

Ultrasonic characterization of conductive epoxy resin/polyaniline composites

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ABSTRACT: This study presents the ultrasonic characterization of conductive epoxy resin (ER)/polyaniline (PANI) composites. The prepared PANI is mixed with ER matrix at weight percentages of 5%, 10%, and 15% for preparing the ER/PANI composites. The effects of PANI amount on the mechanical properties of ER/PANI composites are investigated by ultrasonic pulse-echo-overlap method. Also, electrical conductivity, ultrasonic wave velocity and ultrasonic micro-hardness values of ER/PANI composites are correlated. Experimental results show that there is an excellent correlation between ultrasonic micro-hardness and ultrasonic shear wave velocity. Also, the results of ultrasonic velocities and elastic constants values illustrate that the appropriate combination ratio is 95 : 5 for ER and PANI in ER/PANI composites. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42748.

KEYWORDS: composites; conducting polymers; mechanical properties; properties and characterization

Received 10 November 2014; accepted 19 July 2015

DOI: 10.1002/app.42748

INTRODUCTION

Traditionally, determination of microstructural properties is done by cutting, polishing, grinding, and etching. While mechanical properties are determined by mechanical tests, such as tension tests, Charpy test, Drop weight test, etc.¹ Such destructive tests can provide very useful information, especially relating to the material's design considerations and useful life. The information obtained through destructive testing is quite precise, but can only apply to the specimen being examined. Since the specimen is destroyed or mechanically changed, it is impossible for it to be used for other purposes beyond the mechanical test. Therefore, most of the destructive test specimens cannot be used again once the test is complete. Furthermore, large and expensive equipments are required for many destructive tests.

The development of Nondestructive test (NDT) methods is important from a technical and an economical point of view. Contrary to destructive methods, NDT plays an important role in assuring that structural and mechanical components perform their function in a safe, reliable, and cost-effective manner. There are many advantages of NDT methods. For example: - The tested sample can be used after examination, -Every item or a large portion of the material can be examined without adverse consequences, - Materials can be examined for conditions internal and on the surface, - Parts can be examined while in service, - Many NDT methods are portable and can be taken

to the object to be examined, - Nondestructive testing is cost effective, - Most of NDT methods give quick test results.² Therefore, nondestructive characterization of material properties assumes a great importance during production as well as service life of the sample. Some of the nondestructive testing techniques, which have been used to characterize material properties, are ultrasonic, magnetic-particle, liquid penetrant, radiographic, remote visual inspection (RVI), eddy-current testing, acoustic emission, shearography and Barkhausen noise, etc.³⁻⁵

Ultrasonic waves are mechanical waves that are commonly used in nondestructive ultrasonic testing, which applied to a wide variety of material analysis applications. Ultrasonic testing is one of the most preferred NDT technique for characterization of material properties. Typical measurement parameters of ultrasonic testing include the time of flight, attenuation, scattering, and the change in the frequency spectrum of a wave in a test object, which, with mathematical modeling, provides the means to obtain information about sample geometry and material properties.⁶ The ultrasonic wave velocity and attenuation are most required parameters for the ultrasonic nondestructive characterization or evaluation of materials. These parameters are significantly affected by changes in both microstructural and mechanical properties of materials. With the advancement in electronics and technology, these parameters can be measured very accurately to correlate them with various material properties with a reasonable confidence level.¹ Ultrasonic techniques

are used for thickness gauging, flaw detection, and acoustic imaging, and can also be used to define and quantify mechanical properties, such as density and elastic modulus, and to characterize internal structural features of parts.

Conductive polymers, which offer an alternative to metals and carbon particles, have attracted a particular attention during the last few years. Among them, PANI, which is easy and inexpensive to produce, is environmentally stable and considered as one of the most promising electrically conducting polymers.^{7,8} However, the PANI has some disadvantages like low electrochemical strain, insolubility in most solvents, and infusibility, which make it unsuitable for melting processes,⁹ exhibiting poor physical and mechanical properties. These disadvantages limit its practical applications. Preparation of the PANI composites or blends is proposed as one of the most promising approaches in avoiding these problems. A large amount of PANI/inorganic composites^{10–14} are synthesized and studied to enhance the overall properties in the past few years. It has been reported that the preparing composite system by blending the PANI with raw polymeric materials, improves its mechanical properties,¹⁵ processibility, and also broaden applicability.

Epoxy resin (ER) is one of the most important high-performance polymers in many composites, and adhesives to high-tech applications.^{16,17} One of the way to form new conductive polymer with better mechanical properties is to prepare epoxy/PANI composites by mixing PANI with ER. Because of their increasing engineering applications, ER and ER-based composites are extensively studied in recent year.^{18–23} However, no investigation of the elastic properties of ER/PANI composites by ultrasonic velocity measurement has been reported. Many studies are carried out to increase the conductivity and mechanical properties of PANI-based composites.^{10–14,24–26} Nevertheless, the mechanical properties of these PANI-based composites are investigated by traditional destructive methods such as tensile test, drop test. To our knowledge, ultrasonic study has not been done yet on ER/PANI composites for investigating their mechanical properties. Therefore, measurement of mechanical properties of ER/PANI composites by ultrasonic velocity measurement method in this research is the first in the related literature, which makes this study unique. In conclusion, the main goal of this study is to evaluate the effects of PANI on the mechanical and electrical properties of ER/PANI composites and to figure out their relationships with ultrasonic velocity measurement method.

EXPERIMENTAL

Materials

ER used is the DER321, which is based on diglycidyl ether of bisphenol-A (Dow Chemical Company, USA). It is figured out that the type of hardeners used to cure ER plays a crucial role to obtain a conductive ER/PANI composites.²⁷ Therefore, a cycloaliphatic polyamine called Polyox H043 (Dow Chemical Company, USA) is used as curing agent in this study. The catalyst (2,4,6-tris [dimethylaminomethyl] phenol) is obtained from Sigma-Aldrich, USA. Aniline hydrochloride is supplied from Beijing Wushi Fine Chemicals Company, China, and ammonium

persulphate (APS) is purchased from Merck (Darmstadt, Germany).

