

ULTRASONIC BEHAVIOR OF EPOXY RESINS/ POLY(ETHYLENE OXIDE) BLENDS CURED WITH PHTHALIC ANHYDRIDE

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ABSTRACT

By means of ultrasonic attenuation apparatus, the ultrasonic velocity and attenuation of anhydride-cured epoxy resins (EP)/poly(ethylene oxide) (PEO) blends were measured on the basis of pulse-echo method. It was found that the sonic velocity of the blends decreased as the temperature increased, but attenuation coefficient increased and possessed a peak value. Larger velocity and smaller attenuation coefficient(α) can be obtained from perfect crosslinking network structures of pure DGEBA cured with phthalic anhydride(PA). As for cured DGEBA/PEO blend systems, sonic velocity decreased as a function of PEO concentration, but attenuation coefficient (α) increased.

INTRODUCTION

The propagation properties of high frequency elastic wave in media have been studied widely, especially in solids^[1]. Ultrasonic attenuation(i. e. high frequency internal friction) in solid polymeric materials^[2] is a kind of energy loss which mainly results from viscoelastic relaxation, plastic flow and scattering factors. Ultrasonic velocity closely relates to the elastic modulus of materials, and the elastic coefficient or effective elastic coefficient of materials will change when the sonic velocity in the materials changes.

The relaxation processes of polymer can be studied over a wide

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frequency range by dynamic mechanical methods, dielectric method or nuclear magnetic resonance etc.. Ultrasonic technology provides a method of investigating high frequency dynamic mechanical properties of polymers.

The ultrasonic behaviors of polymeric materials under condensed state have been studied^[3-8], mostly on the relationship between frequency properties and temperature, absorbance as well as pressure. The studies on epoxy resin systems mainly concerned with the composite materials of epoxy resin matrix^[9,10]. Prassianakis^[11] investigated the ultrasonic properties of epoxy resin with various plasticizer contents and the effect of curing time on sonic velocity.

But the studies on the ultrasonics of epoxy resin blends have been seldom reported yet. In the previous work^[12,14], the conclusion that epoxy resin/PEO blends cured with phthalic anhydride (PA) are miscible has been reached. The resulting cured product is a kind of block and crosslinked copolymer. Various amounts of PA and blend composition both determine different crosslinking network structures. In the present paper, the ultrasonic properties of the same systems are investigated. The main aim of this work is to find how the various curing agent contents and addition of PEO constituent to the systems may affect the ultrasonic attenuation and velocity. An attempt to correlate crosslinking networks of the cured product with ultrasonic properties will be accomplished.

EXPERIMENTAL

1. Materials and preparation of samples

Epoxy resin used in this study is a DGEBA type (E-51) made by Shanghai Resin Factory (China), with equivalent weight: 185—210. Poly (ethylene oxide) (PEO), $M_n = 20,000$, was obtained from Shanghai Chemical Reagent Co., doubly terminated with hydroxyl groups and described elsewhere^[12]. Crosslinking agent is phthalic anhydride (chemical pure grade) PEO, produced by Xiangyang Chemical Reagent Factory of Shanghai.

DGEBA and PEO were mixed at the temperature above the melting point of PEO (87°C) for a period of sufficiently long time, and then PA was added into the mixture at 120°C with continuous stirring until PA was almost in solution and degassed in vacuum. The blends were cured according to the curing schedule: 110°C for 1 hour followed by 160°C for 4 hours.

The cured cylinder samples were carefully polished in order to obtain

the two parallel and plain surfaces to prevent from reflection at interfaces, beam divergence etc.. The thickness of the samples depends on the attenuation degree, and is in the range of 3-9mm.

2. Measurement;

The measurement of attenuation coefficient (α) and sonic velocity were performed on the Ultrasonic Attenuation Apparatus made by our laboratory on the basis of pulse-echo method in vacuum described elsewhere in detail^[8]. Ultrasonic transducer is made from quartz. Silicon oil was used as coupling agent. The frequency was 2.5GHz. The temperature of thermoset was measured by a thermocouple with the heating rate of 2°C/min.

Sonic velocity (V_1): $V_1 = 2L/t_{21}$, where, L is the thickness of the samples and t_{21} is the adjacent time difference between two particular echoes on the oscilloscope, which is directly collected by microcomputer.

Attenuation coefficient (α): $\alpha = (20/2L) \text{Log} (A_1/A_2) \text{ (dB/cm)}$, A_1, A_2 are the particular echo pulse heights respectively. Generally speaking, only one or two echoes are observed for polymer systems because α is very high compared with that of metals.

RESULTS AND DISCUSSION

1. Ultrasonic velocity

Velocity of ultrasound in solid polymers is closely related to their condensed state structures of materials. In addition, the continuity of macromolecular chains, intermolecular interactions and the temperatures etc. greatly affect sonic velocity.

