Correlation of Mechanical and Acoustical Properties of Plasticized Epoxy Polymers

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Synopsis

In the present experimental work the influence of the percentage of plasticizer on the mechanical and acoustical properties of the plasticized epoxy polymers was studied. The velocity c_l of the longitudinal waves and the acoustic attenuation coefficient α were evaluated from the acoustical properties. Also the influence of curing time of plasticized epoxy polymers on the acoustical properties, c_l and α, was examined and it was found out that these quantities tend to their limiting values when the polymerization is completed. Furthermore, the determined acoustical properties are correlated with the corresponding mechanical properties for the same materials, which were also considered in earlier papers. So, a simple and quick experimental nondestructive technique is provided for the evaluation of the elastic properties, as well as of the epoxy polymers composition, by determining the velocity c_l of the longitudinal waves only.

INTRODUCTION

The continuously maturing use of epoxy polymers in research and especially in connection with photomechanics and other destructive and nondestructive (NDT) experimental techniques makes it necessary to study not only the mechanical and optical but also the acoustical behavior of these substances. Since the mechanical, optical, and acoustical behavior of epoxy polymers can vary between broad limits by adding different amounts of plasticizer, epoxy polymers are used as model materials in various experimental techniques. The mechanical and acoustical properties of epoxy polymers are strongly time-dependent, so that these materials can be used to simulate the viscoelastic behavior of other engineering materials. Epoxy polymers hardening is achieved by adding suitable hardener and the products are polymers of high strength with effective adhesive properties.

The study of the mechanical behavior of epoxy polymers has been reported by Lee and Neville.[1] Theocaris and Gdoutos[2] have studied the mechanical and optical viscoelastic behavior of epoxy polymers. Along with the mechanical behavior, Prassianakis[3] and Theocaris and Prassianakis[4] studied the optical behavior of polymers plasticized with different amounts of plasticizer at ambient temperature. They also applied the optical method of caustics, which is introduced by them for the first time in the study of various problems of experimental mechanics where plasticized polymers are used as model materials.

The nondestructive evaluation (NDE) technique used in this study was the ultrasonic pulse–echo technique (Krautkrämer and Krautkrämer[5]). In contra-

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diction to the majority of NDE literature on structures, which deals with metallic materials, this study considers plasticized epoxy polymers. According to the ultrasonic pulse–echo technique when ultrasonic pulses are introduced into a specimen, they will reflect on a discontinuity or on the backwall of the specimen. The magnitudes of the echo reflections depend on the changes in the impedance across the specimen.

Ultrasonic testing has been widely used for nondestructive inspection and evaluation of structural materials. Hale and Ashton[6] related strength reduction and change in ultrasonic attenuation of progressively damaged glass-reinforced plastics. Williams and Lee[7] utilized the NDE technique of ultrasonics to characterize separation mode and fracture strength, for adhesively bonded fiber-reinforced plastics.

In the field of fracture mechanics among the multitude of techniques ultrasonics also were proposed. In order to assess fatigue crack propagation, Bouami and Vadder,[8] using an ultrasonic technique based on wave diffraction by the crack tip, detected and measured both closure and opening of cracks (lengths and loads). Similarly using ultrasonics, Stigh[9] derived the relation between the damage variable and the ultrasonic wave velocity and showed that measuring the ultrasonic velocity on damaged materials one can predict their remaining ultimate strength and hence their remaining life.

In the present paper the acoustical behavior of epoxy polymers, plasticized with different amounts of plasticizer at ambient temperature, was studied and correlated with the corresponding mechanical behavior which was defined by the elastic modulus E, the Poisson's ratio ν, and the shear modulus G. These mechanical constants have been taken from Refs. 3 and 4. Using ultrasonics, acoustical behavior was characterized by the velocity of longitudinal waves c_l, transmitted through the specimen, as well as by the coefficient of acoustical attenuation, α. The variation of these properties with the amount of plasticizer in the epoxy prepolymer was studied in detail.

Finally the variation of the acoustical properties was studied vs. the conditions of polymerization of the epoxy polymers.

