Ultrasonic Properties of Polystyrene-Based Composites

Imran Oral,[1] Hatice Guzel,[1] Gulnare Ahmetli[2]

[1]*Department of Physics Education, Selcuk University, 42090 Konya, Turkey*
[2]*Department of Chemical Engineering, Selcuk University, 42031 Konya, Turkey*

Received 26 February 2011; accepted 17 May 2011
DOI 10.1002/app.34926
Published online 7 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, first the pure polystyrenes (PS) with different molecular weights (350×10^3 and 500×10^3) have been modified by the chemical modification with succinic anhydride (SA), maleic anhydride (MA), and phthalic anhydride (PhA) and then the polystyrene based composites (CPS) prepared by addition of modified polystyrenes (MPS) into pure PS (with the molecular weight of 230×10^3) in weight % ratios of 90 : 10, 80 : 20, and 70 : 30. Ultrasonic measurements were performed on PS/MPS blends of different weight percent of MPSs by use of pulse echo method with 5-MHz frequency at room temperature. Elastic properties namely; longitudinal modulus (L), Young's modulus (E), bulk modulus (K) and shear modulus (G), Poisson's ratio (μ), and acoustic impedance (Z) were calculated from the ultrasonic velocities values measured and densities values obtained experimentally. Atomic force microscopy (AFM) has been used for determining the microstructure of composites. The variations of these parameters with increasing MPSs weight percentage content in PS/MPS from 10 to 30 have been discussed. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1226–1237, 2012

Key words: polystyrene; composites; ultrasound; elastic properties; compatibility

INTRODUCTION

Modern day structural applications demand materials with a specific set of properties. It is usually impossible to achieve all the required properties using a single material. Hence new materials are fabricated by combining two or three different types of materials. Composite materials are developed by the combination of two or more materials which have superior properties than the individual constituents. Some of the primary advantages of composite materials are high strength to weight ratio, high bending stiffness, corrosion resistance, excellent fatigue characteristics (comparable to metals), and good thermal insulation properties. Currently, the primary areas of application of composite materials are aerospace industry, automobile industry, ship building industry and sports equipment.[1]

The blending of polymers offers attractive opportunities for developing new materials with unique property combinations.[2,3] Polymer blending is a widely used technique to improve the physical/mechanical properties of homopolymers. Blending of two polymers may either result in a compatible (miscible) system or incompatible (immiscible) system. The majority of polymers are incompatible.[4–6] It has been increasingly recognized that the interfacial adhesion and morphology control in multiphase polymer blends play an important role in their overall performance.[7] Development of newer properties depends on the degree of compatibility of the polymers at the molecular level. Methods of determining the degree of compatibility of polymeric blends have been reported, both theoretically and experimentally.[8–10] There have been various techniques, such as heat of mixing, glass transition temperature, morphology, dynamic mechanical studies, and ultrasonic testing, for studying the compatibility of the polymer blend. More recently, the use of ultrasonic waves has shown a great potential also as a method for the characterization of materials, especially polymers and composites of polymer.[11–21]

Sound generated above the human hearing range (typically 20 kHz) is called ultrasound. However, the frequency range normally employed in ultrasonic nondestructive testing and thickness gaging is 100 kHz to 50 MHz. Although ultrasound behaves in a similar manner to audible sound, it has a much shorter wavelength. This means it can be reflected off very small surfaces such as defects inside materials.[22] It is this property that makes ultrasound useful for nondestructive testing of materials.

Characterization of mechanical properties of polymer materials using acoustics dates back to the late 1940s whereby A.W. Nolle was one of the first authors to discuss in detail the propagation of sound

Correspondence to: Dr. I. Oral (oralimran@selcuk.edu.tr).
Contract grant sponsor: Scientific Research Projects (BAP) Coordinating Office of Selcuk University; contract grant number: 08101027.
Contract grant sponsor: Selcuk University, Turkey.

waves in rubber materials and also provide a solution to the wave equation taking into consideration damping of waves in polymers. It has been well documented that by using longitudinal and shear wave propagation techniques the corresponding complex dynamic modulus of polymers may be determined. Considering the large amount of literature published over the last 50 years, it may seem surprising that research in this field still remains very important.[23,24]

The simple measurements of ultrasonic velocity reveal various aspects of the compatibility of polymer blends in both highly viscous and solid form. Ultrasonic wave propagation for polymer characterization is a fast, nondestructive, and noninvasive technique based on low-intensity ultrasound. The advantage of using ultrasound velocity measurements for investigating polymer compatibility has been shown by many workers.[25–39] Ultrasound as a non-destructive testing technique is normally associated with the detection of defects, cracking, pores etc. Acoustic techniques are also well suited for determining the effective values of elastic and viscous coefficients for polymer materials. Therefore, establishing a relationship between the microstructural and ultrasonic evaluation results could be very useful for improving the process parameters and controlling the quality of the products.

The most frequent application of ultrasonics to material property measurement involves the study of elastic constants and related strength properties. The ultrasonic testing has been widely used by many researchers for the determination of mechanical properties of the polymers.[30–37] Ultrasound is routinely used also in medical imaging and diagnostics, and it is finding increasing use in the food industry for both analysis and process monitoring.[40–42] According to physical acoustics theory, the elastic behavior of solids can be determined by measurements of ultrasonic wave velocity.[43]

