Storage and Loss moduli Behavior of Plasticized Epoxy Polymers Over a Frequency and Temperature Range, and Damaging Effects Assessment by Means of the NDT Method of Ultrasounds and Moisture Absorption

E. Sideridis, I. N. Prassianakis, V. N. Kytopoulos

Department of Mechanics, Laboratory of Strength and Materials, Faculty of Applied Mathematics and Physics Sciences, National Technical University of Athens, Iroon Polytechniou 5, GR-157 73, Zografou, Athens, Greece

Received 25 January 2006; accepted 24 March 2006
DOI 10.1002/app.24525

ABSTRACT: The first objective of the present experimental work is to evaluate the storage and loss moduli of plasticized epoxy polymers over a temperature and frequency range, and to correlate with the ability of the ultrasounds for the characterization of such polymers. The materials used were a series of cold-setting epoxy polymers, plasticized with different amounts of plasticizer. After the investigation of dynamic properties through vibration tests, the velocities of longitudinal and transverse elastic waves, and the acoustic attenuation coefficient *a* were evaluated and, then, using these quantities, the "dynamic" moduli E', G', and ν' were evaluated. Thereafter, it can be stated that the plasticizer content and measuring frequency range strongly influence the elastic moduli of the material in the sense that the plasticizer tends to reduce, whereas the measuring frequency to increase these. The second objective of this work is to asses and discuss the associated plasticizer-induced microstructural damaging effects by combined methods of ultrasounds, tensile modulus, as well as moisture absorption testing and then to correlate this assessment with the storage moduli behavior. It was shown that, despite the nonneglecting scatter in the experimental data, certain irresistible general trends might be assessed. In this context, it was found that the damage "response" is markedly sensitive to the respective applied "detection" technique and, therefore, the damage evolution data obtained by these different techniques are comparable only under certain circumstances. By comparison between the applied techniques, it seems reasonable to assume that the "moisture" technique due to its inherent microscopic mass transport processes, in the form of H_2O molecules diffusion and therefore its ability to "detect" microstructural detects on a much lower scale, should give a better approach to the internal damage phenomena. J Appl Polym Sci 101: 3869–3880, 2006.

Key words: nondestructive testing; ultrasounds; epoxy polymers; dynamic properties; damage; storage modulus; loss modulus; loss tangent; moisture absorbtion; diffusivity

INTRODUCTION

Epoxy polymers are crosslinked thermosetting polymers whose hardening is achieved by adding suitable agents, and whose mechanical, optical, and acoustical properties are strongly affected and can be modified between broad limits by the addition of an appropriate platicizer.

The polymers prepared by this way are insoluble, unmeltable substances of high strength, with effective adhesive properties.[1,2] These materials can be used to simulate the viscoelastic behavior of other engineering materials, and also in the restoration of damaged constructions, that is, for the repairing of concrete buildings damaged by earthquakes.

The ultrasonic testing[3–5] has been widely used by many researchers for the determination of mechanical properties of the polymers.[6,7] In a series of previous articles, the mechanical, optical, and acoustical properties of platicized epoxy polymers were determined.[2,8–11] Thus, the ultrasound was applied for the examination of adhesively bonded materials.[10] Also, in Refs. 9 and 11, a new experimental technique, based on the ultrasounds, for the evaluation of the damage parameter, *D*, of the materials was developed.

On the other hand, extensive studies have been carried out over wide range of temperatures and amount of plasticizer. In Refs. 12 and 13 by applying the time–temperature superposition principle, the master curves for the extensional or bulk creep and relaxation complicances and moduli were derived. It was proved that, within the range from ambient to 135°C, the aforementioned curves are of simple sigmoidal form, consisting of a glassy region, in which the material behaves elastically, a transition zone, in which the viscoelastic behavior is intense, and a flat rubbery region.

However, at high strain rates or frequencies, the materials exhibit a similar behavior, and the respective

---

Correspondence to: I. N. Prassianakis (prasian@central.ntua.gr).

Journal of Applied Polymer Science, Vol. 101, 3869–3880 (2006)

master curves possess one additional transition zone. As these materials are particularly important for dynamically loaded structures, for which both dynamic stiffness and damping capacity must be maintained at prescribed levels, when frequency or strain rate varies, a complete knowledge of their dynamic properties over wide frequency ranges and for various degrees of plasticization is required.

Previous investigations of the dynamic mechanical properties of some particular amine-cured epoxies are reported in the literature.[14,15] Derivation of storage and loss moduli from the relaxation modulus can be obtained by means of transformations performed on the respective viscoelastic spectra, as in Ref. 16. Dynamic tensile properties of plastics were determined over a wide temperature range.[17–19] The glass transition temperatures determined by dynamic methods were checked by additional tests, by means of thermal expansion measurements.[20] Respective techniques for nonlinear behavior are discussed in Ref. 21. Other viscoelastic parameters, such as relaxation modulus, over a correspondingly wide time range are derived by conversion from storage and loss moduli obtained over a frequency range.[22,23]

In this article, the dynamic moduli of epoxy plasticized with different amounts of plasticizer, ranging between 0% and 60% by weight of the amount of the epoxy prepolymer, were determined over a temperature range in four different frequencies through vibration tests.

On the other hand, the moduli of elasticity and the physical damage parameter in a series of epoxy polymers plasticized in a wider range with different amounts of plasticizer at ambient temperature, using ultrasounds, were determined, and the results were compared with the corresponding ones evaluated from dynamic and from static tensile as well as from moisture absorption test. In this connection, it must be mentioned that, recently, a novel nondestructive approaching technique based on the moisture test has been proposed[24–26] for the damage evaluation in certain polymer composites. This technique is based on the net effects of the internal microstructural changes on the moisture diffusivity of the material. It has been shown that this thermophysical approaching technique can be used in a complementary way to study the internal damage, and can provide a powerful tool to gain a deeper insight into the general phenomenon of damage evolution.

THEORETICAL CONSIDERATIONS

Dynamic mechanical analysis

Experimental studies of viscoelasticity in polymers are extremely extensive, and a very large number of techniques have been developed. To obtain a satisfactory understanding of the viscoelastic behavior, data are required over a wide range of frequency or time and temperature.

By subjecting a specimen to an alternating strain and simultaneously measure the stress when equilibrium is reached, the stress and strain will both vary sinusoidally, but the strain lags behind the stress:

$$\varepsilon = \varepsilon_0 \sin\omega t \text{ and } \sigma = \sigma_0 \sin(\omega t + \delta) \tag{1}$$

where $\omega = 2\pi f$ is the angular frequency, δ is the phase lag, and f is the frequency.