ULTRASONIC PULSE–ECHO EQUIPMENT AND MEASUREMENT PROCEDURES

As is well known, if an ultrasonic stress wave is introduced into a material, the characteristics of the wave after it has propagated through the structure may be related to the material properties.[5] The main purpose of the ultrasonic testing of materials is to look for and to evaluate locations in the materials which contain discontinuities, as well as to determine the interaction effects between sound waves and material properties.

The basic quantities for all ultrasonic measuring methods are the sound velocities and the sound attenuation through the material in which the sound wave travels. From the sound velocities c_l and c_t of the longitudinal and the transverse waves, respectively, and the density ρ of the material, the modulus of elasticity E, the shear modulus G, and the Poisson ratio ν are evaluated from the following relationships (Krautkrämer and Krautkrämer[5]):

$$E = \frac{(1+\nu)(1-2\nu)}{(1-\nu)}\rho c_l^2, \quad G = \rho c_t^2, \quad \nu = \frac{\frac{1}{2}(c_l/c_t)^2 - 1}{(c_l/c_t)^2 - 1} \tag{1}$$

For determining the mechanical characteristics of materials the sound attenuation is often of greater advantage in comparison to the sound velocity because it reacts with far more sensitivity to the changes in the structure.

A schematic of the used ultrasonic pulse–echo measuring system is shown in Figure 1. The system consists of a broadband (0.5–15 MHz) ultrasonic pulser–receiver flaw detector made by Krautkrämer (Model USIP 11) to generate and receive electric pulses up to 15 MHz. As transmitting–receiving transducers of sound waves, the probes K2G and K4N were used, producing ultrasounds of 2 and 4 MHz, respectively. As transducer–specimen interface couplant, a simple machine oil was used. A contact load, for both probes, of 9.88 N was applied to the transducer–specimen interface.

The pulser section produces and injects ultrasonic pulses into the specimen through the transducer, and the reflected signals are received by the same transducer. The voltage signals produced by the transducer are amplified by the receiver section of the equipment and displayed on the oscilloscope.

The sound velocity c_l^x of the longitudinal waves of each specimen was evaluated using the relationship (Krautkrämer and Krautkrämer[5])

$$c_l^x = c_l \frac{d_x}{d_g} \tag{2}$$

where c_l is the sound velocity of the reference block, d_x is the real specimen thickness, and d_g is the equivalent thickness of the specimen, measured on the oscilloscope screen.

In order to eliminate the effects of variations in probe coupling, it was decided to make use of two successive backwall echoes to measure attenuation. The coefficient of sound attenuation α was evaluated from the relationship (Krautkrämer and Krautkrämer[5])

$$\alpha = \frac{20}{2d} \log \frac{H_n}{H_{n+1}} \tag{3}$$

where d is the specimen thickness and H_n and H_{n+1} are the two successive backwall echo heights, measured on the oscilloscope screen.

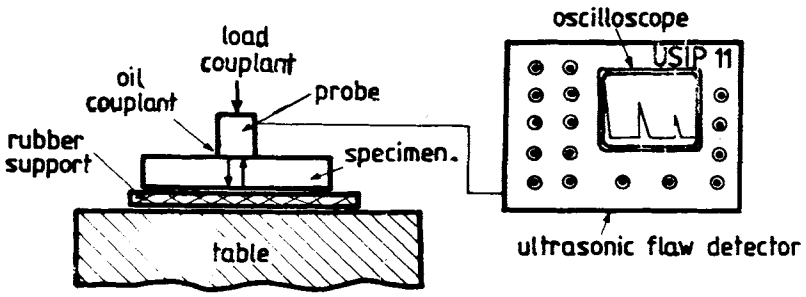

Fig. 1. A schematic diagram of the used ultrasonic pulse-echo measuring system.