In general no standard parameters are employed to describe the material properties using ultrasound. For example several authors just use sound velocity and attenuation[24] to describe the elastic modulus whereas others prefer the longitudinal modulus, real part of the complex Poisson's ratio,[44–46] phase and group velocities,[47,48] relaxation times,[49,50] attenuation per wavelength,[51,52] real and imaginary part of the complex modulus[53–56] and tan δ [tan δ is defined as the ratio of the energy dissipated per cycle to the maximum potential energy stored during a cycle].[57] It is interesting to note from the publishing years that up to the present day this wide distribution concerning the choice of acoustic parameters employed still exists. For example Kumar et al.[58] had stated that the Poisson's ratio decreases with increase in the elastic modulus and ultrasonic velocities for various solid isotropic materials. They stated that ultrasonic shear wave velocity is a better parameter for materials characterization as compared to longitudinal wave velocity. Therefore they stated that Poisson's ratio provides more information about the character of the bonding forces than any of the other elastic constants.[59]

In the first part of this study the physical properties of modified polystyrenes (MPS) had been evaluated by ultrasonic pulse echo method. In the first part of this study, our aim was to improve the physical properties of pure polystyrene (PS) by modifying it with some organic anhydrides. It was seen that this process improved the properties of PS. Modified PSs were found to have higher mechanical and elasticity properties than PS had and they were more durable against impact.[60] But because that this process was an expensive way, as continue of the first part of the study, this study was done. Therefore the aim of this study is to improve the physical properties of PS by a more economical way. For this aim, the PS based composites produced by addition of MPS into PS at 90 : 10, 80 : 20, and 70 : 30 wt % ratios and then the ultrasonic velocity of longitudinal waves and shear waves in the composites of PS/MPS using ultrasonic pulse echo method, were measured. Longitudinal modulus, shear modulus, Young's modulus, bulk modulus, Poisson's ratio and acoustic impedance of the PS based composites using the obtained velocity and density values of the PS based composites, have been calculated.

EXPERIMENTAL

Materials

PSs with different molecular weights (PS_{500}: the pure polystyrene with molecular weight of 500×10^3; PS_{350}: the pure polystyrene with molecular weight of 350×10^3; PS_{230}: the pure polystyrene with molecular weight of 230×10^3), succinic anhydride (SA), maleic anhydride (MA), phthalic anhydride (PhA), chloroform as solvent, methanol as precipitator and cationic catalyst $BF_3.O(C_2H_5)_2$ were purchased from Merck (Darmstadt, Germany).

Synthesis of modified polystyrenes (MPS)

A reactor consisting of a mixer, cooler, and thermometer was used in the experiment. For modifiying the PS_{500}, first 7,8 g of SA (20 % of the polymer amount) was added to the solution of 39 g PS in 300 mL chloroform ($CHCl_3$) by mixing. After anhydride was dissolved completely, 10 mL $BF_3.O(C_2H_5)_2$ was added drop by drop and was stirred for 3 h at 25°C to end the reaction. The mixture was poured into a beaker. Modified PS (MPS) was precipitated by

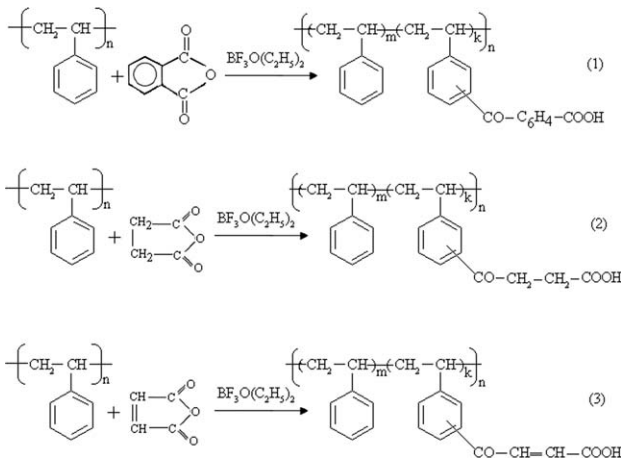

Figure 1 The modification reaction of PS with various organic anhydrides (1: with PhA, 2: with SA and 3: with MA).

methanol (500 mL) from the reaction mixture, filtered and dried under vacuum at 60°C for 5 h. So the modified PS_{500} with SA called SAI was obtained. The chemical modifications of other PS_{500} samples with MA and PhA in the presence of the catalyst $BF_3.O(C_2H_5)_2$ were examined with the same procedure. The other modified PS_{500} with MA called MAI and with PhA called PhAI were obtained too.

The chemical modifications of PS_{350} samples with SA, MA, and PhA in the presence of the catalyst $BF_3.O(C_2H_5)_2$ were examined with the same procedure too. The modified PS_{350} called SAII, MAII, and PhAII were obtained. The modification reactions of PS with various organic anhydrides (PhA, SA and MA) are given in Figure 1.

Preparation of polystyrene-based composites (CPS)

After obtaining all of the MPSs (SAI, SAII, MAI, MAII, PhAI, and PhAII), the polystyrene-based composites (CPS) were produced according this procedure: first 6,5 g of SAI (10 wt % of the pure PS) was added to the solution of 65 g PS_{230} in 300 mL chloroform ($CHCl_3$) by mixing for 2 h at 25°C. Afterward MPS (SAI) was dissolved completely. The mixture was poured into a beaker. The composite of PS that obtained was precipitated by methanol (500 mL) from the reaction mixture, filtered, and dried under vacuum at 60°C for 5 h. So the composite of PS/SAI whose rate is 90 : 10 was obtained. By the same way the other composites of PS with SAI were produced at the wt % ratios of 80 : 20 and 70 : 30 too. On the other hand by the same procedure, the composites of PS/MAI, PS/PhAI, PS/SAII, PS/MAII, and PS/PhAII were prepared too.

All samples of composites were obtained, were melted at the same temperature of 180–200°C during three minutes in a molding machine and then all samples of composites melted were poured into the molds of steel by seven atmosphere pressure. The mold is cooled constantly to a temperature that allows the composites to be cool to the touch. So all composites were obtained by this process. The composition rates of composites were given in Table I.