It can be seen that the stress may be considered to consist of two components: $\sigma_0 \cos \delta$ in phase with the strain and $\sigma_0 \sin \delta$ 90° out of phase with the strain. Then

$$\sigma = \varepsilon_0 E' \sin \omega t + \varepsilon_0 E'' \cos \omega t \tag{2}$$

where

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \text{ and } E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \tag{3a, b}$$

Quantity E' in phase with the strain is called storage modulus, because it defines the energy stored in the specimen due to the applied strain. The quantity E'' out of phase with the strain defines the dissipation of energy and is called the loss modulus. The ratio of these two quantities is called loss factor. That is

$$\frac{E''}{E'} = tg\delta_E \tag{4}$$

When a viscoelastic material, such as epoxy resin, is subjected to sinusoidally varying strain, the relation between complex stresses and strains is formally the same, as that between stresses and strains in an elastic material, but the moduli are now complex quantities with varying frequency. Thus

$$E_m^* = E'_m(t) + iE''_m(t) \tag{5}$$

where $E'_m(t)$ and $E''_m(t)$ are the storage modulus and loss modulus of the plasticized matrix material, respectively.

The complex shear modulus and the complex Poisson ratio can be introduced in a similar manner as follows:

$$G_m^* = G'_m(t) + iG''_m(t) \tag{6}$$

with

$$\frac{G''_m}{G_m} = tg\delta_G \tag{7}$$

and

$$v_m^* = v'_m(t) - iv''_m(t) \tag{8}$$

where v''_m is a positive quantity.

It can be proved that $tg\delta_G > tg\delta_E$. This relation can be written as follows:

$$\frac{G''_m}{G'_m} > \frac{E''_m}{E'_m} \tag{9}$$

It is valid that $G_m^* = \dfrac{E_m^*}{2(1 + v_m^*)}$. Thus

$$\begin{aligned} G'_m + iG''_m &= \frac{E'_m + iE''_m}{2(1 + v'_m - iv''_m)} \\ &= \frac{(E'_m(1 + v'_m) - E''v''_m) + i[E'_m v''_m + E''_m(1 + v'_m)]}{2[(1 + v_m^{''2})]} \end{aligned} \tag{10}$$

By equating the real and imaginary parts of the relationship, we obtain

$$G''_m = \frac{E'_m v''_m + E''_m(1 + v'_m)}{2[(1 + v'_m)^2 + v_m^{''2}]} \tag{11a, b}$$

and

$$G'_m = \frac{E'_m(1 + v'_m) - E''_m v''_m}{2[(1 + v'_m)^2 + v_m^{''2}]}$$

Substituting eqs. (11a) and (11b) into eq. (9) we have

$$\frac{E'_m v''_m + E''_m(1 + v'_m)}{E'_m(1 + v'_m) - E''_m v''_m} > \frac{E''_m}{E'_m} \tag{12}$$

After doing some algebra we obtain

$$(E_m^{'2} + E_m^{''2})v''_m > 0 \tag{13}$$

which is valid, because $E_m^{'2} + E_m^{''2}$ is a positive quantity, and $v''_m > 0$.

Therefore, the loss tangent in shear is always greater than the loss tangent in extension.

The ultrasonic evaluation of the moduli of elasticity and the associated damage parameter

The ideally elastic solids when subjected to a small deformation obey Hooke's law:

$$\sigma = E\varepsilon \quad \text{and} \quad \tau = G\gamma$$

where σ, τ, ε, and γ are the normal and shear stresses and strains, E the static Young's moduli, and G the static shear moduli of elasticity.

On the other hand, by using the velocities of longitudinal c_l and transverse c_t elastic waves, one can evaluate the corresponding dynamic moduli of elasticity E', G', and the Poisson ratio ν', from the following equations:

$$E' = 4\rho c_1^2 \frac{\frac{3}{4} - (c_t/c_l)^2}{1 - (c_t/c_l)^2} \tag{13a, b, c}$$

$$G = \rho C_1^2$$

$$v' = \frac{\frac{1}{2}\left(\frac{c_l}{c_t}\right)^2 - 1}{\left(\frac{c_l}{c_t}\right)^2 - 1}$$

where ρ is the density of the material.

It is well known that these moduli are strongly affected by the frequency of the elastic wave as well as by the viscosity and the elasticity of the materials, as it comes out from the following relation given in Ref. 23:

$$c^2 = c_0^2 + \int_0^\infty \frac{H(\tau)\omega^2\tau^2}{\rho(1 + \omega^2\tau^2)} d\tau \tag{14}$$

where $\tau = \eta/E$ is the relaxation time, η is the viscosity of the material, $H(\tau)$ is the density of the spectrum of relaxation times, and c_0 is the limit velocity that corresponds to the static modulus of elasticity E.

From this equation, one can see that when $\omega\tau \to 0$ the phase velocity c tends to be equal to c_0 ($c \to c_0$). This means that either the frequency $f \to 0$ (static loading) or the relaxation time $\tau \to 0$ case corresponds to highly elastic states (low viscosity and high elasticity).

In the other limiting case, when $\omega\tau \to \infty$, it follows from eq. (14) that with a growth of frequency f or of the relaxation time τ (high viscosity and low elasticity) the velocity of waves should increase tending to a limiting value.

The attenuation coefficient, a, can be evaluated for each composition of plasticized epoxy polymer, using the following well-known relationship:

$$\alpha = \frac{20}{2d} \log \frac{h_0}{h} \tag{15}$$

where d is the specimen thickness, and h_0 and h are the two successive backwall echo (the first and the second) heights, measured on the screen of the ultrasonic equipment.

A simple definition of the damage parameter, D, in the continuum mechanics is given in Refs. 27 and 28 as follows: If A_a is the apparent area of the cross-section of a bar subjected to a tensile load (when damage microcavities are created within the specimen as voids, micropores, microcracks, etc.), the area occupied by microcavities is A_d and the effective cross-sectional area is A_ε, and the damage parameter D_0 is given by the following relation:

$$D_0 = \frac{A_a - A_\varepsilon}{A_a} = \frac{A_d}{A_a} \tag{16}$$

where, when $A_a = A_\varepsilon$ and $A_d = 0 \rightarrow D_0 = 0$ means that there is no damage, while when $A_a = A_d$ and $A_\varepsilon = 0 \rightarrow D = 1$ there is damage.

There are a lot of different experimental methods of measuring the damage. On the basis of the ultrasounds, a new simple and accurate NDT method for the damage determination was introduced in Ref. 9 through the following relation of "attenuation" damage as follows:

$$D_1 = \frac{h_0 - h}{h_0} \tag{17}$$

The same relation is used for the damage determination versus the loading when a specimen is loaded by a stress σ_i, taking into consideration that in this case h is the echo height on CRT-screen at zero stress ($\sigma = 0$) and h is the height of the same echo on the screen at stress σ_i. This one has been verified in a lot of problems, as in the case of marble loading of Ref. 11. Using eq. (17), one can determine the damage variation in accordance to any influence to the material as, for example, the loading, the temperature, the polymerization as well as the content of the plasticizer in epoxy polymers, as was examined in the present article.