Synthesis of PANI

The polyaniline (PANI) is synthesized by chemical oxidative polymerization method by using APS. Aniline hydrochloride is dissolved in 0.04M of ethanol while ammonium persulfate is dissolved in 0.05M of distilled water. The beaker, which has oxidizing solution and monomer solution in it, is placed on a magnetic stirrer at room temperature. After stirring for 24 h a dark green solution is obtained. Thus, emeraldine salt form of PANI is obtained. The solution is filtered through filter paper under vacuum. The PANI deposited on the filter paper is washed repeatedly with 0.2M HCl solution till light color of water poured out. This washing operation is made in order to remove the unreacted monomers. The PANI obtained is dried in an oven at 60°C for one day and it is ground into fine powder which has particle size of <63 μm .

Preparation of ER/PANI Composites

The ER matrix in 95 wt % and PANI in 5 wt % are mixed with mechanical stirring during 3 h at 1200 rpm speed. Afterwards, 30 wt % of Polyox Hardener 043 and 1 wt % of (2,4,6-tris [dimethylaminomethyl] phenol) catalyst are added. The mixture is outgassed in an ultrasonic bath for 1 h at 40°C temperature and then transferred into the stainless steel moulds (20 \times 20 \times 20 mm³). The curing procedure is realized in an oven within 24 h by increasing the temperature from 60°C to 120°C. The ER/PANI composite obtained by ER/PANI addition at 95 : 5 ratio is abbreviated as EPC1. This process is done for ER/PANI addition at 90 : 10 and 85 : 15 ratios as well. The composites, which obtained by ER/PANI addition in ratios of 90 : 10 and 85 : 15 are abbreviated as EPC2 and EPC3, respectively. Only one sample with 20 \times 20 \times 20 mm³ dimensions is obtained for each kind of composites. This size of dimension is useful for figuring out if a sample is isotropic or not.

Measurements

Density and Ultrasonic Wave Velocity Measurements. An analytical balance (Radwag AS220/ C/2, capacity 220 g, readability 0.1 mg, Poland) and a density kit (Radwag 220, Poland) are used to measure the samples' density at room temperature (25°C).

The ultrasonic velocity measurements are carried out by using the pulse-echo-overlap method²⁸ at room temperature. In this method, only one transducer is used to transmit and receive the ultrasonic signals like pulse echo method. The entire received pulse-echo train is first displayed on an oscilloscope; then two echoes are selected and brightened by a delayed strobe generator connected to the z-axis input of the oscilloscope for detailed observation. The horizontal sweeps of the oscilloscope and the ultrasonic pulses are triggered by a continuous wave (CW) sinusoidal signal whose period is approximately equal to the travel time between the two echoes. When the sweep speed, intensity, and the trigger threshold of the oscilloscope are properly adjusted, the two echoes are optically superimposed (overlapped). These two echoes are actually interfering with each other visually on the oscilloscope screen. Because this interference effect is not affected by the amplitude or shape of the

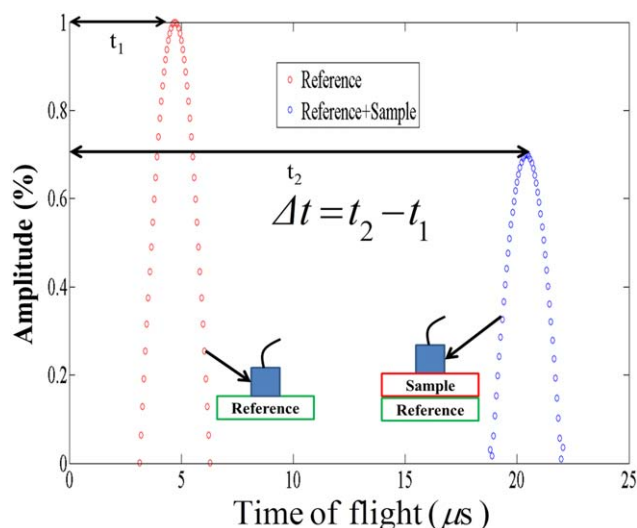


Figure 1. Time of flight measurement technique with pulse-echo-overlap method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

echoes, and also because it is always adjusted to a null-phase-shift condition, the accuracy of the velocity measurement is greatly improved. The proper adjustment of the CW frequency permits a cycle-for-cycle alignment of these two echoes so that the CW period exactly corresponds to the travel time between these two echoes. The phase velocity of the waves can then be calculated. For more precise measurement, a polymethylmethacrylate (PMMA) sample as a reference material is used in this study. The time of flight of first backwall echo for reference sample is determined. The composite sample is put over reference (PMMA sample) sample and the data of first backwall echo for reference + composite samples is determined (Figure 1).

As mentioned above, the time of flight between two measurements is determined by overlapping the first backwall echoes of two measurements. After defining the time of flight between these backwall echoes, the ultrasonic velocity is determined by the equation below:

$$V = \frac{2d}{\Delta t} \quad (1)$$

where d is the sample thickness and Δt is the time interval. The concept of the pulse-echo-overlap method may be regarded as a combination of the delay-line technique and the interferometer technique. More information about the discussion of the possible errors of the absolute-velocity measurement can be found in the study carried out by Papadakis.²⁸

A pulser/receiver generator (5800PR-35 MHz Panametrics Olympus, USA) and a digital oscilloscope (60 MHz GW Instek GDS-2062, Taiwan) are used to measure the ultrasonic velocities. Initially, thickness of samples are measured by an analog micrometer (Sommet, Czechoslovakia). A 20 MHz longitudinal (V116-Panametrics Olympus, USA) and a 5 MHz shear (V155-Panametrics Olympus, USA) contact transducers are used. The coupling medium of the specimens has a profound effect on the ultrasonic velocity measurements.²⁹ Therefore, the glycerin (BQ-

Panametrics Olympus, USA) is used for the longitudinal wave velocity measurements, and shear wave couplant (SWC) (SWC-Panametrics Olympus, USA) is used for the shear wave velocity measurements as the coupling mediums. A constant force is applied to the probe for providing a constant thickness of couplant layer at the probe-specimen interface. The measurements are repeated 10 times to check the reproducibility of the data. The estimated accuracy of measured ultrasonic wave velocity is about 0.1%.