Measurements

Density measurements

The density of the composites was measured using Archimedes' principle with doubly distilled water as the liquid medium[61] by an analytical balance (Radwag AS220/C/2, capacity 220 g, readability 0.1 mg, Poland) and a kit of density (Radwag 220, Poland). First, the temperature of the room inserted into the balance; next, the mass of the samples were measured in air and in water, and finally, the densities of the samples were measured by the balance automatically. The percentage error was 0.001% for the density measurements of the samples.

Ultrasonic velocity measurements

The ultrasonic wave velocities measurements were done by pulse echo method at room temperature. The ultrasonic pulses are provided by a 5800PR (35 MHz Panametrics Olympus, USA) generator. An electrical impulse with high amplitude and short duration excites the piezoelectrical transducer vibrating on the fundamental mode through the sample, and after reflections on the opposite face returns to the transducer. After propagation in the material, the output signal is displayed on the screen of a numerical oscilloscope (60 MHz GW Instek GDS–2062, Taiwan). A 5 MHz (V109- Panametrics Olympus, USA) longitudinal and 5 MHz shear (V155- Panametrics Olympus, USA) contact transducers were used. As the coupling medium, glycerin (BQ - Panametrics Olympus, USA) was used for the longitudinal wave measurements, and shear wave couplant (SWC) (SWC-Panametrics Olympus, USA) for the shear wave measurements. Because that shear waves do not propagate in liquids, it is necessary to use a very viscous couplant as SWC when making measurements with these waves. The thicknesses of the specimens were measured using an analog micrometer and the samples were found to possess plane

TABLE I
The Composition Rates and Amounts of PS_{230}/MPS Components

Components	Composition rate	PS_{230}, g	MPS, g
PS : MPS	90 : 10	65	6.5
PS : MPS	80 : 20	60	12
PS : MPS	70 : 30	55	16.5

parallelism to an accuracy of ±0.002 mm. The knowledge of the transit time through the thickness of the sample allows the determination of the wave velocities by eq. (1)

$$V = \frac{2d}{t} \tag{1}$$

where V, d, and t are the velocity of sound, the thickness of the sample, and the time-of-flight between subsequent backwall signals on the oscilloscope, respectively. The measurements were repeated ten times to check the reproducibility of the data. The accuracy of velocity measurements is about 0.04%.

Calculation of elastic constants

The elastic properties were calculated according to the following formulae.[62–66]

$$L = \rho.V_L^2 \tag{2}$$

$$G = \rho.V_s^2 \tag{3}$$

$$K = L - \frac{4}{3}G \tag{4}$$

$$E = 2G(1 + \mu) \tag{5}$$

$$\mu = \frac{L - 2G}{2(L - G)} \tag{6}$$

$$Z = \rho.V_L \tag{7}$$

where $V_L V_S$, L, G, K, μ, E, Z, and ρ are longitudinal ultrasonic wave velocity, shear ultrasonic wave velocity, longitudinal modulus, shear modulus, bulk modulus, Poisson's ratio, Young's modulus of elasticity, acoustic impedance, and density of the samples, respectively. The estimated accuracy of elastic constants and acoustic impedance is about 0.04% and for Poisson's ratio measurements is about 0.02 %.

Morphological measurements

Atomic Force Microscopy (AFM) is a versatile technique, which can be used for the characterization of the polymer films, polymer–filler interactions, etc. AFM is one of the most important microscopic techniques used for the surface analysis of polymers on a nanometer scale. The added advantage of using AFM is that it can give distinguished surface topography and surface heterogeneity. The morphology of the PS and composites was examined with a Solver P47H atomic force microscope (NT-MTD) (Moscow, Russia) operating in tapping mode in air at room temperature. Diamond-like carbon (DLC) coated NSG01 DLC silicon cantilevers (from NT-MTD) with a 2-nm tip apex curvature were used at the resonance frequency of 150 kHz. The Nova 914 software package was used to control the SPM system and for the analysis of the AFM images.

RESULTS AND DISCUSSION

The experimental data of the ultrasonic velocity of longitudinal wave (V_L) and that of shear wave (V_S), density (ρ), as well as the elastic parameters (L, G, K, E, μ, Z) of composites of the PS/MPS_{500} and PS/MPS_{350} samples for different compositions are tabulated in Tables II and III and Figures 2–17. Also some figures of atomic force microscopy (AFM) that F2-F17 show the microstructure of composites are given in Figure 18.

Density and sound velocity

As seen from Tables II and III, the densities ranged between 1038 and 1054 kg m^{-3} for composites of PS/MPS (SAI, MAI, PhAI) and ranged 1042–1052 kg m^{-3} for the composites of PS/MPS (SAII, MAII, PhAII). The highest density value was found at composite of PS/PhAI at wt. ratio of 80 : 20 for composites of PS/MPS_{500} and at composite of PS/PhAII at wt. ratio of 80 : 20 for composites of PS/MPS_{350} too. It can be seen that the density of PS/SAI composite was decreased with increase in weight percent of SAI from 10 to 30 (Table II). But the density of PS/MAI composite was increased with increase in weight percent of MAI from 10 to 30. Also density of PS/PhAI increase with the increase of PhAI at 90 : 10 and 80 : 20 wt. ratios of compositions and then decreased with increase in weight percent of PhAI from 20 to 30. The addition amount of SAII and PhAII into the PS/SAII and PS/PhAII, respectively, showed a similar behavior of PhAI. Furthermore density of PS/MAII composite was decreased with increase in weight percent of MAII from 10 to 20 and then increased with increase in weight percent of MAII from 20 to 30.