Elastic modulus as damage measure

Considering several most common techniques to evaluate damage (ultrasonic waves, cyclic softening and damping, electrical resistance, elastic modulus, i.e., stiffness reduction) the most appropriate one for damage evaluation is the measurement of the tensile static modulus of elasticity. This technique is derived directly from the coupling between elasticity and damage and is deduced from the principle of strain equivalence:[27,28]

$$\tilde{\sigma} = \frac{\sigma}{1 - D} = E\varepsilon_e \tag{18}$$

or

$$\sigma = E(1 - D)\varepsilon_e \tag{18a}$$

where $E \times (1 - D) = \tilde{E}$ may be interpreted as the elastic modulus of the damaged material. If E_0, the Young's modulus of the virgin, undamaged, material, is known, and $\tilde{E}_i$, can be measured, the stiffness damage is defined as follows:

$$D_i = 1 - \frac{\tilde{E}_i}{E_0} \tag{19}$$

where i denotes the number (steps) of damaging loads. It must be mentioned that the measurement of $\tilde{E}$ is often difficult because of the following factors: first, the localization of damage which requires the use of very small strain gauges; second, the small nonlinearities which always exist in the elastic range even during unloading; and third, microplasticity phenomena which, usually neglected, must be considered when damage occurs in the elastic modulus range, even if macroscopic plastic strain does not exist. Because of such elastic-induced microplastic structural changes, the stiffness (elastic modulus) degradation measurement may represent in fact a quasi nondestructive testing technique.

Mass diffusivity as damage measure

The diffusion phenomenon, in general, represents certain thermodynamic-passive mass/molecular transport processes in the materials. This microscopic behavior of the material is macroscopically determined by its mass. Diffusivity $\tilde{D}$ is a measure of the speed by which the moisture concentration changes inside the material. It was found that many transport phenomena can be described by means of the linear and nonlinear law of the Fickian diffusion mechanisms, from which the corresponding mass diffusivity, $\tilde{D}$, can be calculated.[29,30] Moreover, the linear Fickian law plays a very important, role because of its relative simplicity in the calculation of the formulae of diffusivity $\tilde{D}$. This, in turn, can be measured by the standard experimental procedure given elsewhere[29] and concerning relative simple moisture absorption/desorption test. In addition, this is an usual test for material characterization, which can be assessed in terms of thermomechanical as well as viscoelastic behavior. We can define a diffusivity damage measure in a similar way to eqs. (17) and (18), which is given as follows[24–26]:

$$D_i = 1 - \left(\frac{\tilde{D}_i}{\tilde{D}_0}\right)^n \tag{20}$$

with $n = 1$ if $\tilde{D}_{i1} \leq \tilde{D}_0$ and $n = -1$ if $\tilde{D}_i \geq \tilde{D}_0$, where $\tilde{D}_0$ and $\tilde{D}_i$ are the corresponding mass diffusivity of the virgin and the mechanically as well as physically damaged material, respectively.

EXPERIMENTAL

Material and specimens

The specimens used for the ultrasonic measurements of the velocity of longitudinal waves, the static elastic moduli, E, G, and ν , and the fracture stress σ_f were prepared in 1989 and were conserved properly until today at ambient conditions in our laboratory. They were made from a pure cold-setting commercial epoxy [repolymer (Epikote 828)] with an epoxy equivalent of 185–192, a molecular weight between 370 and 384, and a viscosity of 15,000 cP at 25°C, polymerized by addition of 8% triethylene tetramine (TETA) hardener per weight of the epoxy resin.[2,8] The amount of plasticizer, consisting of a polysulfide polymer Thiokol LP_3 added in the prepolymer, varied between 0% and 80% by weight of pure epoxy prepolymer.

The materials were produced as follows: The prepolymer was heated up to 30°C to decrease the viscosity. Proper amounts of curing agent and plasticizer were then added, and the mixture, after being stirred thoroughly, was put in a vacuum chamber for degassing. Subsequently, it was put in a Plexiglas mold of suitable form and capacity. The pot life, that is, the gelation time, was of the order of 15 min at 25°C.

The molding was removed 24 h later, and it was subjected to thermal processing, aiming for hot only at complete curing but also to stress-free specimens: Temperature was raised at 5°C/h from ambient to 100°C, maintained constant for ~3 days and then decreased at 1°C/h back.

Using this procedure, simple orthogonal plate specimens of dimensions $10 \times 50 \times 120$ mm^3 for each composition of epoxy polymer were prepared to determine the elastic moduli and the damage of each substance. The letter p indicates the percentage of the plasticizer added to each mixture, which varied from 0% to 80% by amounts of 10% for each batch.

Also, for the dynamic tests, cylindrical specimens with the percentage of plasticizer varying from 0% to 50% by amounts of 10% prepared in the same way, having 50-mm length and 3.5-mm diameter, were used.

Experimental procedure

For dynamic measurements, the specimens were tested on a Dynastat and a Dynalizer apparatus, by which the dynamic tensile properties of plastics can be determined over a wide range of temperatures. This apparatus applies a sinusoidal load of maximum amplitude (100 N) on cylindrical specimens. By taking into account the rigidity of the load-cell and the type and dimensions of the specimen, the storage and loss moduli, E' and E'', can be evaluated.

In fact, the dynamic measurements were carried out at temperatures covering the range from 20°C to 80°C, at steps of 10°C and in a subsonic range at frequencies 1, 10, 50, and 100 Hz.

For the determination of the velocities of the ultrasonic longitudinal and transversal elastic waves ,the attenuation coefficient and the damage parameter of all the specimens were tested under exactly the same conditions, using the Krautkramer USIP-11 ultrasonic equipment and ultrasonic waves of frequency equal to 2 MHz.

First, the velocities of longitudinal and transversal waves were determined. Then, using the eq. (13), the ultrasonic dynamic elastic moduli of elasticity, E', G', and ν', were determined. Also, using the eqs. (15) and (16), the attenuation coefficient α and the damage parameter D were evaluated for each composition of epoxy polymer and for the longitudinal waves.

All values of the physical, that is, nonmechanical-induced microstructural damage D_1 are normalized to the pure epoxy polymer, which is produced without plasticizer ($p = 0$). Thus, the damage values have been evaluated, taking h_0 as the height of the echo of the epoxy polymer plate made with $p = 0$ and h as the echo heights taken from the other compositions of the epoxy polymer plates, containing plasticizers varying from 0% to 80%.

The stiffness reduction testing procedure, to obtain the elastic modulus damage measure, was performed on an Instron-type loading machine by applying a quasistatic strain rate of about 10^{-4} s^{-1}. The elastic modulus was measured by means of adequate electrical strain gauges.

As mentioned previously, the saturating moisture absorption experiments were performed following the test procedures given elsewhere.[29,30] Especially, in the present study, we have tried to shorten the testing time by using "high" water conditioning temperature of about 80°C, which was significantly lower than the glass transition temperature $T_g \cong 115°$ of the composite material fact, which can eliminate free volume-induced effects. In this way, the saturation time (in days) required for each tested specimen was shortened by about 10 times. Moreover, by means of preliminary cycling sorbtion/desorbtion testing experiments, it was shown that possible high temperature hygrothermal damaging effects, such as osmotic degradations, surface blistering, surface peeling, resin leaching and dissolution (mass loss effects), surface microcracking, and other physical or microstructural damage, may be minimized but not totally avoided.