Determination of Elastic Constants. Elastic properties are very informative about the structure of solids and they are directly related to the inter-atomic potentials.³⁰ The pure PANI and ER/PANI composites have amorphous structures.^{31,32} Therefore, the elastic properties of composites are calculated according to the following equations, which are valid for isotropic materials.³³

$$L = \rho V_L^2 \quad (2)$$

$$G = \rho V_s^2 \quad (3)$$

$$K = L - \frac{4}{3}G \quad (4)$$

$$\mu = \frac{L - 2G}{2(L - G)} \quad (5)$$

$$E = 2G(1 + \mu) \quad (6)$$

$$H = \frac{(1 - 2\mu)E}{6(1 + \mu)} \quad (7)$$

$$Z = \rho V_L \quad (8)$$

where V_L , V_s , L , G , K , μ , E , H , Z , and ρ are, respectively, the longitudinal wave velocity, shear wave velocity, longitudinal modulus, shear modulus, bulk modulus, Poisson's ratio, Young's modulus of elasticity, ultrasonic micro-hardness, acoustic impedance, and density of the samples. The estimated accuracy for elastic constants is about 0.2–0.4%, for acoustic impedance is about 0.2% and for Poisson's ratio measurements is about 0.06%.

Conductivity Measurement. Conductivity of composites is measured in the range of 1–10 Volts. Conductivity is measured by means of the standard in-line four point probe method using an Entek FPP-470 instrument, Entek Electronics, Ankara, Turkey. An average of 10 measurements are taken to check the reproducibility of the data.

Scanning Electron Microscopy Analysis. Scanning electron microscopy (SEM) is performed to investigate the interface between ER and PANI (Philips XL30 SFEG, Eindhoven, Netherlands). For SEM examinations, the specimens are sectioned to observe the microstructure through the thickness.

RESULTS AND DISCUSSION

In related literature, PANI is added into polyethylene and polypropylene,^{34–37} polyamide,^{38–42} poly (vinyl alcohol), polycarbonate, poly (methylmethacrylate),^{43–47} rubbers and elastomers,^{48–52} and epoxies^{24–26,32,53–63} at different wt % amounts (1–60 wt %) for obtaining conductive composites, which have better materials properties (Mechanical, electrical, elastic, etc.). It is found that increasing amount of PANI causes an increase in