The variation of velocity as a function of composite composition is presented in Tables II and III and Figures 2–5. The variations of V_L and V_S with MPS addition are illustrated in Table II, Figures 2 and 4 for the PS/MPS_{500} composites and in Table III, Figures 3 and 5 for the PS/MPS_{350} composites. Moreover, both longitudinal and shear ultrasonic velocities of PS/MPS_{500}, as shown in Tables II and III and Figures 2–5, are higher then pure PS. V_L and V_S data for pure PS were obtained as 2344 and 1147 m s^{-1}, respectively. The longitudinal ultrasonic velocities of PS/MPS_{500} with the increase in weight percent of MPS_{500} from 10 to 30 are ranged from 2390 to 2409 m s^{-1} and the shear ultrasonic velocities are ranged from 1157 to 1173 m s^{-1}. The longitudinal ultrasonic velocities of PS/MPS_{350} with the increase in weight percent of MPS_{350} from 10 to 30 are ranged from

TABLE II
Variation of Density (ρ), Longitudinal Wave Velocity (V_L), Shear Wave Velocity (V_S), Poisson's Ratio (μ), Longitudinal Modulus (L), Shear Modulus (G), Bulk Modulus (K), Young's Modulus (E), Acoustic Impedance of PS and PS-Based Composites Made with MPS_{500}

Composition in wt %		ρ (kg m^{-3})	V_L (m s^{-1})	V_S (m s^{-1})	μ	L (GPa)	G (GPa)	K (GPa)	E (GPa)	Z (10^6 kg m^{-2} s^{-1})
PS/SAI	100 : 0	1041	2344 ± 0.04	1147 ± 0.04	0.3425 ± 0.01	5.725 ± 0.04	1.371 ± 0.03	3.896 ± 0.04	3.683 ± 0.06	2.442 ± 0.04
	90 : 10	1052	2399 ± 0.03	1159 ± 0.04	0.3475 ± 0.01	6.057 ± 0.04	1.415 ± 0.04	4.169 ± 0.04	3.815 ± 0.06	2.524 ± 0.04
	80 : 20	1047	2403 ± 0.04	1167 ± 0.03	0.3454 ± 0.02	6.048 ± 0.03	1.428 ± 0.03	4.143 ± 0.03	3.844 ± 0.07	2.517 ± 0.03
	70 : 30	1046	2409 ± 0.03	1171 ± 0.04	0.3451 ± 0.02	6.076 ± 0.04	1.436 ± 0.04	4.160 ± 0.03	3.865 ± 0.07	2.521 ± 0.04
PS/MAI	100 : 0	1041	2344 ± 0.04	1147 ± 0.04	0.3425 ± 0.01	5.725 ± 0.04	1.371 ± 0.03	3.896 ± 0.04	3.683 ± 0.06	2.442 ± 0.04
	90 : 10	1038	2404 ± 0.03	1168 ± 0.04	0.3455 ± 0.02	6.002 ± 0.03	1.416 ± 0.03	4.113 ± 0.04	3.812 ± 0.07	2.496 ± 0.03
	80 : 20	1044	2398 ± 0.03	1161 ± 0.03	0.3467 ± 0.01	6.006 ± 0.04	1.409 ± 0.04	4.127 ± 0.03	3.795 ± 0.06	2.504 ± 0.03
	70 : 30	1053	2393 ± 0.04	1157 ± 0.04	0.3473 ± 0.02	6.034 ± 0.03	1.411 ± 0.03	4.152 ± 0.04	3.803 ± 0.07	2.521 ± 0.04
PS/PhAI	100 : 0	1041	2344 ± 0.04	1147 ± 0.04	0.3425 ± 0.01	5.725 ± 0.04	1.371 ± 0.03	3.896 ± 0.04	3.683 ± 0.06	2.442 ± 0.04
	90 : 10	1049	2399 ± 0.03	1173 ± 0.03	0.3428 ± 0.01	6.045 ± 0.04	1.446 ± 0.04	4.116 ± 0.03	3.884 ± 0.07	2.519 ± 0.03
	80 : 20	1054	2394 ± 0.04	1168 ± 0.04	0.3438 ± 0.02	6.044 ± 0.03	1.439 ± 0.03	4.125 ± 0.03	3.867 ± 0.06	2.524 ± 0.03
	70 : 30	1046	2390 ± 0.04	1167 ± 0.03	0.3434 ± 0.01	5.981 ± 0.04	1.426 ± 0.04	4.079 ± 0.04	3.831 ± 0.07	2.501 ± 0.04

SAI, MAI, PhAI.

TABLE III
Variation of Density (ρ), Longitudinal Wave Velocity (V_L), Shear Wave Velocity (V_S), Poisson's Ratio (μ), Longitudinal Modulus (L), Shear Modulus (G), Bulk Modulus (K), Young's Modulus (E), Acoustic Impedance of PS and PS-Based Composites Made with MPS_{350} (SAII, MAII, PhAII)