TABLE 1
Mechanical and Acoustical Properties of Various Compositions of Epoxy Polymers

p (%) (1)	ρ (g/cm^3) (2)	E (GPa) (3)	G (GPa) (4)	ν (5)	σ_f (MPa) (6)	c_l (km/s) (7)	c_l (km/s) (8)	c_t (km/s) (9)	E' (GPa) (10)	G' (GPa) (11)	ν' (12)	∂ (dB/mm) (13)	D (14)
0	1.182	3.30	1.23	0.338	57.3	2.900	2.750	1.230	4.95	1.80	0.374	0.81	0.00
10	1.194	3.22	1.20	0.338	57.3	2.850	2.720	1.220	4.87	1.77	0.375	0.88	0.09
20	1.208	3.00	1.12	0.340	59.8	2.810	2.650	1.200	4.85	1.74	0.371	0.94	0.19
30	1.224	2.50	0.92	0.358	55.9	2.760	2.610	1.180	4.68	1.70	0.372	1.03	0.30
40	1.243	1.82	0.64	0.430	52.4	2.680	2.600	1.150	4.52	1.64	0.378	1.12	0.46
50	1.242	1.30	0.44	0.480	46.8	2.580	2.490	1.060	3.85	1.38	0.391	1.18	0.60
60	1.240	0.90	0.31	0.490	22.7	2.500	2.400	960	3.22	1.15	0.400	1.32	0.70
70	1.238	0.50	0.17	0.495	16.0	2.480	2.320	910	2.87	1.02	0.410	1.28	0.76
80	1.236	0.32	0.11	0.499	14.6	2.400	2.280	850	2.54	0.89	0.420	1.25	0.81

RESULTS AND DISCUSSION

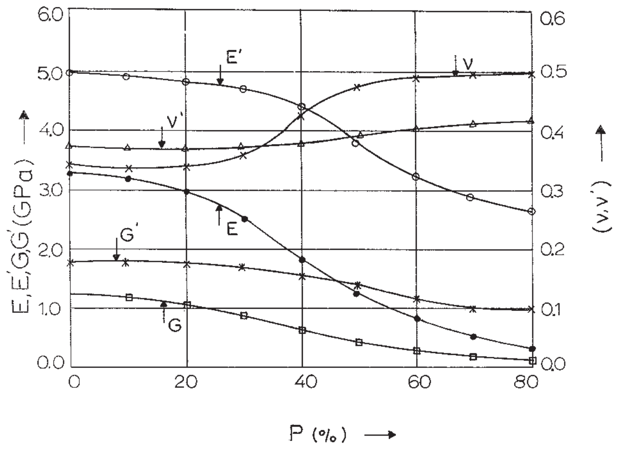
"Acousto-mechanical" behavior

The ultrasonic NDT method can be applied with facility, and provides precise information for epoxy polymers' mechanical properties even with very large contents in plasticizer. The determined properties (by this method) are the velocities of the longitudinal and transversal waves, the ultrasonic dynamic elastic moduli E', G', and ν', as well as the attenuation coefficient, α, and the associated damage parameter, D, of these materials.

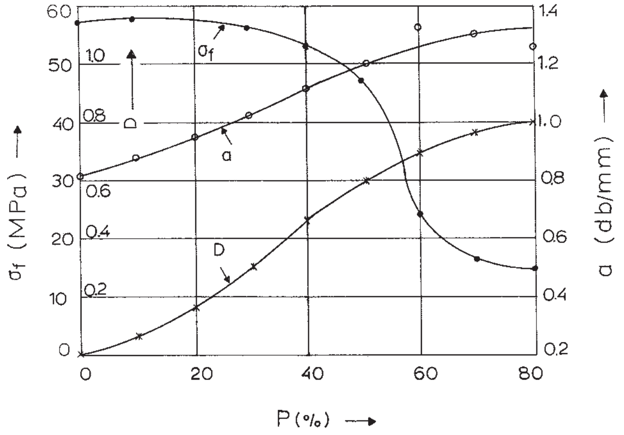
The static moduli of elasticity E, G, andν, the fracture strength σ_f, obtained from tensile tests and the velocity of longitudinal waves c_l (columns 3–7 of Table I).[8] All the experimental results are included in Table I and have also been drawn in the respective Figures 1(a) and 1(b).

Figure 1(a) illustrates the variation of the static and dynamic moduli of elasticity, and Figure 1(b) the variation of the fracture stress σ_f, together with the attenuation coefficient α, and the associated damage parameter D, for the longitudinal ultrasonic waves, versus the amount of plasticizer p, ranging between 0% and 80% of the amount of the epoxy prepolymer.

First, we can observe from these results that the velocities of longitudinal waves, for all of these polymers compositions (column 8), are slightly lower than the corresponding compositions mentioned in Ref. 8 (column 7) which were determined 12 years ago, in fact caused by the aging of the polymer. Also, from the curves of the Figure 1 arise that the variation of the ultrasonic dynamic elastic moduli E' and G' versus the percentage of plasticizer p is similar to the corresponding variation of the static moduli E and G, tending asymptotically to small values, but remaining continuously greater than them. This behavior can be explained if we take into consideration the influence of the frequency of the elastic waves and of the relaxation time on the moduli of the material, according to eq. (14).

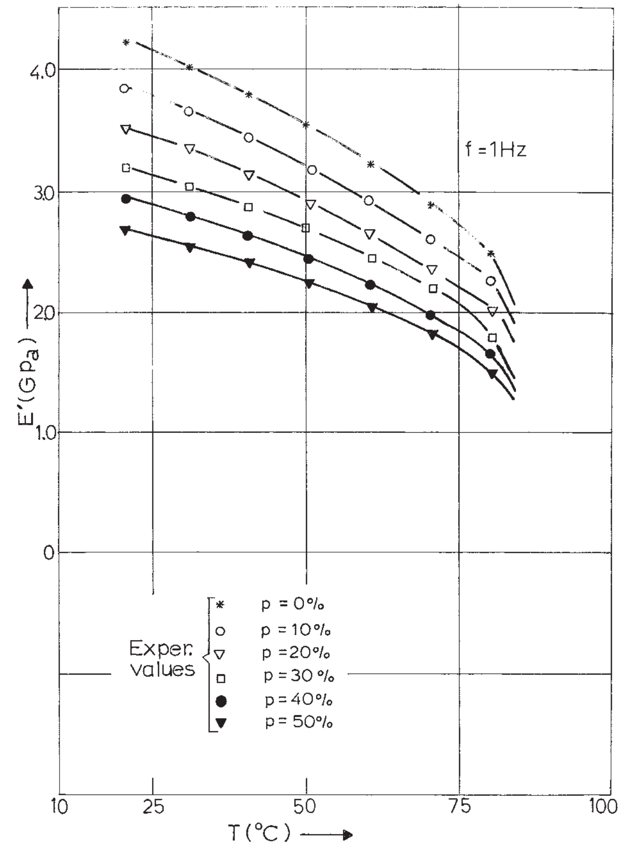


(a)



(b)

Figure 1 (a) Variation of the static E, G, ν and ultrasonic dynamic E', G', v' moduli of elasticity, versus the amount of plasticizer p of epoxy prepolymer, ranging between 0% and 80% of the amount of the epoxy prepolymer. (b) Variation of the fracture stress, σ_f, the attenuation coefficient, α, and the damage parameter, D, versus the amount of plasticizer p of epoxy prepolymer, ranging between 0% and 80% of the amount of the epoxy prepolymer.



