure, DER 332.

There are some attempts to find the variation of viscosity of epoxy resins during cure by experiment and analysis, but not by the constitutive equations.

Here, we can find the variation of viscosity of epoxy resins with cure time by the developed constitutive equations except at zero cure time. Because the constitutive equations are not defined exactly at this point. The obtained absolute wave attenuation for Epon 828/Z and Epon 815/V140 by this experiment using Sonoray 303B ultrasonic flaw detector and Alphaseris 10 MHz transducer are 6.0 and 4.0 (1/cm), respectively, at zero cure time. From these values absolute wave attenuation can be obtained.

The calculated values of viscosity by using the absolute wave attenuation which were obtained by experiment and using the constitutive equations are shown in Figure 6, for Epon 828/Z, 815/V140 and DER 332. This viscosity variation with cure time has a good agreement with the results of Ref.

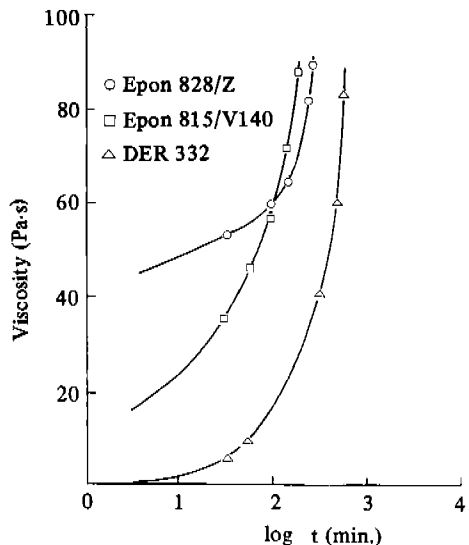


Fig. 6. Variation of Viscosity During Cure.

(12, 13).

But in the absence of any experimental viscosity data for the above epoxy resins during cure, no quantitative correlation between the calculated values and the experimental data is made in this paper. Yet the theory provides a frame work in which the variation of viscosity can be determined from the constitutive equations.

The variation of mechanical properties can be calculated during cure by the constitutive equations.

$C_{11}'$  can be obtained from experiment and  $C_{11}''$  is calculated from Eq. (6) after  $\alpha$  is calculated from Eqs. (13) and (14). If we assume that  $k_f$  and  $g_s$  are constant, the variation of  $k_s$  can be obtained by the Eqs. (11) and (12). The calculated values of  $k_s$  are 6.6 (Gpa) and 3.85 (Gpa) for Epon 828/Z and 815/V140 at fully cured state. The experimental values of them are 6.81 (Gpa) and 3.868 (Gpa), respectively. So the calculated and experimental values are not much different.

Figure 7 shows the variation of  $k_s$  during cure.

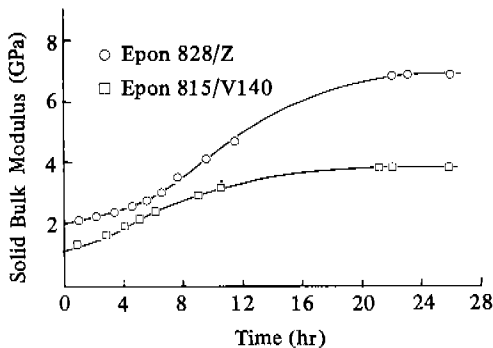


Fig. 7. Variation of Solid Bulk Modulus During Cure.

As evidenced in the above results, the constitutive equations developed by Hahn

can be used to monitor the cure and to calculate the mechanical properties of the epoxy resins during cure.

#### 4. Conclusion

Quantitative correlation between the theory and the ultrasonic experimental data is made. The developed constitutive equations can be used to monitor cure and calculate the variation of mechanical properties of epoxy resins with cure time. Application of these equations to three epoxy resins has demonstrated its validity that is in excellent agreement with experimental results.

#### REFERENCES

1. Stansbarger, D.L. et al., Air Force Contract F 33615-74-c-5753, Northrop Corp., 2nd Quarterly Report IR-406-4 (II), 31 OCT. (1974).
2. J.F. Carpenter, Instrumental techniques for developing epoxy cure cycles, MCAIR 76-003, McDonnell Douglas (1976).
3. C.D. Han and K.W. Lem, Chemorheology of Thermosetting Resins. I. The Chemorheology and curing kinetics of Unsaturated Polyester Resins, J. Appl. Polym. Sci. Vol. 28, 3155-3183 (1983).
4. A.M. Lindrose, Ultrasonic wave and moduli changes in a curing epoxy resins, Exp. Mech. 18:227 (1978).
5. R.S. Williams, Ultrasonic Assesment of Cure Rate Effects in Bonded Honeycomb Structure, ACS 47th Mtg. (Sept. 1982).
6. J.B. Enns and J.K. Gillham, The time-temperature-transformation (TTT) cure diagram: Modeling the cure behavior of thermosets, ACS, Div. Org., Coating,

- & *Plastics Chem., Preprint*, 48:575 (1982).
7. H.T. Hahn, Application of Ultrasonic technique to cure characterization of epoxies, Presented at the Symposium on Nondestructive Methods for Material Property Determination Hershey, PA. (April 6-8, 1983).
  8. G.J. Curtis, Measurement of the cure of resins by Ultrasonic Techniques, Presented at the conference on the testing of polymers for services, Buxton, Derbys (Oct. 5-6, 1972).
  9. H.J. Sutherland and R1 Lingle, An acoustic characterization of polymethyl methacrylate and three epoxy formulations, *J. Appl. Phys.*, Vol. 43, No. 10 (Oct. 1972).
  10. B.W. Shaffer and M. Levitsky, Thermoelastic Constitutive Equations for Chemically Hardening Materials. *J. Appl. Mech.* (Sept. 1974).
  11. R.M. Christensen, "Theory of Viscoelasticity: An Introduction", Academic Press (1971).
  12. W.I. Lee and G.S. Springer, Heat of Reduction, Degree of Cure, and Viscosity of Hercules 3501-6 Resin, *Journal of Composite Materials*, Vol. 16, pp. 510-520 (1982).
  13. K.W. Lem and C.D. Han, Chemorheology of thermosetting resins. II Effect of particles on the chemorheology and curing kinetics of unsaturated polyester resin, *J. Appl. Polym. Sci.*, Vol. 28, 3185-3206 (1983).