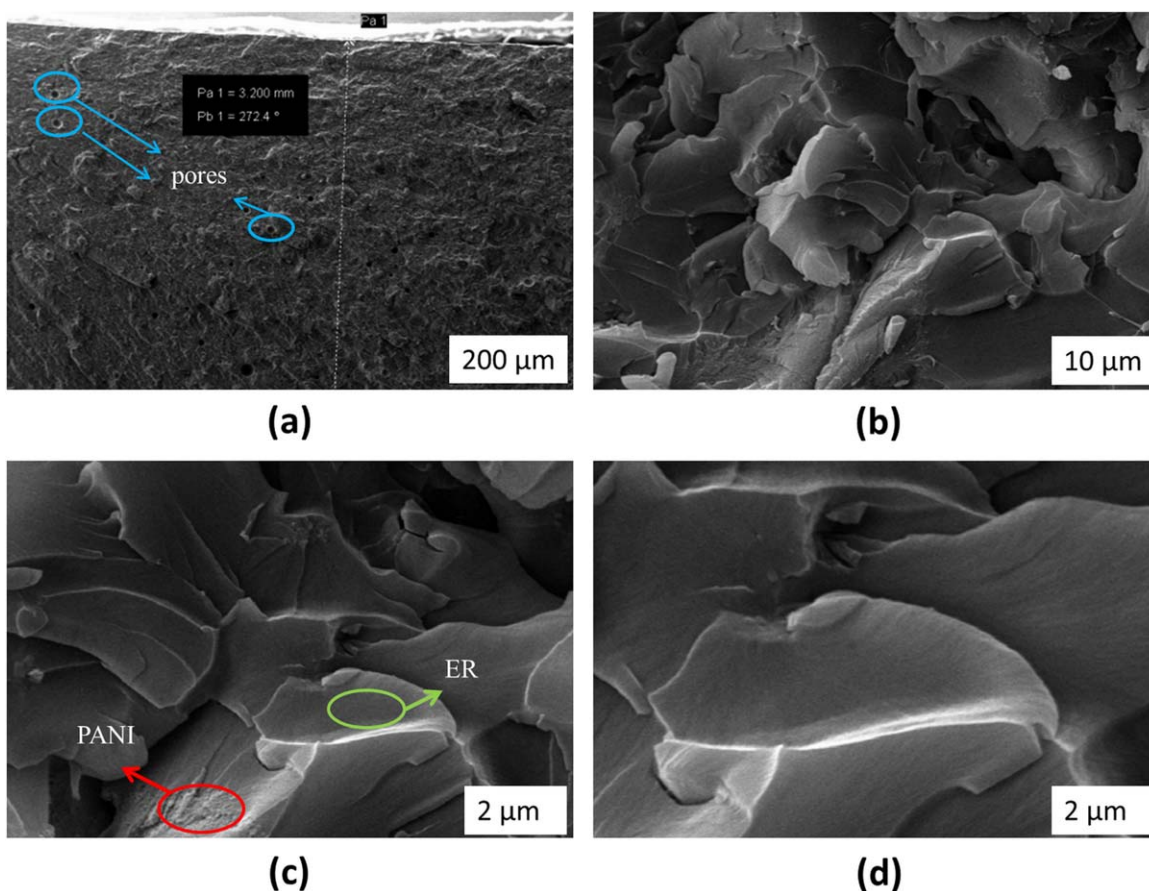


Figure 2. The SEM images of fracture surface of composite with 5% PANI, obtained at different magnifications: (a) 20 X, (b) 1.00 KX, (c) 2.50 KX, (d) 5.00 KX. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conductivity, but meanwhile, after 7 wt % amount of PANI addition, a decrease in mechanical properties occurs. Another interesting result obtained from the related literature is that mechanical properties of PANI composites are only investigated by traditional destructive methods. As it is known that there are many factors (hardener, accelerator, matrix system, temperature, etc), which have important effects on conductivity and mechanical properties of PANI composites. Therefore, this study is only carried out with 5, 10, and 15 wt % concentrations of PANI in ER. And then the mechanical properties of PANI composites are determined by ultrasonic wave velocity measurement method.

The morphology of the composite containing 5 wt % of PANI is shown in Figure 2, reveals the uniform dispersion of PANI in the epoxy matrix. The small quantity of pores observed by naked eyes, are attributed to the inefficient gas releasing during the curing process [Figure 2(a)]. This small quantity of pores and quite small amount of agglomeration of PANI can be seen in Figure 2(c), which is favorable for improving the conductivity and mechanical properties of the composite materials.

There is not a proper phase boundary between the PANI particles and the epoxy matrix (Figure 2). This implies that the PANI particles are well-distributed within the matrix and there

Table I. The Density (ρ) and Ultrasonic Wave Velocities Values of Cured ER and ER/PANI Composites

Sample ID	Composition ratio of ER/PANI (wt %)	ρ (kg/m ³)	V_L (m/s)	V_S (m/s)
ER	100 : 0	1164 ± 0.02	2160 ± 0.1	1048 ± 0.1
EPC1	95 : 5	1178 ± 0.02	2767 ± 0.1	1134 ± 0.1
EPC2	90 : 10	1173 ± 0.02	2762 ± 0.1	1135 ± 0.1
EPC3	85 : 15	1169 ± 0.02	2752 ± 0.1	1104 ± 0.1

V_L : Longitudinal wave velocity, V_S : Shear wave velocity.

Note: The accuracy given in Table I is the percentage [%] uncertainty.

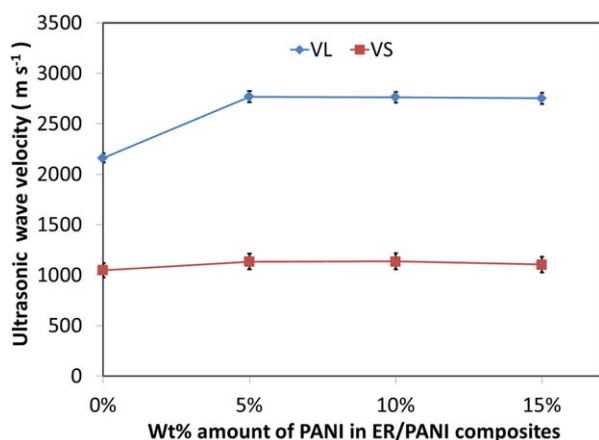


Figure 3. Variation in ultrasonic wave velocities for wt % amount of PANI in ER/PANI composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is a strong interaction between the matrix and the filler. The small agglomeration seems in Figure 2(c), shows that with increasing the loading of PANI from 5 to 10 wt % and from 10 to 15 wt %, the amount of agglomerated PANI may increase.

As it can be seen from the data of Table I, that using different amount of PANI into pure ER has caused an increase in density of cured ER. The densities ranged between 1169 and 1178 kg/m³ for composites of ER/PANI. All the ER/PANI composites' density values are higher than the pure ER's values. The highest density value is found for composite named as EPC1.

Figure 3 shows variation in ultrasonic wave velocity with wt % concentration of PANI. The longitudinal wave velocities ranges between 2752 and 2767 m/s and shear wave velocities ranges between 1104 and 1135 m/s for ER/PANI composites. Both of longitudinal wave velocity and shear wave velocity values of ER/PANI composites are higher than pure ER. Mixing of PANI with pure ER has caused a significant increase for V_L and V_S values, especially for PANI addition in 5 wt %. But increasing the amount of PANI in pure ER from 5 to 10 wt % or from 10 to 15 wt %, the V_L and V_S values have decreased slightly. This can be attributed to the increasing of volume fraction of PANI particles. When the ultrasonic waves start to interact with the particles of PANI more extensively, may increase the scattering of ultrasonic waves. Because of this reason, the wave takes longer time to transfer through the composite sample and thus the ultrasonic velocity decreases. Furthermore, the differences in sound velocity have showed the same behavior of densities (Table I). It shows that there is a strong relationship between ultrasonic wave velocities and materials' densities.

The conductivity of the ER increases with the increase in PANI concentration from value of 1.03×10^{-14} to 3.02×10^{-3} S cm⁻¹ for 15 wt % PANI concentration. This behavior is attributed to the formation of conducting channels by the distribution of PANI particles inside the epoxy matrix. For smaller concentrations of PANI, the conductivity remains low. For example, the conductivity of pure ER is increased from 1.03×10^{-14} to 7.04×10^{-4} S cm⁻¹ at 5 wt % PANI loading, from

Table II. The Electrical Conductivity Values of Cured ER and ER/PANI Composites

Sample ID	Composition ratio of ER/PANI (wt %)	Electrical conductivity (S cm ⁻¹)
PANI	0 : 100	59.00×10^{-2}
ER	100 : 0	1.03×10^{-14}
EPC1	95 : 5	7.04×10^{-4}
EPC2	90 : 10	2.10×10^{-3}
EPC3	85 : 15	3.02×10^{-3}

1.03×10^{-14} to 2.10×10^{-3} S cm⁻¹ at 10 wt % PANI loading. The highest value for electrical conductivity is observed for EPC3 composite, which is prepared by 15 wt % PANI loading (see Table II and Figure 4).