Figures 2–5 Variation of the dynamic (subsonic) storage modulus E' versus temperature for the amounts of plasticizer p of epoxy prepolymer, ranging between $p = 0\%$ and $p = 50\%$ and for frequencies 1, 10, 50, and 100 Hz, respectively.

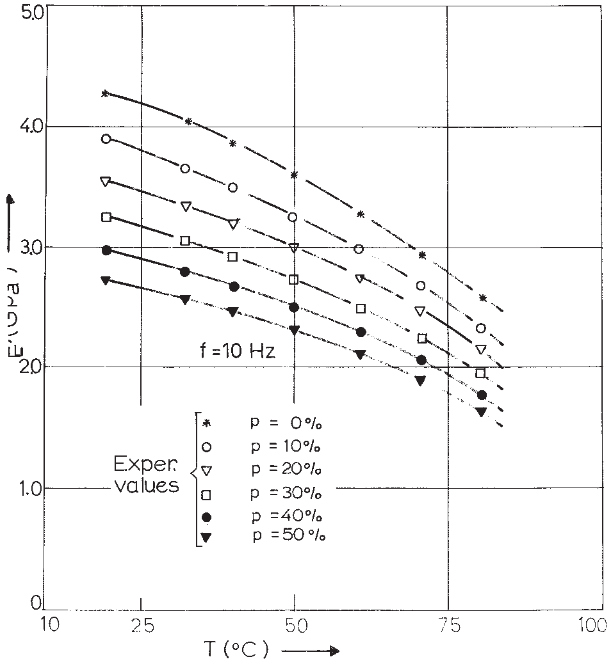


Figure 3

As to the change of the dynamic Poisson's ratio ν', we observe that it is altered as the other moduli smooth up to the content of plasticizer equal to 30%. However, beyond this content, the static Poisson's ratio ν takes higher values than the corresponding dynamic ones, tending to a limit value equal to 0.5, which is attained for the content in plasticizer equal with 80%.

The experimental values obtained from dynamic tests carried out on plasticized epoxy materials both for storage and loss moduli were plotted versus temperature in the range from 20°C to 80°C, for $p = 0\%$ up to $p = 50\%$ plasticizer are illustrated in Figures 2–5 and Figures 6–9, respectively. These curves are given for the four distinct frequencies used during the experiments. Although the two sets of curves essentially retain their main characteristics, certain differences in form exist.

The storage modulus decreases with increasing temperature and, according to the slope of the respective curve, certain characteristic parts of them can be distinguished, to which the respective parts of the loss modulus curve correspond. Thus, in the range from 20°C to 80°C, the storage modulus decreases while the loss modulus increases considerably. In this article, the epoxy resin exhibits a quasielastic behavior, and no characteristic energy dissipating mechanisms develop. At higher temperatures ($T > 80°C$) the glass transition occurs, which is associated with maximization of the slope of the storage modulus curve and the

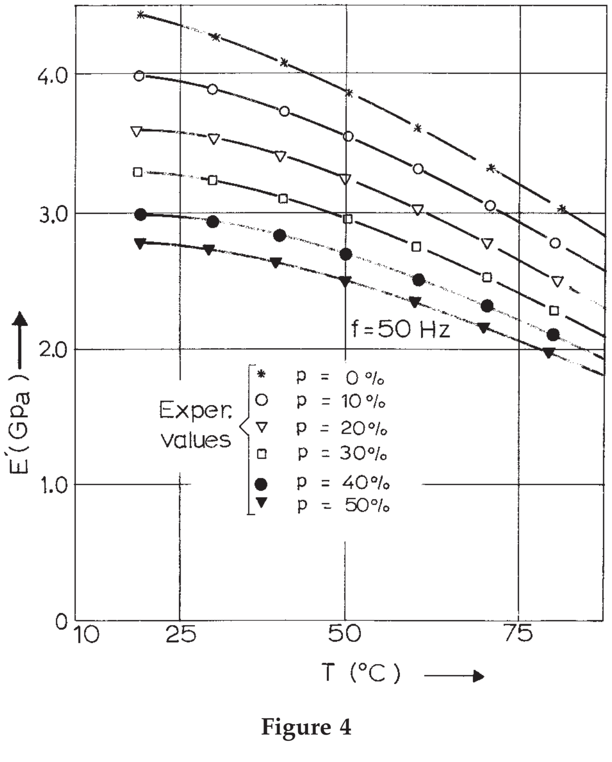


Figure 4

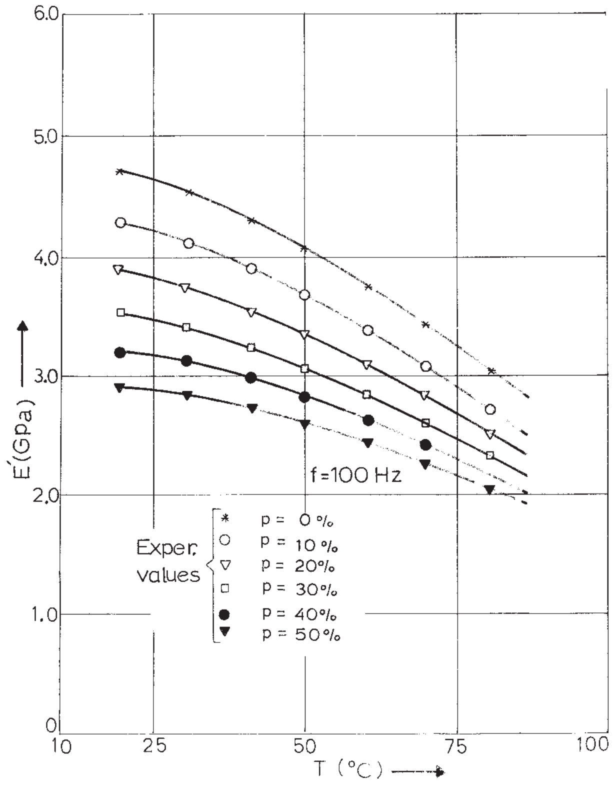


Figure 5

value of the loss modulus, which means that certain characteristic energy dissipative mechanisms should occur.

Transitions at low temperatures have been observed by other authors[14,15] as well, where the effect of the amounts of TETA as curing agent on the dynamic properties of the present epoxy resin was investigated.

The effect of plasticizer appears in the same figures. The storage modulus decreases when the amount of plasticizer is increasing. On the contrary, increase of the plasticizer amount causes increase of the loss modulus. This behavior should be indicative of the onset of certain internal damping or energy dissipating effects favored by an increase in the plasticizer content.

From Figures 2–5, it can be observed that when the amount of plasticizer increases, the slope of the E' curve versus temperature decreases. This may be due to the fact that the higher amount of plasticizer, because of its large macromolecules, enters the network of the matrix and shift the interchain distance almost up to the limit. For this reason, by the increase of the temperature which tends to shift the interchains, there is no way to increase the interchain distance, namely more than the already existing situation.