PREPARATION OF SPECIMENS

The specimens used in this paper, were made exactly in the same way as those of Refs. 3 and 4. They were prepared from a pure cold-setting commercial epoxy prepolymer (Epikote 828) polymerized by addition of 8% triethylenetetramine (TETA) hardener per weight of the epoxy resin (phr). The amount of plasticizer, consisting of a polysulfide polymer Thiokol LP_3 added in the prepolymer, varied between 0 and 100% by phr. The epoxy–plasticizer mixtures were thoroughly mixed in an open cup before the hardener was added. The mixture was then degassed in a vacuum chamber for 10 min to remove all bubbles. Then the mixture was ready for casting. The casting was made in orthogonal molds of dimensions $10 \times 50 \times 120$ mm^3 coated with Silicon oil in order to eliminate adhesion of the mixture to the mold. The 11 types of epoxy polymer plates, prepared as described above, were denoted as C-100-p-8, where the letter C stands for the type of the epoxy polymer, which is a cold-setting one, and the two numbers in sequence indicate the percentage by weight of the epoxy prepolymer and of the amine hardener, respectively, added in each preparation. The intermediate letter p indicates the percentage of the plasticizer added to each mixture, which varied from 0 to 100% by amounts of 10% for each batch.

Using this procedure, two simple orthogonal specimens for each composition of epoxy polymer were made, which, after the removal of the molds 2 days after the casting, were tested as follows:

(1) Undercure specimens. The ultrasonic parameters were evaluated in the specimens at the fifth day after the casting when the polymerization of the epoxy polymers was not yet completed.
(2) Proper cure specimens. The ultrasonic parameters were evaluated in the same specimens which were cured by being heated at 110°C, and then slowly being cooled to ambient temperature. The duration of curing cycle lasted approximately 7 days in order to insure complete polymerization of each plate, Refs. 3 and 4.

The tensile specimens used in Refs. 3 and 4, for the determination of the mechanical properties of plasticized epoxy polymers, were made exactly the same way as the proper cure specimens of the present paper.

EXPERIMENTAL PROCEDURE AND RESULTS

For the determination of the attenuation coefficient and velocity of the longitudinal waves five specimens from each composition of epoxy polymer were tested ultrasonically at ambient temperature ($\sim$ 25°C). All the specimens of all the different compositions of plasticized epoxy polymers were prepared and tested under exactly the same environmental conditions in order to yield comparable results. For the generation and reception of sound waves the pulse–echo technique was used.

In order to examine the influence of aging in the acoustical properties c_l and α, new appropriate specimens of epoxy polymers were made, and c_l and α were evaluated in both undercured (5 days old after the casting) specimens, as well as in proper cured specimens (after the appropriate thermal curing of 7

TABLE I
Velocity and Attenuation of Longitudinal Waves at 2 and 4 MHz for Undercure and Proper Cure New Specimens and Density, at Room Temperature, in Various Compositions of Epoxy Polymers

		c_l (m/s)		α (dB/mm)			
		2–4 MHz		Undercure 5 days old		Proper cure	
p (%)	ρ (g/cm^3)	Undercure 5 days old	Proper cure	2 MHz	4 MHz	2 MHz	4 MHz
0	1.182	2640	2685	0.518	0.844	0.789	1.419
20	1.208	2545	2615	0.772	1.176	1.069	1.620
40	1.243	2336	2545	1.020	1.387	1.246	1.978
60	1.240	2229	2378	—	—	1.706	2.155
80	1.236	2156	2256	—	—	1.868	—
100	1.278	2058	2102	—	—	—	—

days). These results along with the density ρ and the percentage of plasticizer p, for various compositions of epoxy polymers, are presented in Table I.

In Table II the experimental values of the mechanical constants of the various compositions of epoxy polymers, as they have been given in Refs. 3 and 4, along with their density ρ, as well as the corresponding velocities of the longitudinal and transverse waves, evaluated using eqs. (1), are listed.

The tensile stress was evaluated in completely polymerized specimens,[3,4] and it was found out that for every composition of epoxy polymer it is greater than the tensile stress in the corresponding undercure specimen. However, the quantities c_l and α were evaluated for both undercured and properly cured compositions of epoxy polymers. In Figures 2 and 3 it is observed that as the polymerization progresses, the velocity of longitudinal waves c_l, as well as the attenuation of the epoxy polymers, both increase.