Composition in wt %		ρ (kg m^{-3})	V_L (m s^{-1})	V_S (m s^{-1})	μ	L (GPa)	G (GPa)	K (GPa)	E (GPa)	Z (10^6 kg m^{-2} s^{-1})
PS/SAII	100 : 0	1041	2344 ± 0.04	1147 ± 0.04	0.3425 ± 0.01	5.725 ± 0.04	1.371 ± 0.03	3.896 ± 0.04	3.683 ± 0.06	2.442 ± 0.04
	90 : 10	1043	2398 ± 0.03	1171 ± 0.03	0.3435 ± 0.02	6.004 ± 0.03	1.431 ± 0,04	4.095 ± 0.04	3.845 ± 0.05	2.502 ± 0.03
	80 : 20	1048	2404 ± 0.04	1176 ± 0.04	0.3427 ± 0.03	6.066 ± 0.04	1.451 ± 0.03	4.131 ± 0.05	3.898 ± 0.07	2.522 ± 0.04
	70 : 30	1044	2407 ± 0.03	1185 ± 0.04	0.3400 ± 0.02	6.055 ± 0.03	1.467 ± 0.02	4.098 ± 0.04	3.934 ± 0.06	2.515 ± 0.04
PS/MAII	100 : 0	1041	2344 ± 0.04	1147 ± 0.04	0.3425 ± 0.01	5.725 ± 0.04	1.371 ± 0.03	3.896 ± 0.04	3.683 ± 0.06	2.442 ± 0.04
	90 : 10	1050	2406 ± 0.05	1168 ± 0.05	0.3457 ± 0.03	6.082 ± 0.04	1.434 ± 0.02	4.169 ± 0.05	3.860 ± 0.06	2.527 ± 0.04
	80 : 20	1042	2395 ± 0.04	1160 ± 0.03	0,3466 ± 0.02	5.983 ± 0.03	1.404 ± 0.03	4.110 ± 0.04	3.783 ± 0.05	2.497 ± 0.03
	70 : 30	1051	2387 ± 0.03	1157 ± 0.04	0.3463 ± 0.03	5.989 ± 0.03	1.408 ± 0.04	4.111 ± 0.05	3.791 ± 0.05	2.508 ± 0.03
PS/PhAII	100 : 0	1041	2344 ± 0.04	1147 ± 0.04	0.3425 ± 0.01	5.725 ± 0.04	1.371 ± 0.03	3.896 ± 0.04	3.683 ± 0.06	2.442 ± 0.04
	90 : 10	1049	2405 ± 0.03	1171 ± 0.03	0.3447 ± 0.02	6.076 ± 0.03	1.440 ± 0.03	4.156 ± 0.05	3.873 ± 0.05	2.525 ± 0.03
	80 : 20	1052	2396 ± 0.04	1164 ± 0.04	0.3456 ± 0.03	6.043 ± 0.04	1.425 ± 0.04	4.142 ± 0.04	3.837 ± 0.06	2.521 ± 0.04
	70 : 30	1046	2388 ± 0.03	1163 ± 0.03	0.3444 ± 0.02	5.971 ± 0.03	1.417 ± 0.03	4.081 ± 0.04	3.810 ± 0.07	2.499 ± 0.04

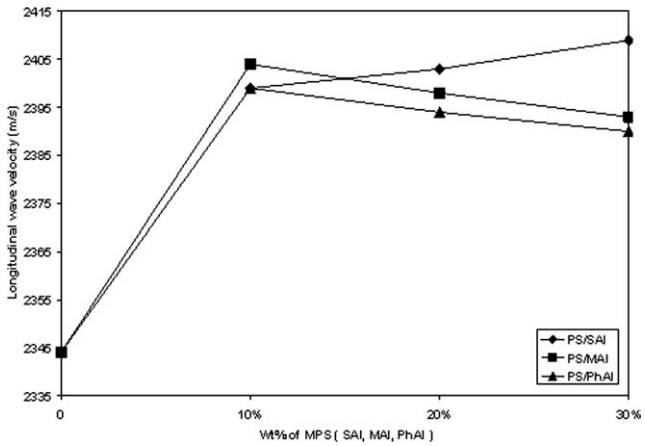

Figure 2 Variation of longitudinal ultrasonic wave velocity with weight percent of MPSs (SAI, MAI, PhAI) in composite of PS/MPS.

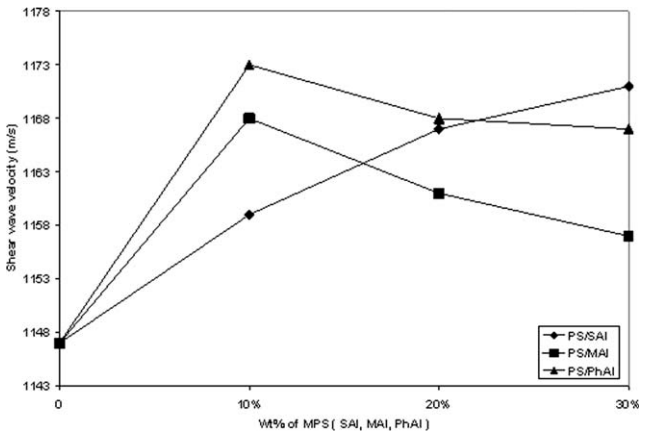

Figure 4 Variation of shear ultrasonic wave velocity with weight percent of MPSs (SAI, MAI, PhAI) in composite of PS/MPS.

2387 to 2407 m s^{-1} and the shear ultrasonic velocities are ranged from 1157 to 1185 m s^{-1}. These experimental results of V_L and V_S for pure PS are in good agreement with the findings of Higazy et al.[66]

As seen in Figures 2–5, it was found a proportional relationship between ultrasonic velocities and composition of SAI and SAII in the range 10–30 wt % of PS/MPS system. It was reported[67–70] in polymeric liquid blends that ultrasound velocity varies linearly with composition in compatible blends. So according to this result it can be stated that composites of PS/SAI and PS/SAII showed a good harmony with each other. Also there is an inversely proportional relationship between ultrasonic velocities and composition of MAI, MAII, PhAI, PhAII in the range 10–30 wt % of PS/MPS system.

Elastic constants

The longitudinal modulus (L), Young's modulus (E), bulk modulus (K), and shear modulus (G) of the PS, PS/MPS_{500} and PS/MPS_{350} were calculated employing eqs. (2)–(5). The calculated values of elastic constants (L, E, K, G) of pure PS and CPSs as a function of weight percent of MPS_{500} (SAI, MAI, PhAI) and MPS_{350} (SAII, MAII, PhAII) are presented in Tables II and III and Figures 6–13.