The PANI is generally classified into two types, emeraldine base and emeraldine salt. Emeraldine base is the nonconductive form of PANI which is blue in color, is generally doped with hydrochloric acid (HCL) in order to obtain PANI emeraldine salt that has a dark green color. The dark green colored emeraldine salt form of PANI has conductivity on a semiconductor level of the order of 10^0 S cm⁻¹, which is many orders of magnitude higher in comparison to common polymers ($<10^{-9}$ S cm⁻¹) but much lower than typical metals ($> 10^4$ S cm⁻¹).⁶⁰

The conductivity has increased by increasing the amount of PANI in ER/PANI composites (Figure 4). The lowest concentration of filler at which conductive composites can be formed is known as the percolation threshold. When an adhesive is loaded with a critical or higher concentration of conductive filler, the transition of the composite adhesive is observed from insulator to electrical conductor.³² The composite containing 5 wt % percolation concentration of PANI is at the semiconductive level. The conductivity of ER is risen up to 15 wt % PANI concentration and changes in the range of 7.04×10^{-4} – 3.02×10^{-3} S cm⁻¹. It is clear that the conductivity of pure ER is about 10^{-14} (S cm⁻¹), which shows that conductivity of pure ER is at the nonconductive level.

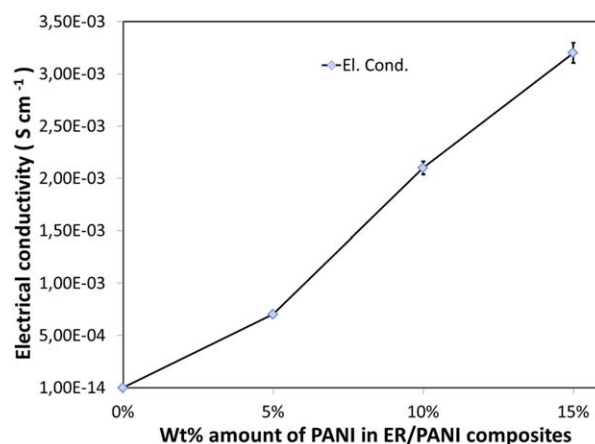


Figure 4. Variation in conductivity for wt % amount of PANI in ER/PANI composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