In a series of old specimens of dimensions $10 \times 50 \times 200$ mm^3, which had been made at the same time with the specimens of Refs. 3 and 4 and which had been properly cured and kept until today, two types of measurements of the acoustical constants c_l and α were carried out as follows. First these

TABLE II
Mechanical and Acoustical Constants for Old Specimens of Epoxy Polymers

p (%)	E (10^9 N m^{-2})	ν	σ_f (10^7 N m^{-2})	c_l (m/s)	c_t (m/s)	ρ (g/cm^3)
0	3.30	0.338	5.73	2065	1021	1.182
10	3.22	0.338	5.73	2029	1004	1.194
20	3.00	0.340	5.98	1955	963	1.208
30	2.50	0.358	5.59	1844	867	1.224
40	1.82	0.430	5.24	2042	716	1.243
50	1.30	0.480	4.68	3032	595	1.242
60	0.90	0.490	2.27	3524	494	1.240
70	0.50	0.495	1.60	3675	368	1.238
80	0.32	0.500	1.46	—	294	1.236

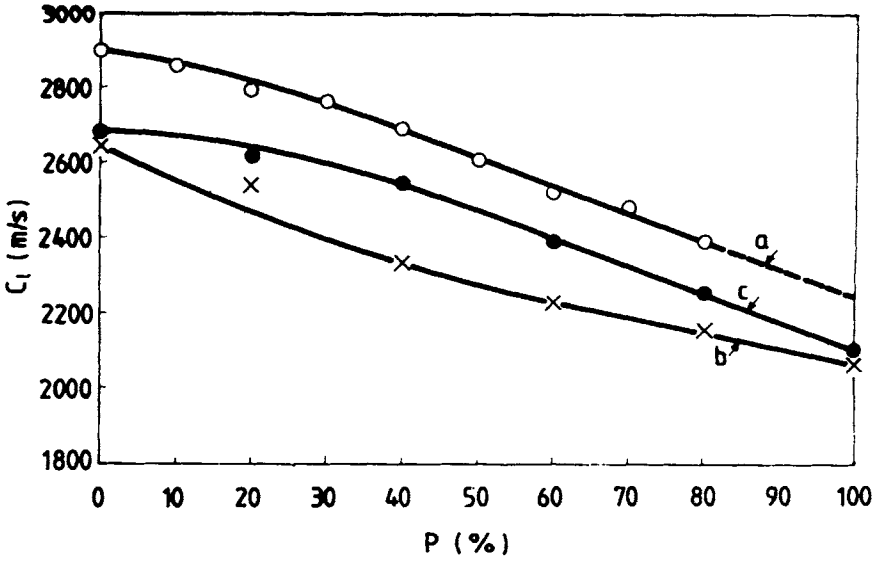

Fig. 2. Variation of longitudinal waves velocity c_l vs. amount p of the plasticizer of the epoxy prepolymer, ranging between 0 and 100% of the amount of the epoxy prepolymer; (○), (x), and (●) indicate results obtained by the old, the new undercure, and the new proper cure specimens, respectively.