The values of elastic constants of pure PS and MPS_{500} (SAI, MAI, PhAI) are presented in Table II, Figures 6, 8, 10, and 12. For the PS/SAI composite, the shear and Young's modulus increase with increasing in weight percent of SAI addition from 10 to 30, but longitudinal and bulk moduli decrease with increasing in weight percent of SAI from 10 to 20 and increase again with increasing in weight percent of SAI addition from 20 to 30. For the PS/MAI composite, the shear and Young's modulus increased when 10 wt % MAI was incorporated, decreased when MAI addition was increased from 10 to 20 wt % and increased again when MAI addition was increased from 20 to 30 wt %. The longitudinal and bulk modulus of PS/MAI increased when

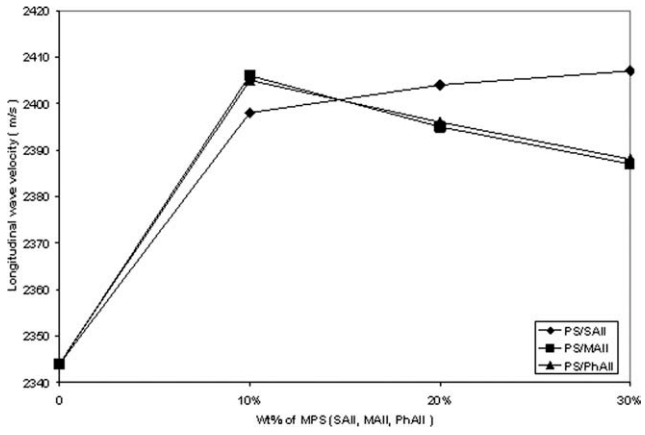

Figure 3 Variation of longitudinal ultrasonic wave velocity with weight percent of MPSs (SAII, MAII, PhAII) in composite of PS/MPS.

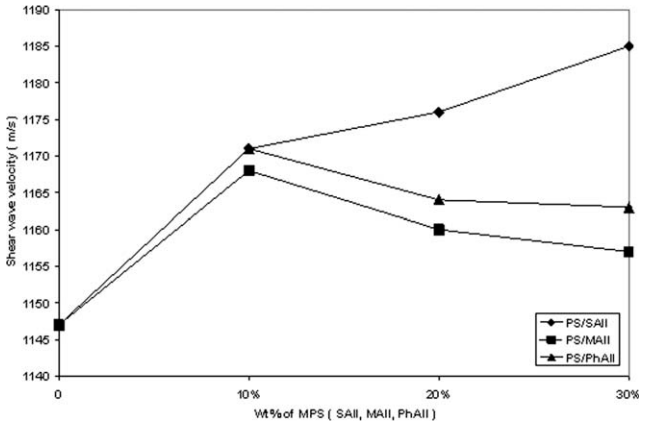

Figure 5 Variation of shear ultrasonic wave velocity with weight percent of MPSs (SAII, MAII, PhAII) in composite of PS/MPS.

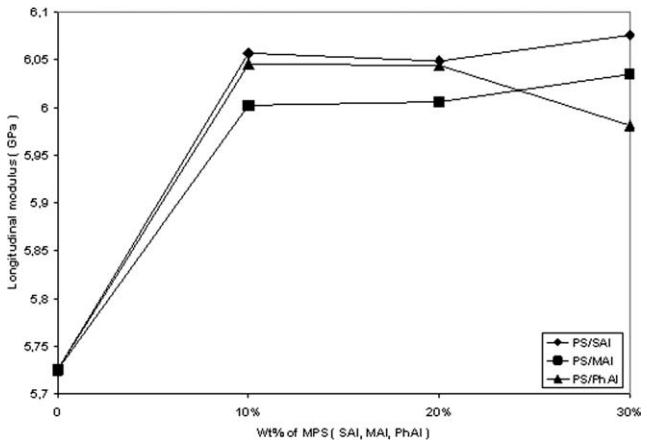

Figure 6 Variation of longitudinal modulus with weight percent of MPSs (SAI, MAI, PhAI) in composite of PS/MPS.

MAI addition was increased from 10 to 30 wt %. For the PS/PhAI composite, the longitudinal, shear, and Young's modulus decreased when PhAI addition was increased from 10 to 30 wt %. The bulk modulus of PS/PhAI increased when 10 wt % PhAI was incorporated, increased when PhAI addition was increased from 10 to 20 wt % and then decreased when PhAI addition was increased from 20 to 30 wt %.

The values of elastic constants of pure PS and MPS_{350} (SAII, MAII, PhAII) are presented in Table III, Figures 7, 9, 11, and 13. For the PS/SAII composite, the shear and Young's modulus increase with increasing in weight percent of SAII addition from 10 to 30, longitudinal and bulk moduli increase with increasing in weight percent of SAII from 10 to 20 and decrease with increasing in weight percent of SAII addition from 20 to 30. For the PS/MAII composite, the longitudinal, shear, bulk, and Young's modulus increased when 10 wt % MAII was incorporated, decreased when MAII addition was increased from 10 to 20 wt % and increased again when MAII addition was increased from 20 to 30 wt %. For the PS/PhAII composite, the longitudinal, shear, bulk and Young's modulus increased when 10 wt % PhAII was incorporated, decreased when PhAII addition was increased from 10 to 30 wt %.

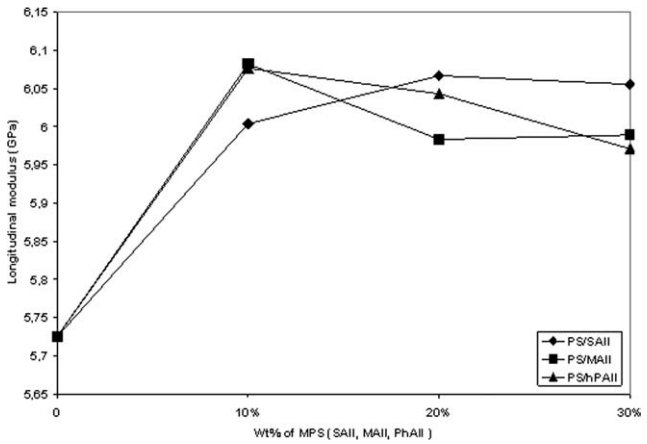

Figure 7 Variation of longitudinal modulus with weight percent of MPSs (SAII, MAII, PhAII) in composite of PS/MPS.