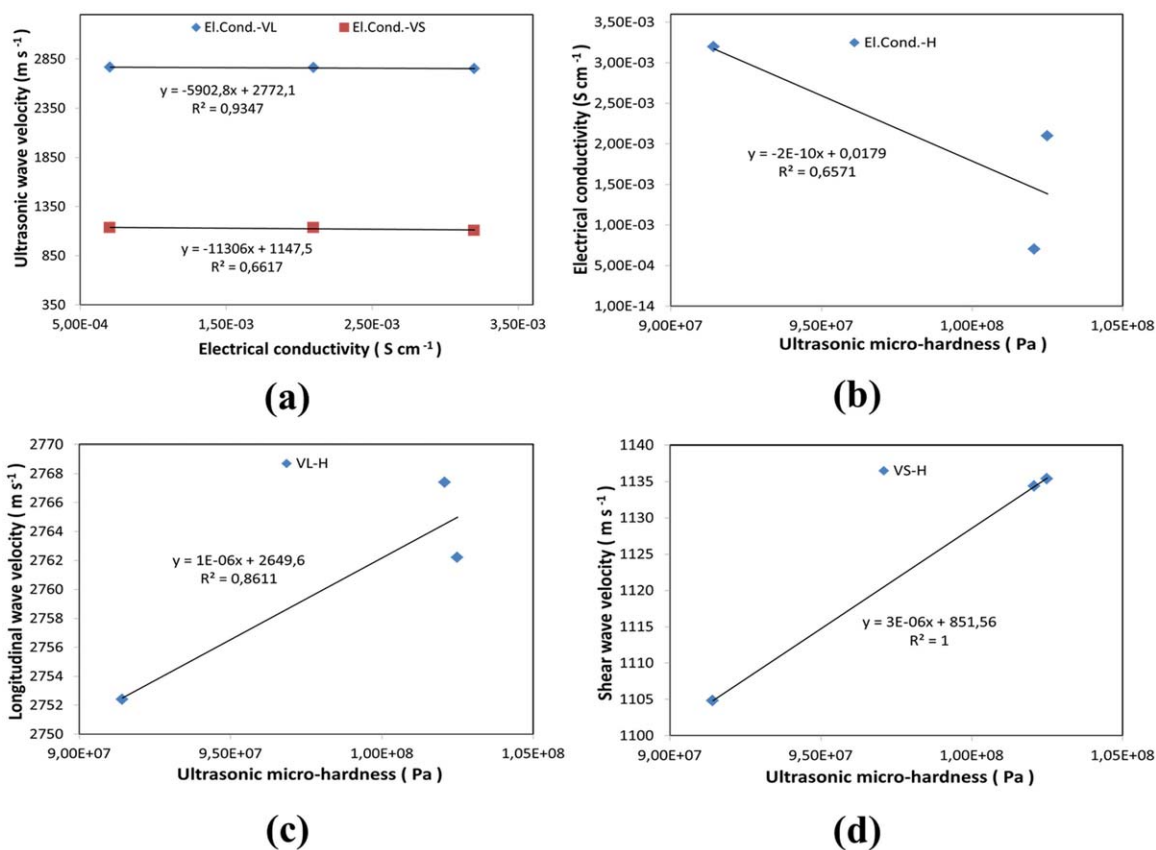


Figure 5. Correlation of conductivity, ultrasonic wave velocities (V_L, V_S), and microhardness: (a) Conductivity- ultrasonic wave velocities, (b) Conductivity-micro hardness, (c) Longitudinal wave velocity-micro hardness, (d) Shear wave velocity-micro hardness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, the conductivity of ER/PANI composites has reached to about semiconductors' conductivity level by increasing the amount of PANI in ER/PANI composites. Similar trend in electrical conductivity with wt % PANI concentrations is also reported earlier.^{25,57} On the other hand, the different values of maximum conductivity are obtained in literature.^{25,54,64} For example, Yang *et al.*²⁵ have obtained maximum conductivity as 10^{-5} S cm⁻¹ at 7.5 wt % of PANI, Jang *et al.*⁵⁴ have obtained maximum conductivity as 10^{-3} S cm⁻¹ at 20 wt % of PANI and Moreira *et al.*⁶⁴ have obtained maximum conductivity as 10^{-8} S cm⁻¹ at 30 wt % of PANI.

As it can be seen in Figure 4, the maximum conductivity is obtained as 3.02×10^{-3} S cm⁻¹ at 15 wt % of PANI and also the conductivity of ER/PANI is obtained as 7.04×10^{-4} S cm⁻¹ at 5 wt % of PANI. The results of research show that matrix (DER321 type of ER, which is based on diglycidyl ether of bisphenol-A), hardener (cycloaliphatic polyamine called Poly-pox H043), and catalyst (2,4,6-tris [dimethylaminomethyl] phenol) are compatible with each other for forming conductive ER/PANI composites.

Figure 5 illustrates the relationship of ultrasonic wave velocity with electrical conductivity, ultrasonic micro-hardness with electrical conductivity and ultrasonic wave velocities (V_L, V_S). The linear reverse correlation between electrical conductivity and

ultrasonic wave velocities (V_L, V_S) is existed [Figure 5(a)]. The correlation coefficient R^2 of about 0.93 is obtained between longitudinal wave velocity and electrical conductivity of ER/PANI composites. On the other hand, the correlation coefficient R^2 of about 0.66 is obtained between shear wave velocity and electrical conductivity of ER/PANI composites. Meanwhile, the correlation coefficient R^2 of about 0.65 is obtained between electrical conductivity and ultrasonic micro-hardness of ER/PANI composites. The analysis of results suggests that correlation between ultrasonic longitudinal wave velocity and electrical conductivity is higher than any other parameters.

Linear regression curve shows a reverse correlation between electrical conductivity and ultrasonic micro-hardness [Figure 5(b)]. From Figure 5(b), it is clearly seen that the relatively weak relationship exists among hardness and electrical conductivity (R^2 of about 0.65). It is observed that towards the highest values of hardness, the electrical conductivity shows rapid increase without any appreciable increase in hardness. Linear relationship of hardness with correlation coefficient of 0.86 is calculated for longitudinal wave velocity [Figure 5(c)] and 1.00 for shear wave velocity [Figure 5(d)]. It is observed that ultrasonic shear wave velocity correlates more perfectly than any other parameters and could be used for hardness prediction with reasonable accuracy and high confidence level.

Table III. The Elastic Properties Values of Cured ER and ER/PANI Composites

Samples' ID	L (GPa)	G (GPa)	K (GPa)	E (GPa)	H (GPa)	μ	Z ($10^6 \text{ kg m}^{-2} \text{ s}^{-1}$)
ER	5.43 ± 0.4	1.27 ± 0.2	3.72 ± 0.4	3.44 ± 0.2	0.131 ± 0.2	0.34 ± 0.06	2.51 ± 0.2
EPC1	9.02 ± 0.4	1.52 ± 0.2	7.00 ± 0.4	4.24 ± 0.2	0.102 ± 0.2	0.39 ± 0.06	3.26 ± 0.2
EPC2	8.95 ± 0.4	1.51 ± 0.2	6.93 ± 0.4	4.23 ± 0.2	0.103 ± 0.2	0.39 ± 0.06	3.24 ± 0.2
EPC3	8.86 ± 0.4	1.43 ± 0.2	6.96 ± 0.4	4.01 ± 0.2	0.091 ± 0.2	0.40 ± 0.06	3.22 ± 0.2

L: Longitudinal Modulus, G: Shear Modulus, K: Bulk Modulus, E: Young's Modulus, H: Ultrasonic Micro-Hardness, μ : Poisson's Ratio, Z: Acoustic Impedance.

Note: The accuracy given in Table III is the percentage [%] uncertainty.

As seen from Table III, the longitudinal modulus values ranges between 5.43 and 9.02 GPa, shear modulus values ranged between 1.27 and 1.52 GPa, bulk modulus values ranges between 3.72 and 7.00 GPa and Young's modulus values ranges between 3.44 and 4.24 GPa for pure ER and composites of ER/PANI. The longitudinal modulus, which defines the resistance to elongation, is related with bonds, which creates the polymer chains between monomers and the shear modulus, which defines the resistance to transverse contraction, is related with bonds between molecular chains.⁶⁵ The enhanced elastic moduli in the ER/PANI with PANI is associated with the formed covalent bonds between epoxy matrix and the amine groups in PANI, which can restrain the movements of the epoxy chains. Compared with the cured epoxy, the improved

elastic moduli of the ER/PANI composites is attributed to the chemical bonds.

As it is seen in Figure 6, a maxima is obtained at 5 wt % of PANI content. It is clear that value of elastic moduli (L , G , K , and E) of ER/PANI composite, which is prepared in ratio of 95 : 5, is higher than that of pure ER and other ER/PANI composites as well. However, the difference in elastic moduli of cured ER and ER/PANI composites is seen as 20% of improved value. After 5 wt % of PANI addition in ER matrix, the longitudinal modulus (L) of ER/PANI composites decreases as the loading increases above 5 wt %. Similar trend is observed for the shear modulus (G), bulk modulus (K), and Young's modulus (E).