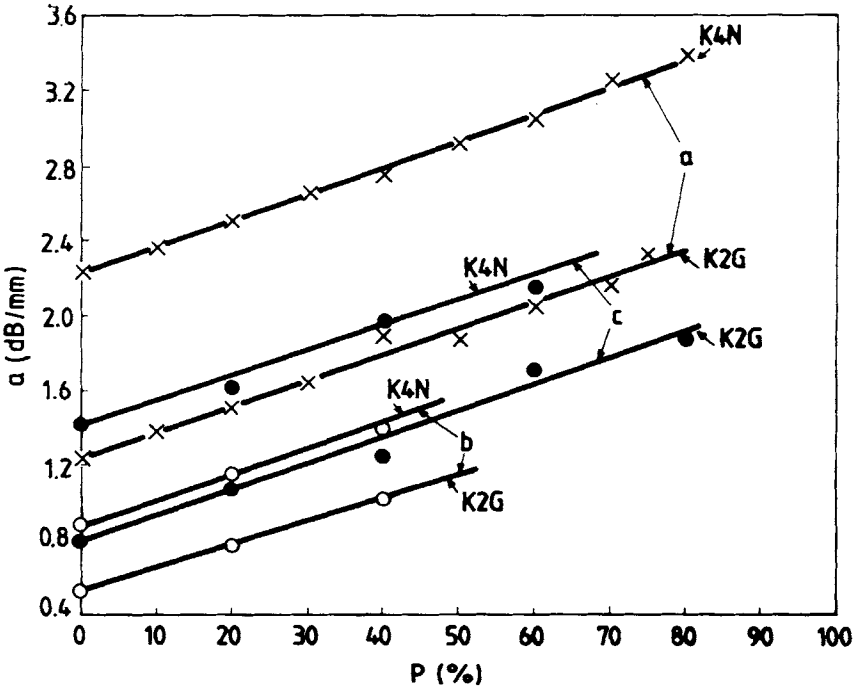

Fig. 3. Variation of acoustic attenuation coefficient α vs. amount p of the plasticizer of the epoxy prepolymer, ranging between 0 and 80% of the amount of the epoxy prepolymer for the wave frequencies 2 and 4 MHz; (a), (b), and (c) indicate results obtained by the old, the new undercure, and the new proper cure specimens, respectively.

TABLE III
Velocity and Attenuation of Longitudinal Waves at 2 and 4 MHz for Undercure and Proper Cure Old Specimens and Density, at Room Temperature, in Various Compositions of Epoxy Polymers

p (%)	ρ (g/cm^3)	c_l (m/s) 2–4 MHz		α (dB/mm)			
				Undercure		Proper cure	
		Undercure	Proper cure	2 MHz	4 MHz	2 MHz	4 MHz
0	1.182	2897	2899	1.180	2.227	1.221	2.218
10	1.194	2856	2854	1.385	2.367	1.295	2.307
20	1.208	2781	2807	1.521	2.522	1.368	2.530
30	1.224	2781	2765	1.655	2.597	1.531	2.578
40	1.243	2686	2675	1.905	2.778	1.802	2.815
50	1.242	2614	2575	1.872	2.923	1.734	2.823
60	1.240	2522	2501	2.042	3.067	2.147	3.014
70	1.238	2485	2477	2.162	3.263	2.257	3.218
80	1.236	2374	2397	2.341	3.387	2.298	3.316

constants were evaluated in the specimens as they were and second the same constants were reevaluated in the same specimens after they had been submitted in the 7 days appropriate curing thermal program, as it was applied in the new specimens of the present paper. The obtained results are presented in Table III.

Figure 2 presents the variation of the velocity c_l of the longitudinal waves vs. the percentage p of plasticizer in epoxy polymers, for the following cases:

(a) Old specimens, curve a,
(b) New undercure specimen (5 days age), curve b,
(c) The new proper cured specimens, curve c.

From these curves one observes that, as the polymerization progresses, the velocity c_l increases. Also in the same figure it is observed that while for the undercured specimens curve b is concave upward, on the contrary in the case of properly cured specimens, the corresponding curves a and c are concave downward.

Figure 3 shows the variation of the acoustic attenuation coefficient α vs. the percentage in plasticizer p of epoxy polymers for the following cases:

(a) Old specimens, lines (a),
(b) New undercured specimens (5 days age), lines (b),
(c) New proper cured specimens, lines (c).

From this figure it is seen that, in all cases, the attenuation coefficient α increases monotonically with the increase of plasticizer p, and takes higher values for higher frequencies. Furthermore, from the same figure it can be observed that for the same sound frequency, in the case of old specimens before and after the curing process (lines a) the coefficient α remains un-