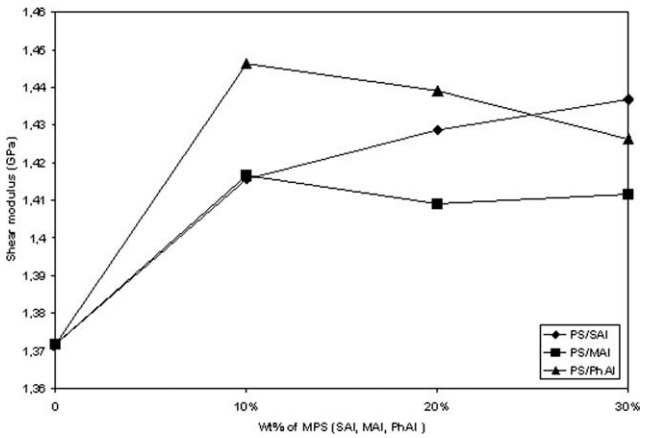

Figure 8 Variation of shear modulus with weight percent of MPSs (SAI, MAI, PhAI) in composite of PS/MPS.

As seen from Table II and Figures 6–13, the values of elastic constants of CPSs are higher then pure PS. For example, longitudinal modulus of PS was measured 5,725 GPa. When SAI added into PS at 10 wt %, it was increased from 5.725 to 6.057 GPa. For samples of PS/MPS_{500} (SAI, MAI, PhAI) composites, longitudinal modulus ranged from 5.981 to 6.076 GPa, shear modulus ranged from 1.409 to 1.446 GPa, bulk modulus from 4.079 to 4.169 GPa and Young's modulus from 3.815 to 3.865 GPa. For samples of PS/MPS_{350} (SAII, MAII, PhAII) composites, longitudinal modulus ranged from 5.971 to 6.082 GPa, shear modulus ranged from 1.404 to 1.467 GPa, bulk modulus from 4.081 to 4.169 GPa and Young's modulus from 3.791 to 3.934 GPa.

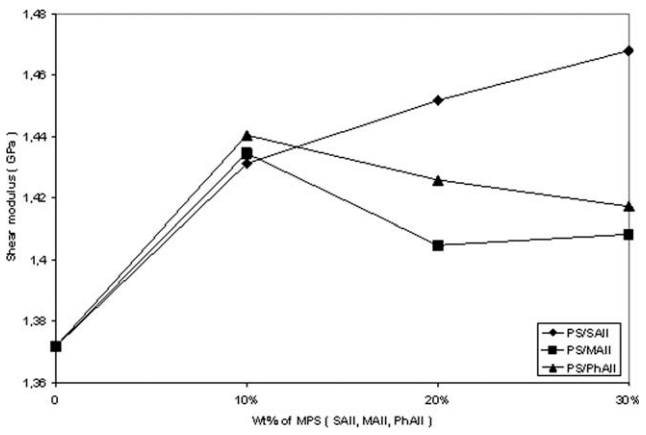

Figure 9 Variation of shear modulus with weight percent of MPSs (SAII, MAII, PhAII) in composite of PS/MPS.

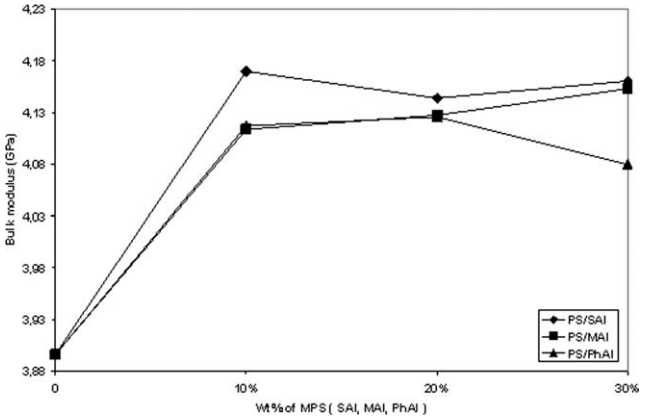

Figure 10 Variation of bulk modulus with weight percent of MPSs (SAI, MAI, PhAI) in composite of PS/MPS.

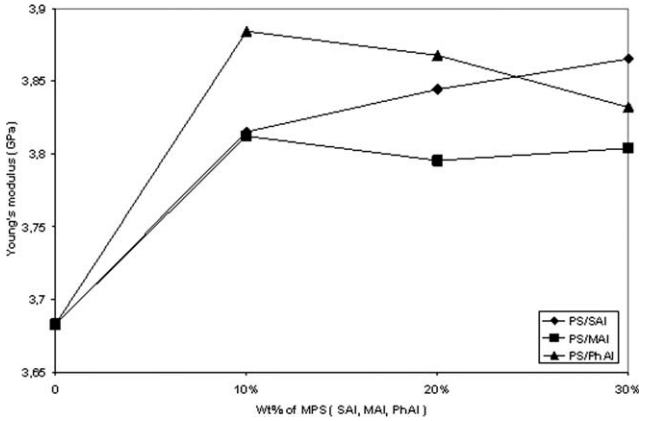

Figure 12 Variation of Young's modulus with weight percent of MPSs (SAI, MAI, PhAI) in composite of PS/MPS.

According to results of Tables II and III and Figures 6–13, the values of *L*, *G*, *K*, and *E* of pure PS are in good agreement with the findings of investigations made before.[66,71,72] When a comparison is made between the elastic properties of the PS/MPS_{500} composites and its corresponding PS/MPS_{350} composites, in generally PS/MPS_{350} composites had higher longitudinal, shear, bulk, and Young's modulus than the PS/MPS_{500} composites.