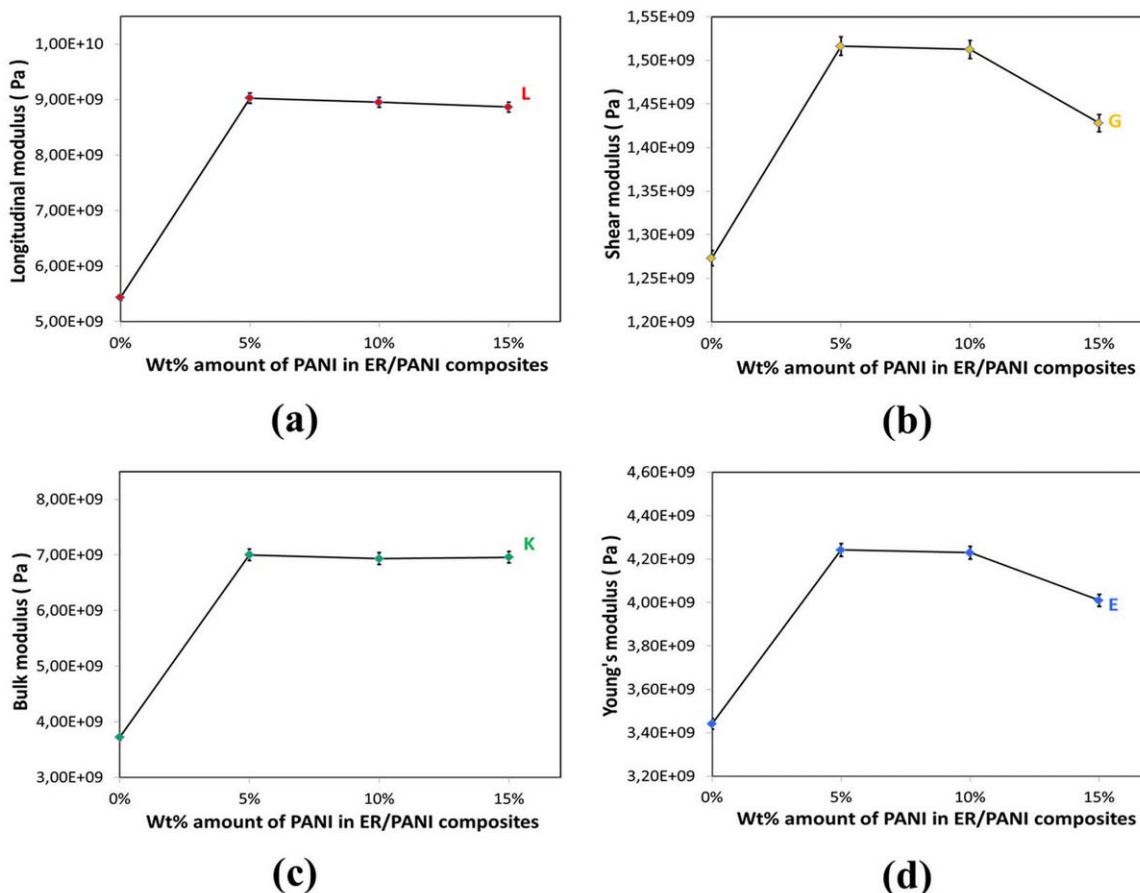


Figure 6. Variation in elastic moduli for wt % amount of PANI in ER/PANI composites: Longitudinal modulus (L), (b) Shear modulus (G), (c) Bulk modulus (K), (d) Young's modulus (E). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

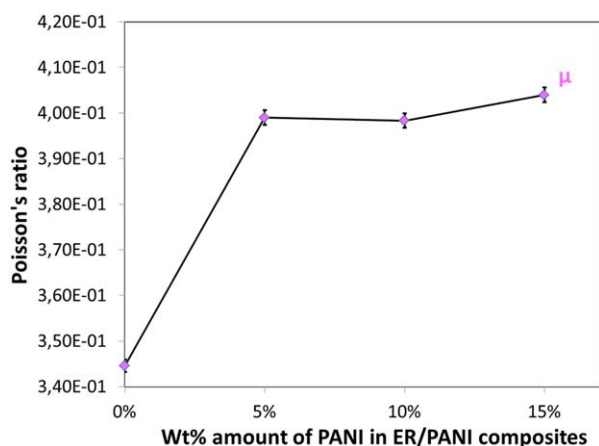


Figure 7. Variation in Poisson's ratio for wt % amount of PANI in ER/PANI composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This decrease in elastic moduli reveals weak two-phase interaction of the ER and PANI. It has been figured out that the introduction of PANI reduces the mechanical properties of EP resin.^{57,59,61} For example, Mir and Kumar⁵⁷ investigated the impact properties of ER/PANI composites as a function of PANI concentration by traditional destructive methods such as drop test and lap shear strength test. They figured out that increasing the amount of PANI in ER/PANI system caused poor impact on properties. This can be because of the polarity difference and pores. Because that the PANI is highly polar and it tends to agglomerate in the nonpolar matrix.⁶⁶ The pores, which is attributed to inefficient gas releasing during the curing process, is shown in the Figure 2(a) and agglomeration of PANI because of the polarity difference, may affect the elastic properties of ER/PANI composites. Therefore, the conclusion, related with elastic moduli behavior after 5 wt % of PANI concentration in ER/PANI composites, is in agreement with the results reported before.^{57,59,61}

The changes in Poisson's ratio for ER/PANI composites with varying PANI weight percent is shown in Figure 7. While Poisson's value is 0.34 for pure ER, the values of Poisson's ratio of the composites of ER/PANI range between 0.39 and 0.40.