The inverse situation can be observed for the loss modulus E'' from Figures 6–9. With large amount of plasticizer and due to the large interchain distance, the internal damping increases and this is reflected to the loss modulus, which is an indication of damping.

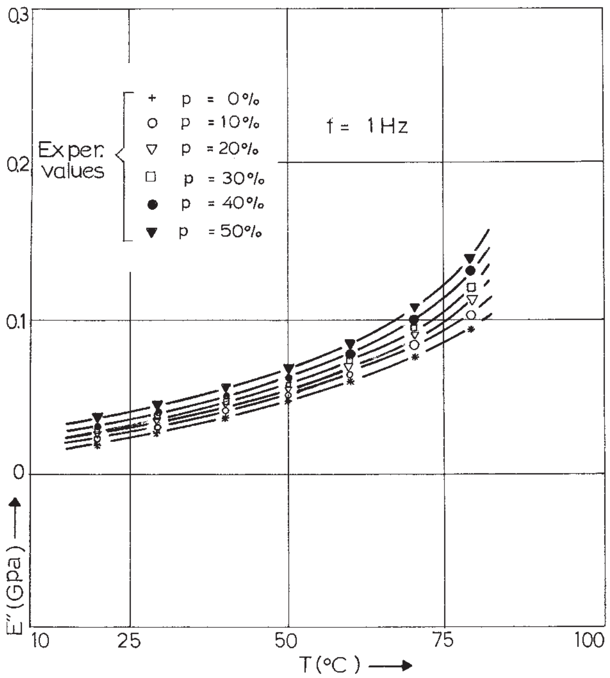


Figure 6–9 Variation of the dynamic (subsonic) loss modulus E'' versus temperature for the amounts of plasticizer p of epoxy prepolymer, ranging between $p = 0\%$ and $p = 50\%$ and for frequencies 1, 10, 50, and 100 Hz, respectively.

The dynamic properties of these materials depend on the frequency. It can be observed that both storage and loss moduli are "shifted" more or less to higher values, as frequency increases.

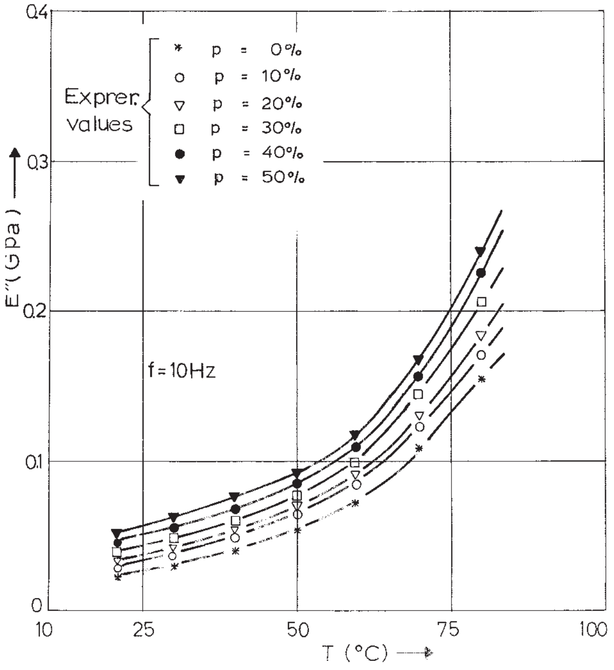


Figure 7

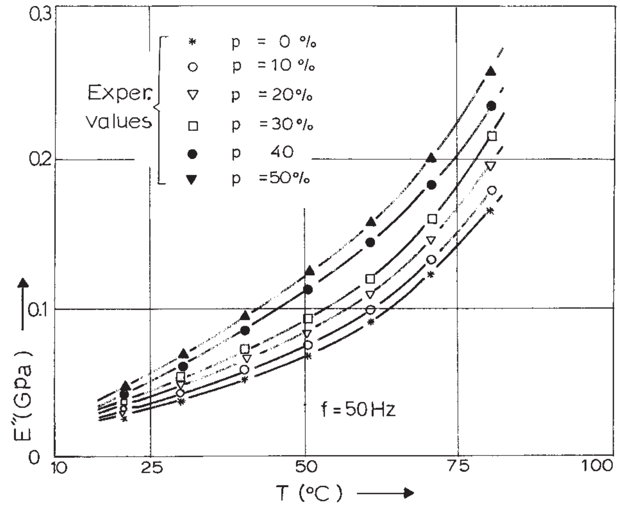


Figure 8

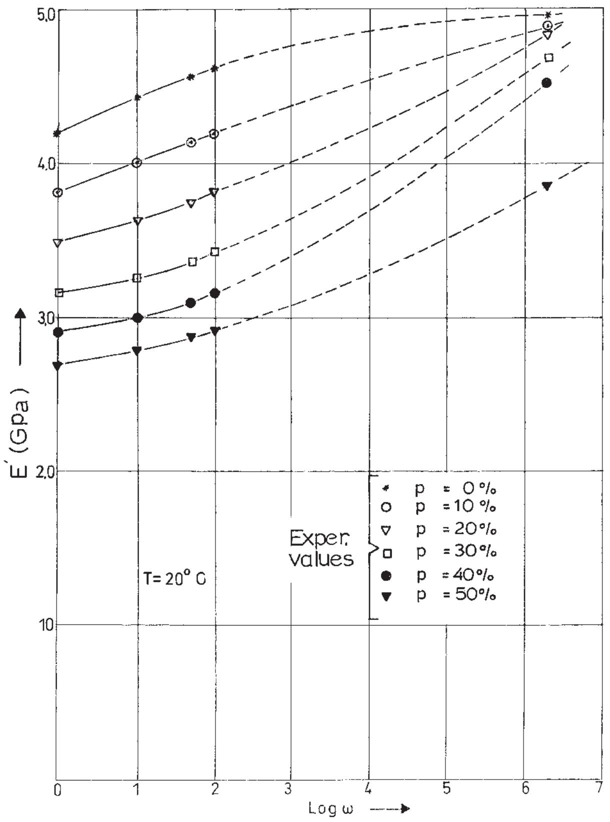


Figure 10 Variation of the dynamic (subsonic) storage modulus E' versus frequency for the amounts of plasticizer p of epoxy prepolymer, ranging between p = 0% and p = 50% and at T = 20°C. Correlation with the dynamic modulus E' derived from ultrasonic tests.

In relation to the frequency dependence, some more information can be observed from the respective figures for E' and E''. Thus, it can be seen that the frequency almost does not influence (or it influences to a less extent) the rate for the storage modulus.

On the contrary, in the loss modulus, the frequency influences too much. Increase of the frequency increases also the rate, which can be interpreted as increase of the intermolecular friction.