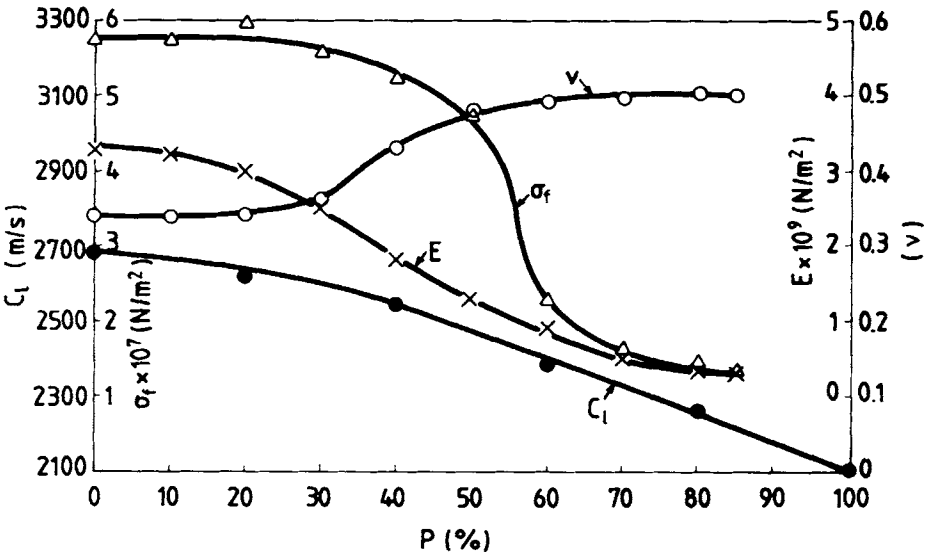

Fig. 4. Variation of longitudinal waves velocity c_l, elastic modulus E, Poisson's ratio ν, and the fracture stress σ_f vs. amount p of plasticizer of epoxy prepolymer, ranging between 0 and 100% of the amount of the epoxy prepolymer.

changed, while in the case of new specimens before and after the curing (lines b and c) the coefficient α changes. That means that as the polymerization progresses the sound attenuation increases. This phenomenon is continued until the polymerization of epoxy polymers is completed. Therefore, in the case of old specimens where the polymerization was over before the curing process, the attenuation does not change with the new curing cycle.

Figure 4 presents the variation of the fracture tensile stress σ_f, the elastic modulus E, and the Poisson's ratio ν of old specimens,[3,4] together with the variation of the velocity c_l of the longitudinal waves of new proper cured specimens, vs. the percentage p of plasticizer of epoxy polymers. It can be observed from this figure that the velocity c_l of the longitudinal waves decreases as the percentage p of the plasticizer in the epoxy polymer increases. From the same figure it can also be seen that the velocity c_l vs. the percentage p decreases in the same way as the fracture tensile stress and the elastic modulus decrease vs. the same quantity.

Comparing the velocity c_l of the longitudinal waves which was evaluated from eqs. (1) and the known elastic constants (Table II), with the corresponding values as they were evaluated experimentally in this work using ultrasonics (Table I), one can observe significant differences. The latest are in accordance with those in the literature.

To investigate the reasons of these differences, the same quantities were evaluated in PMMA-GS-222 and steel specimens, the mechanical and the acoustical properties of which are well known from the relative literature. First from the above materials the appropriate specimens were made for the tension and the ultrasonic tests. Then from the tension test the elastic constants E, ν, and G of these materials were evaluated and afterwards from

these constants and eqs. (1) the velocity c_l was evaluated. The same velocity was also evaluated from the ultrasonic test.

So, for the PMMA-GS-222 specimens the following elastic constants were found: $E = 3.295 \times 10^9$ N/m^2, $\nu = 0.33$, and $G = 0.9924 \times 10^9$ N/m^2 and from these values the corresponding velocity of the longitudinal waves was found equal to $c_l^p = 2026$ m/s.

On the other hand, from the ultrasonic test the same velocity was found equal to $c_l^p = 2730$ m/s. Furthermore, the velocity c_l was evaluated by the same two ways in steel specimens, and from these evaluations there was not observed any significant difference between the resulting two values. This velocity was found equal to $c_l^s = 5920$ m/s. These results agree exactly with those of the corresponding literature. From these measurements one can conclude that, although the ultrasonic method gives results in metals which coincide exactly with the corresponding results computed by the destructive method, the same is not valid for polymers.

This difference seems to be owed to the viscoelastic behavior of the materials. So, in the case of steel where viscoelastic behavior is insignificant for the tension test, the two values of c_l computed either from tension test or ultrasonically are the same. However, in the case of PMMA, which is a strongly viscoelastic material, the elastic constants change during the tension test. So, the velocity c_l^p computed from the elastic constants differ from that evaluated ultrasonically.

In the above way the differences between the values of the velocity c_l in epoxy polymers, computed from the known elastic constants from Refs. 3 and 4 and the corresponding values evaluated ultrasonically in the present experimental work, can be explained.

Returning back to the curves of Figure 4, it is observed that from the velocity of the longitudinal waves one can evaluate quickly, easily, and with great accuracy the percentage p of plasticizer of some epoxy polymer of unknown composition; furthermore, from the same figure one can also evaluate the corresponding elastic constants σ_f, E, and ν, without the necessity of any destructive test.