From Figure 7, it can be seen that Poisson's ratio increases with increasing in the percentage of PANI from 0 to 5 wt %. When the amount of PANI increases from 5 wt % to 10 wt %, a big change is not seen in Poisson's ratio and then it increases again when PANI amount reaches to 15 wt %. Poisson's ratio is formally defined, for any structure, as the ratio of lateral to longitudinal strain, produced when tensile forces are applied,⁶⁷ is reported to provide more information about the character of the bonding forces than any of the other elastic coefficients.^{68–71} It has been reported that Poisson's ratio decreased with increasing Young's and shear moduli, and it is maximal when elastic moduli is minimal.⁶⁹ Therefore, the decrease in elastic moduli and increase in Poisson's ratio are in good agreement in this study.

The Figure 8 illustrates the acoustic impedances of ER/PANI composites as a function of PANI. Each material is given a factor that is used to calculate reflectivity at an interface. This fac-

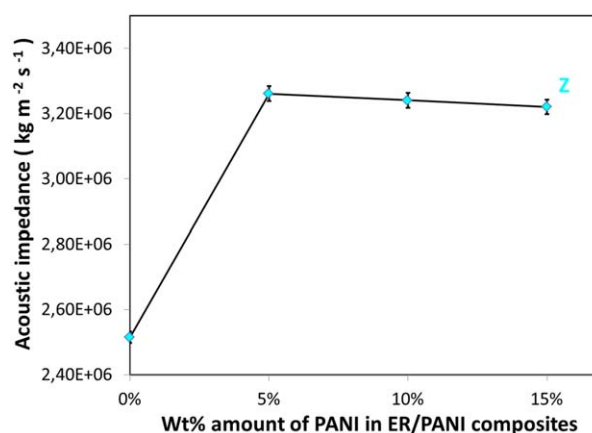


Figure 8. Variation in acoustic impedances for wt % amount of PANI in ER/PANI composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tor is called the “acoustic impedance (Z)”². The acoustic impedance values range from 3.22×10^6 to 3.26×10^6 kg m⁻² · s⁻¹ for ER/PANI composites.

It is clear that ER/PANI composites abbreviated as EPC1 have the highest acoustic impedance value (3.26×10^6 kg m⁻² · s⁻¹). The acoustic impedance value of pure ER is measured as 2.51×10^6 kg m⁻² · s⁻¹ and the acoustic impedance values of EPC3, EPC2, and EPC1 composites are measured as 3.22×10^6 , 3.24×10^6 , and 3.26×10^6 kg m⁻² · s⁻¹, respectively. Therefore, the acoustic impedances of the ER/PANI composites are higher than that of pure ER. Because that acoustic impedance is depend on longitudinal wave velocity and density values of composites [see eq. (8)]. The variation in acoustic impedance may be attributed to the change in longitudinal wave velocity and density values of composites.

Hardness is also an important material characteristic, which expresses the stress required to eliminate the free volume of materials. The values of ultrasonic micro-hardness ranges between 0.091 and 0.103 GPa for ER/PANI composites (Figure

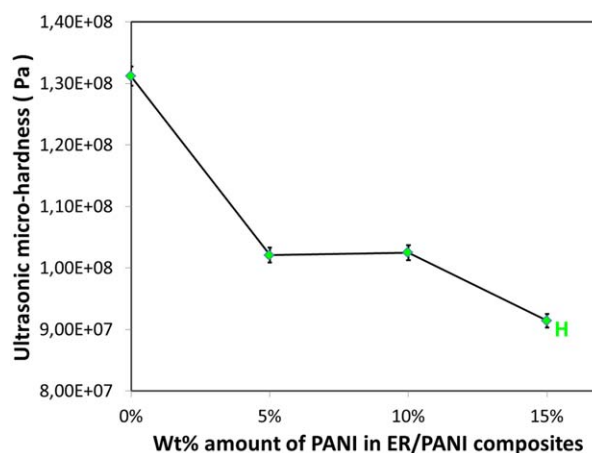


Figure 9. Variation in ultrasonic micro-hardness for wt % amount of PANI in ER/PANI composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

9). The micro-hardness value of pure ER is measured as 0.131 GPa. Therefore, these results show that PANI addition into pure ER has caused a decrease in micro-hardness value.

All ultrasonic velocities and elastic moduli values of composites are higher than that of pure ER. Contrary, as it can be seen from Table III and Figure 9, the micro-hardness value of pure ER is higher than that of the ER/PANI composites. In the region above 5 wt % of PANI, the micro-hardness shows a small increase but after 10 wt % of PANI addition, it is decreased again. Micro-hardness also measures the material's resistance to plastic deformation.² The decrease in hardness of the composites may also be interpreted by the weak intermolecular interaction among composites, which decrease the resistance to plastic deformation. This may be probably attributed to small agglomeration of PANI powder and pores in the composite.

CONCLUSIONS

Based on the experimental results of this study, which is carried out by using ultrasonic pulse-echo-overlap method, the following conclusions can be drawn:

1. With increasing loadings of wt % PANI, conductivities of the composites are increasing linearly and the highest conductivity is observed for EPC3 composite.
2. The highest ultrasonic velocities and elastic constants values are observed for EPC1 composite. So, it can be stated that the appropriate combination ratio for ER and PANI in ER/PANI composites is 95 : 5.
3. The correlation between ultrasonic longitudinal wave velocity and electrical conductivity is higher than any of the other parameters.
4. The ultrasonic shear wave velocity correlates with ultrasonic micro-hardness more perfectly than any other parameters and can be used for hardness prediction with reasonable accuracy and high confidence level.
5. The obtained results display that the ultrasonic pulse echo overlap method is useful for evaluating the elastic properties of ER/PANI composites.

ACKNOWLEDGMENTS

This study was supported by The Scientific and Technological Research Council of Turkey (TUBITAK) within the International Postdoctoral Research Scholarship Programme (2219/2014-1/1059B191400765) and Konya Necmettin Erbakan University. The author is grateful for the support provided by TUBITAK and Konya Necmettin Erbakan University, Turkey.

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