To investigate the correlation with the experimental values for dynamic modulus derived from ultrasonic tests, the E' curves produced for the whole range of temperature are now illustrated for T = 20°C versus frequency in Figure 10 for the amounts of platicizer considered. These curves maintain their main characteristics as plasticizer increases. It can be observed that ultrasonic E' increases with frequency and that if we extend the curves beyond the subsonic range of 100 Hz, as it is shown by the discontinuous part, we may arrive to the moduli obtained by ultrasounds around the frequency of 2 MHz. Therefore, it can be concluded that in viscoelastic materials the results for moduli obtained from ultrasonic measurements are closer to the results obtained from dynamic experiments than to those obtained from static tensile tests because of the strong variations in the properties of these materials with frequency. Furthermore, it can be said that the wave velocities are material properties that depend on the discrete nature of the internal structure of epoxy resin, which may be altered by changes in the row material resin content. As it will be discussed in the next section in epoxy polymers, certain physical or microstructural damage nucleation takes the form of microvoid or microcavities formation or both as well as configurational changes. Thus, the occurrence at the microstructural level of a com-

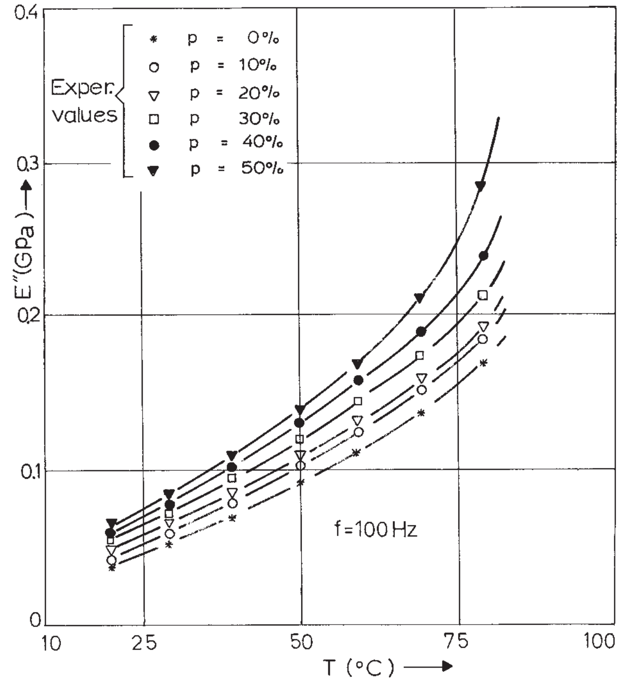


Figure 9

plex series of events, such as microvoids and microcavities or accumulation in the form of channels and holes, degrade the structural integrity.

It can be said that the study of the mechanical and acoustical (acousto-mechanical) behavior of epoxy polymers is of great interest in experimental and fracture mechanics, where these substances are used as model materials. The mechanical and acoustical properties of epoxy polymers vary according to their particular composition and, therefore, they can be used to simulate the elastic or viscoelastic behavior of other materials, metals, or plastics.

Damage assessment and correlations

The fracture stress σ_f, Figure 1(b), also decreases continuously with the increase of the plasticizer, tending to very small values, equal to the value of 25% of fracture stress of the epoxy polymer without plasticizer ($p = 0$), for large contents in plasticizer. In the same figure, we observe the variation of the attenuation coefficient, α, as well as the attenuation damage parameter, D, versus the amount of plasticizer, p, of the epoxy polymer. The values of damage have been normalized to that of the epoxy polymer without plasticizer ($p = 0$). The damage increases continuously from the value equal to 0, tending asymptotically to the limit value equal to 1, which may be virtually attained for very large contents in plasticizer of the epoxy prepolymer. Similar behavior also appears in the variation of the attenuation coefficient, which increases continuously from the value of 0.81 dB/mm, for the pure epoxy polymer ($p = 0$), to the limit value equal to 1.3 dB/mm for the epoxy polymer with plasticizer $p = 80\%$. Also, from the corresponding curves of Figure 1(b), as should be expected, arise that the curves of attenuation coefficient $\alpha = f_1(p)$ and of the damage parameter $D = f_2(p)$ are mirror reflection of the curve of the fracture strength $\sigma_1 = f(p)$.

The variation of all these quantities, versus the amount of plasticizer, is of a sigmoid type. They present an intermediate transition region, which corresponds to the values of plasticizer content p changing between 30% and 60%, for which the variation of all these quantities is very strong.

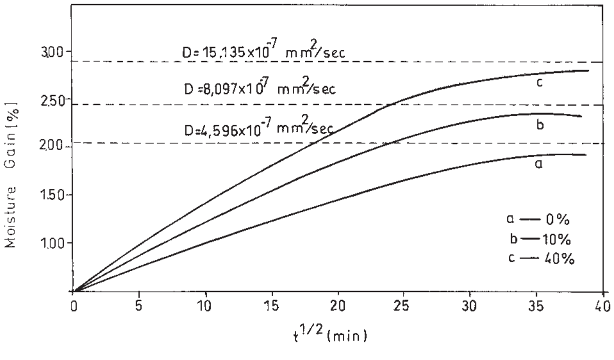


Figure 11 High temperature moisture sorption profile (80°C) for specimens with different plasticizer contents.

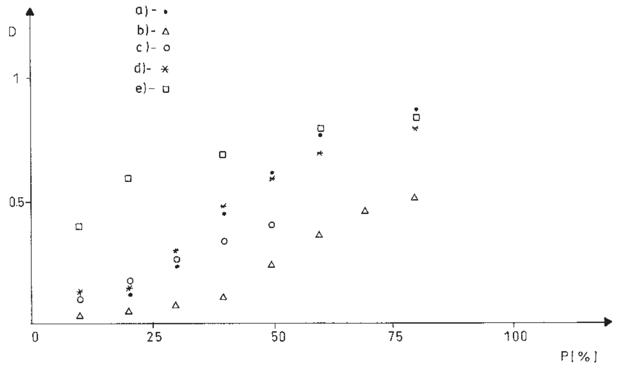


Figure 12 Plasticizer dependence of damage variation evaluated by (a) static moduli, (b) ultrasonic moduli, (c) storage (subsonic) moduli, (d) attenuation factor, and (e) mass diffusivity.

From all the aforementioned variations, it can be deduced that it would be valuable to try to measure and to assess the internal damage by means of other approaching techniques. Among these techniques, a new one is introduced in Refs. 24–26, which is based on the thermophysical phenomenon of diffusion or molecular mass transport. The required testing technique was applied as given in Refs. 27 and 28 and was based on moisture absorption of the investigated material. In Figure 11, the curves show the procentual moisture gain of net epoxy specimens and two epoxy specimens with different plasticizer content p. From these curves, a linear Fickian (single stage) diffusivity was evaluated by the corresponding formulae given in Refs. 29 and 30. In this way, the needed mass diffusivity (diffusion rate) was determined and by means of eq. (20) the so-called "diffusional" damage was calculated. Also, by means of eq. (19) and by substituting the (static) elastic modulus and the other moduli, such as ultrasonic (dynamic) storage, the corresponding damage measures were calculated. Furthermore, as described previously by means of eq. (17), the attenuation damage was also calculated.