CONCLUSIONS

The ultrasonic behavior of plasticized epoxy polymers was studied. The used specimens were prepared applying different amounts of plasticizer in epoxy resin. As representative quantities of the ultrasonic behavior, the velocity of the longitudinal waves and the sound attenuation coefficient were considered using pulse–echo measurements. The ultrasonic quantities were correlated with the mechanical quantities as they are presented in Refs. 3 and 4, where the variation of the elastic modulus, the Poisson's ratio, and the fracture tensile stress with the amount of plasticizer of the epoxy polymers were studied.

The variation of the above acoustical (computed here) and mechanical (taken from Refs. 3 and 4) quantities is presented in appropriate diagrams vs. the amount of plasticizer in the epoxy polymers, which ranges between 0 and 100% of the amount of the epoxy prepolymer. It was shown that although the

curves representing the variation of the mechanical properties vs. the amount of plasticizer p are all of a sigmoid type, the corresponding curves representing the variation of the acoustical properties vary monotonically with p.

Also it was shown that the velocity of ultrasonic longitudinal waves propagating in the plasticized epoxy polymers decreases nonlinearly as the percentage p of the plasticizer in the epoxy polymer increases. On the other hand, the attenuation coefficient α increases linearly as the amount of plasticizer p increases. Furthermore, for the examination of the influence of the progress of the polymerization on the acoustical properties of the epoxy polymers, two batches (undercured and properly cured) of specimens were tested. Thus, it was found that, for all compositions of epoxy polymers, as the polymerization progresses, the velocity of the longitudinal waves and the attenuation coefficient both increase.

Finally from the above experimental analysis it follows that because of the fact that the ultrasonic attenuation through the epoxy polymers shows significant dispersion, the determination of the velocity of the longitudinal waves is suggested to be used as more accurate for the study of the polymers. This is very important for another reason too. Since the attenuation takes very high values as the percentage of plasticizer in the epoxy polymers increases, it is impossible to measure this quantity for the used high sound frequencies, when the values of p are greater than 40%. Also since the transverse waves, produced by special probes, show high attenuation when passing through the polymers, the use of this type of waves is very difficult and sometimes impossible for the study of the acoustical behavior of the epoxy polymers.

From all the acoustical properties of epoxy polymers, the velocity of the longitudinal waves is determined more simply and with greater accuracy than the other quantities. With the determination of this velocity in some epoxy polymer of unknown composition, it is possible to find out the corresponding mechanical properties of the same composition. So, evaluating once the velocity c_l in some epoxy polymer specimen, using the results presented in this work, one can evaluate the correct percentage of plasticizer, p, in that specimen, as well as the fracture tensile stress, the Poisson's ratio, and the modulus of elasticity, without the necessity of fracture of the specimen or of some other destructive analysis.

In order to estimate the accuracy of the presented experimental data in this paper, the computed velocity of longitudinal waves, c_l, for each material is compared to the corresponding velocity given in the literature. So, for the used specimens, made from steel and plexiglas, the mean deviation of the velocity c_l was found to be less than 1%, while for the epoxy polymers the mean value of deviation of c_l was found equal to 4.3%. This error is not considered high in our measurements, for the reason that it is not known if the given value in the literature corresponds to exactly the same compositions of epoxy polymers as those of the present paper. This accuracy is considered good enough for our experiments.

Furthermore, I have to observe also the following: The wave velocity or attenuation are material properties that depend on the discrete nature of the internal structure. The internal structure of epoxy polymer may be altered by changes in the raw material resin content. In epoxy polymers microphysical

damage accumulation takes the form of void formation. So, the occurrence of a complex series of events in an initially intact material, at the microstructural level, such as microvoids or microcracks accumulation, degrade structural integrity.

A sound wave propagating in an epoxy polymer is scattered on encountering included voids. Also, in addition to the action of internal defects, during the curing of epoxy polymers, the backwall echo decreases at shorter transit time as a result of increased attenuation and acoustic velocity. All the aforementioned remarks are confirmed by the results presented in the present experimental work.

The NDE of the acoustical and mechanical properties of epoxy polymers is of a great interest in experimental mechanics, where these substances are used as model materials and they can be used to simulate the elastic or viscoelastic behavior of other materials (plastics or metals). This method can be extended to solve various mechanical problems for single or composite materials.

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