The velocity of the longitudinal acoustic waves measured for pure epoxy resins cured with various amounts of PA are plotted versus temperature in Fig. 1(a). In the temperature region (0–120°C), the velocity decreased as the temperature increased, and decreased dramatically in the vicinity of glass transition temperature. It is observed that there exists significant difference for cured blend systems with various curing agent contents. Thus, in comparison with the system of 40 phr PA used, the curves of sonic wave velocity of the systems with larger or smaller amounts PA both shift dramatically with the increasing temperature. Based on the previous results^[12,14,15], it has been known that the variation of curing agent amounts (PA) determine the varied crosslinking network structures of epoxy resins. In the case of the stoichiometry of PA used, the perfect crosslinking network

strucure can not be formed, and there are many surplus of epoxide groups in the system. Even at the stoichiometry of PA (75phr), the cured pure DGEBA systems still possessed some unreacted anhydride molecules and epoxide group acted as plasticizer due to incomplete curing reaction generated from the activity of curing agent, gelation and vitrification process^[15]. These unreacted epoxide groups or PA molecules would provide the systems with more free volume. From Fig. 1(a) it can also be seen that, at 50°C (<T_gs, e. g. all systems is in the glassy state), the system at 40 phr of PA possesses higher sonic velocity than the systems containing 30, 50, 75 phr of PA. These experimental results are in good agreement with dynamic mechanical analysis. Theoretically, velocity change in materials corresponds to the common contributions of both modulus and density, which also closely relate to the changes of free volume. The elastic modulus of polymers correlate with the sonic velocity. The velocity is related to the real component E' of complex longitudinal modulus E* :

$$E^* = \rho v^2 / (1 - i(2v/\omega)) \quad E' = \rho v^2 \text{ and } E'' = (2\rho v^3)\alpha$$

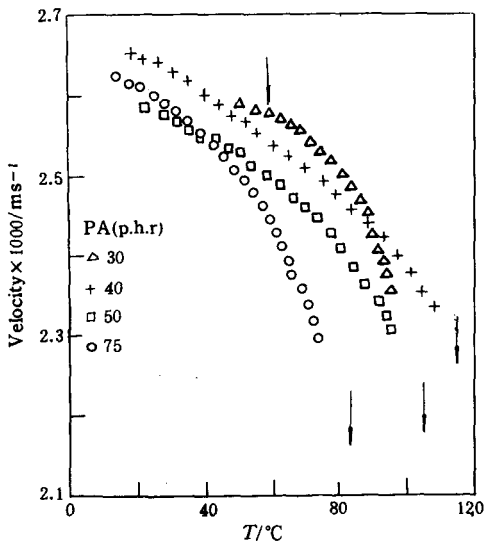


Fig. 1(a) Variation of longitudinal wave velocity (m/s) versus temperature (°C) for pure epoxy resins cured with various amounts of PA

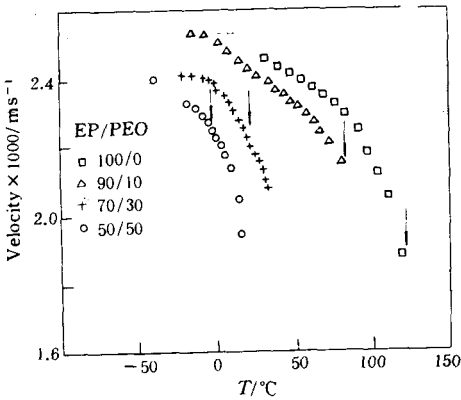


Fig. 1(b) Variation of longitudinal wave velocity (m/s) versus temperature (°C) for DGEBA/PEO cured with PA (40phr)

The arrows indicated the T_gs of the samples from attenuation measurement

where ρ is the density of the thermoset, ω is the angular frequency of the acoustic wave, v is longitudinal velocity and i is imaginary number unit. Obviously, unreacted PA and epoxide groups which act as plasticizer in the

systems will result in the depression of modulus and increment of density^[11], and conjointly to cause the depression of sonic velocity. The more PA and epoxide in the system are, the more sonic velocity will be decreased, Fig. 1(a) also shows that the system under stoichiometry of crosslinking agent (PA: 30phr) possesses the highest sonic velocity at 60°C. For the system, both the modulus and density of materials are lower due to lower crosslinking degree, therefore these factors determine the higher sonic velocity of the cured products.

For DGEBA/PEO blends cured with phthalic anhydride, the results are similar to that of cured DGEBA. In the same state (e. g. glassy state), it is also found that the addition of PEO to the system gives rise to the decrease of sonic velocity. The higher concentration of PEO is, the more the velocity is depressed. Similarly, the phenomena may be contributed to the effects of both modulus and density. For miscible polymer blends, introducing of supple macromolecule (PEO) into the system will result in modulus depression and density increase. It should be pointed out that the blends possess a kind of crosslinked, block and graft structure as PEO doubly terminated by hydroxyl groups participates in the crosslinking reaction. Therefore, the depression of sonic velocity may have a direct relationship to the crosslinking network structure. Further research is needed in this respect (See Fig. 1(b)).