All the data based on these damage measures are given in Figure 12 which, in other words, shows the influence of the plasticizer content on damage. This damage is in fact plasticizer-induced and it is termed physical damage in contrast to the mechanical damage induced by mechanical loading of the material. By comparing the data, relatively, great discrepancies between the five applied measuring techniques are observed. It can, thus, be deduced a "lower" and an "upper" bound of damage data, where the ultrasonic technique represents the "lower" and the diffusional technique the "upper" bound. In other words, the sensitivity of damage detection of the applied techniques seems to increase by sequentially passing from ultrasonic and subsonic and up to static frequency range. A reasonable explanation of the earlier behavior seems to be the following: physical damage can be seen as intermolecular or network loosening effects caused by the interchain displacement because of the infiltration of the (big) plasticizer molecules. Because of these appreciate displacement fields around damage sites, the material reduces its ability of vibrating stress transfer. Because of this fact, these fields cannot "follow" the external high vibration (ultrasonic) field. On the other hand, with decreasing frequency, the displacement fields can better "follow" the external vibration field, a fact which leads to a better "detection" of the damage sites. In the limiting frequency case of static modulus technique, one has a considerable increase in damage detection, approaching those of an attenuation technique. The latter is based on the absorption and scattering of the elastic waves on the damage sites, thus, giving a better resolution or detection ability. The upper limit given by the moisture absorption technique seems to better approach the real internal damage state. This is so because water molecules (H_2O) as microscopic particles or traces can penetrate into very small holes, pores, or channels and, in this way, can "see" damage sites at a very small scale level.

CONCLUSIONS

The effect of plasticizer into an epoxy resin on dynamic mechanical behavior has been investigated. The application of the NDT method of ultrasounds for the determination of the mechanical properties of the same materials was also examined, and the correlation with the results from dynamic tests and those from tensile was considered. At the same time, certain plasticizer-induced damaging effects by means of combined methods of ultrasounds, static stiffness, storage modulus as well as mass diffusivity were assessed.

The following conclusions can be drawn:

1. From the tensile experiments carried out on the plasticized epoxy resins, it was found that the tensile strength and the elastic modulus decreases whereas the Poisson ratio increases.
2. The dynamic properties of the plasticized epoxy resin are temperature-dependent. The storage modulus E' decreases with increasing temperature, while the loss modulus E'' increases (the fact which should facilitate internal damping).
3. The amount of plasticizer has a considerable effect on the dynamic properties. In this sense, the storage modulus decreases, whereas the loss modulus increases with increasing plasticizer amount (the fact which facilitates the internal damping).
4. The dynamic properties of these materials are frequency-dependent. Both storage and loss moduli are shifted to higher absolute values with increasing frequency, whereby the second ones are more affected.
5. The frequency strongly influences the rate of changes and the slope of the curves of the loss moduli with the temperature, whereby the rate increases with increasing frequency. Intermolecular loosening effects due to high plasticizer contents facilitate further increase in this rate, which may be indicative of occurrence of enhanced internal damping or frictional processes.
6. The static moduli derived from tensile tests of the plasticized epoxies are lower than those derived from dynamic (subsonic) tests and significantly lower than those measured by ultrasounds because of the strong variations in the mechanical properties of these materials with frequency.
7. The velocity of longitudinal waves for all plasticized epoxy resins decreases with the aging of the material.
8. From the five damage-measuring approach assessed to estimate the plasticizer-induced damage, the "diffusional" one seems to be the most reliable because of its inherent physical basis of molecular mass transport and hence of its ability to "detect" microstructural defects on a much lower scale.
9. From the executes in the present study experimental work, the ability of the NDT method of ultrasounds to be applied on epoxy polymer materials for the evaluation of their mechanical properties was proved. This "acousto-mechanical" method can be extended to solve experimental and fracture mechanics problems for pure plastics as well as composite materials.

References

1. Lee, H.; Neville, K. Epoxy Resins Their Applications and Technology; McGraw-Hill: New York, 1957.
2. Theocaris, P. S.; Prassianakis, I. N. J Appl Polym Sci 1978, 22, 1725.
3. ASNT. Nondestructive Testing Handbook, 2nd ed., Vol. 7: Ultrasonic Testing; ASNT: USA, 1993.
4. Krautkrämer, J.; Krautkramer, H. Ultrasonic Testing of Materials; Springer-Verlag: Berlin, 1977.
5. Prassianakis, I. N. NDT of Materials—The Ultrasonic Method; National Technical University of Athens (NTUA): Athens, Greece, 2002.
6. Hale J. M.; Ashton, J. N. Comp Struct 1985, 83.
7. Stigh, U. Eng Fract Mech 1987, 28, 1.
8. Prassianakis, I. N. J Appl Polym Sci 1990, 39, 2031.
9. Prassianakis, I. N. Eur J Nondestr Test 1994, 3, 93.
10. Prassianakis, I. N. Insight 2000, 42, 158.
11. Prassianakis, I. N.; Kourkoulis, S.; Vardoulakis, I.; Exadaktylos G. Proceedings of the 2nd International Conference in NDT of HSNT-BAND, Athens, Greece, May 24–26, 1999.
12. Theocaris, P.S. Colloid Polym J 1970, 236, 59.
13. Theocaris, P.S. Rheol Acta 1967, 6, 246.
14. Hirai, T.; Kline, D. E. J Appl Polym Sci 1972, 16, 3145.

15. Hirai, T.; Kline, D. E. J Appl Polym Sci 1973, 17, 31.
16. Theocaris, P. S. Exp Mech 1964, 4, 153.
17. Takayanagi, M. Mem Fac Eng Kyushu Univ 1963, XIII, 2.
18. Murayama, T. J Appl Polym Sci 1975, 19, 3221.
19. Paipetis, S. A.; Theocaris, P. S.; Marchese, A. Colloid Polym Sci 1979, 257, 478.
20. Hwo, C. H.; Johnson, J. F. J Appl Polym Sci 1974, 18, 1433.
21. Warnaka, G. E.; Miller, H. T. Trans ASME J Eng Ind 1968, 53, 491.
22. Schwarzl, F. R. Rheol Acta 1975, 14, 581.
23. Ferry, J. Viscoelastic Properties of Polymers; Wiley: New York, 1961.
25. Kytopoulos, V. N.; Prassianakis, I. N.; Sideridis, E. The 8th International. Conference of the Slovenian for Non-Destrictive Testing, Applications of Contemporary Non-Destructive Testing in Engineering, Portoroz, Slovenia, 2005.
26. Prassianakis, I. N.; Sideridis, E.; Kytopoulos, V. N.; Prassianakis, N. I.; Papapetrou, V. The 3rd International Conference on NDT, Greece, 2003.
27. Krajeinoric, D.; Lemaitre, J.; Eds. Continuum Damage Mechanics, Theories and Applications; Springer-Verlag: Wien, 1987.
28. Kachanov, L. M. Introduction to Continuum Damage Mechanics; Kluwer: Dordrecht, The Netherlands, 1986.
29. Shen, C.-H.; Springer, G. S. J Compos Mater 1976, 10, 2.
30. Shirrell, C. D.; Halpin, J. In Composite Materials: Testing and Design, 4th Conference, 1977; pp 514–528. ASTM-STP, Vol. 617.