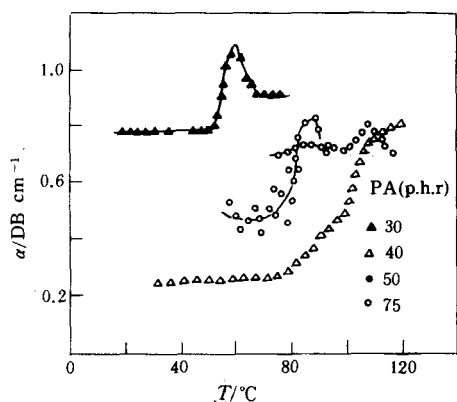


Fig. 2 (a) Relation between attenuation coefficient (α) (dB/m) and temperature ($^{\circ}\text{C}$) for pure epoxy resins cured with various amounts of PA

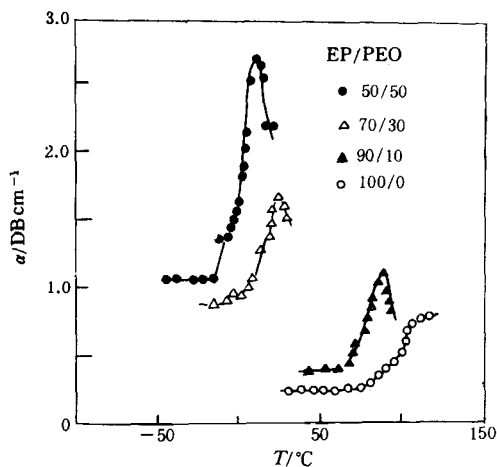


Fig. 2(b) Relation between attenuation coefficient (α) (dB/m) and temperature ($^{\circ}\text{C}$) for DGEBA /poly (ethylene oxide) cured with PA(40phr)

2. Ultrasonic Attenuation

Ultrasonic attenuation is mainly contributed to viscoelastic relaxation and scattering effect. While ultrasonic longitudinal wave propagates in solid polymeric materials, energy loss will occur as there exist retardation phenomenon between strain and stress, which is closely related to dilating effect of volume and motion of free ends. Attenuation due to scattering factors are usually produced because of the presence of the heterogeneity in polymeric materials, e. g. multiphase and semicrystalline polymers. As for the present polymer blend system, the attenuation is ascribed to viscoelastic relaxation. The blend pairs are miscible and investigated by DSC, DMA^[12]. On the other hand, PEO in the samples used for ultrasonic measurement will not crystallize since the T_g s of cured polymers are over ambient temperature (about -20°C). So we can say that the systems are effectively ‘transparent’ to ultrasonic.

Fig. 2(a, b) presents the variation of the attenuation coefficient (α) of the longitudinal waves against temperature. From the figure, it is seen that, for cured DGEBA system, the attenuation coefficient (α) almost remains unchanged at lower temperature, while α increases rapidly in the vicinity of certain temperatures and forms sharp single peak corresponding to glass transition region. Comparing with dynamic mechanical analysis results, it can be observed that ultrasonic attenuation method, as a high frequency dynamic mechanical technique, gives lower values of glass transition temperature (see Table 1.)

Table 1 Comparison between the ultrasonic attenuation T_g s (UAT $_g$) and dynamic mechanical loss T_g (DMAT $_g$)^[15] for the anhydride-cured DGEBA/PEO blends

PEO (wt %)	amount of curing agent (phr)	UA T_g ($^{\circ}\text{C}$)	DMA T_g ($^{\circ}\text{C}$)
0	30	67	93
	40	120	164
	50	110	160
	75	88	124
10	75	87	123
30	75	29	53
50	75	15	33

Fig. 2(a) shows that α of DGEBA with 30 Phr of PA is the highest

comparing with other system containing various amounts of PA under glassy state. In fact, undue amount of epoxide groups will draw a great amount of free ends into the systems and result in energy loss of acoustical wave vibration. For the system containing PA of 40phr, attenuation coefficient (α) is smaller since there are few free ends due to formation of the crosslinking network structure with the largest crosslinking density. From Fig. 2(b), it is observed that addition of PEO to the systems brings greater attenuation, and α increases with the increase of concentration of PEO. This result may be explained with respect of the following aspects: (1) addition of PEO as a supple macromolecule component to the DGEBA systems forms miscible polymer blends, PEO actually acts as plasticizer which gives rise to larger attenuation^[11]. (2) PEO doubly terminated with hydroxyl groups participates crosslinking reaction and forms a kind of crosslinked, block and graft copolymers, which results in incomplete crosslinking reaction, e. g. heterogenous crosslinking networks.

CONCLUSION

The ultrasonic properties of DGEBA/PEO cured with PA were investigated on the basis of pulse-method. It was found that velocity of ultrasound decreased as a function of temperature, and attenuation coefficient (α) increased to reach a peak value, corresponding to glass transition region of the epoxy polymers. Besides, the velocity of ultrasound and attenuation depend on the internal structure as other properties of materials. The experimental results indicate that larger sonic velocity and smaller attenuation can be obtained from network structures of cured epoxy resins with the largest crosslinking density under the glassy state. For the blend system, the addition of PEO to the systems results in depression of sonic velocity and increment of attenuation.

Keywords:

Pulse-echo method; Ultrasonic velocity; Attenuation coefficient (α); Epoxy resins/poly(ethylene oxide) blends; Crosslinking network

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