Poisson's ratio

Poisson's ratio, defined as the lateral contraction per unit breadth divided by the longitudinal extension per unit length in simple tension.[73] Poisson's ratio has been calculated using eq. (6). Figures 14 and 15 illustrate the Poisson's ratio values as a function of the weight percent of MPSs. For PS/MPS (MPS—SAI, MAI, PhAI) composites, it can be seen that the Poisson's ratio decreased from 0.3475 to 0.3428 when SAI, MAI, PhAI contents increased from 10 to 30 wt % (Table II). For PS/MPS (MPS—SAI, MAI, PhAI) composites, Poisson's ratio decreased from 0.3475 to 0.3400 when SAII, MAII, PhAII contents increased from 10 to 30 wt % (Table III). These values of Poisson's ratio of pure PS are close to the related literature results.[71,74] From the results of Tables II and III and Figures 14 and 15, we can obviously notice that the Poisson's ratio decreases as the percentage of SAI, SAII contents in PS/MPS increased from 10 to 30 wt %.

Acoustic impedance

The acoustic impedance of a material is the opposition to displacement of its particles by sound. The boundary between two materials of different acoustic impedances is called an acoustic interface. When sound strikes an acoustic interface at normal incidence, some amount of sound energy is reflected and some amount is transmitted across the boundary. The acoustic impedance of CPSs has been calculated using eq. (7). The acoustic impedance ranged from 2.496 to 2.524 $\times$ 10^6 kg m^{-2} s^{-1} for PS/MPS (MPS—SAI, MAI, PhAI) composites (Table II and

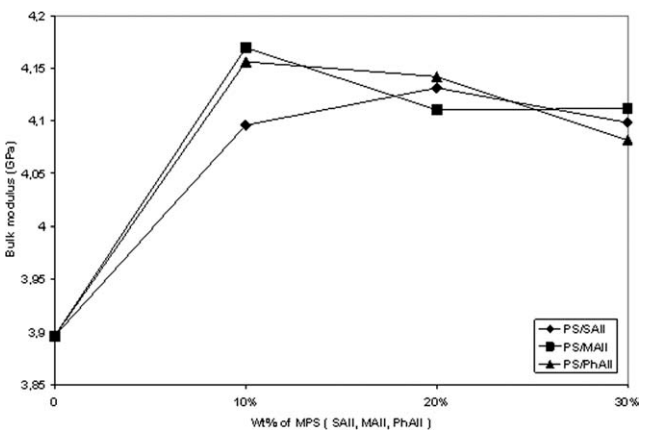

Figure 11 Variation of bulk modulus with weight percent of MPSs (SAII, MAII, PhAII) in composite of PS/MPS.

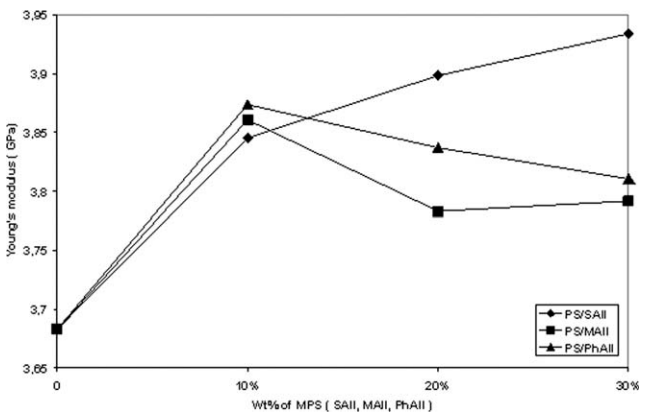

Figure 13 Variation of Young's modulus with weight percent of MPSs (SAII, MAII, PhAII) in composite of PS/MPS.

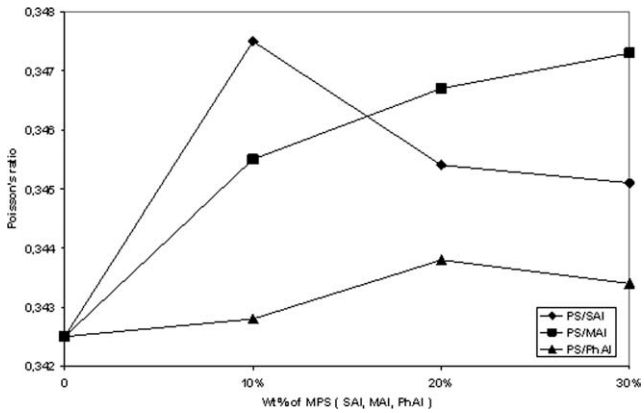

Figure 14 Variation of Poisson's ratio with weight percent of MPSs (SAI, MAI, PhAI) in composite of PS/MPS.

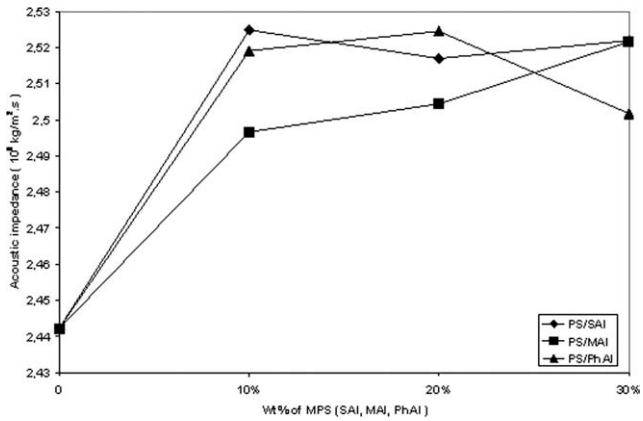

Figure 16 Variation of acoustic impedance with weight percent of MPSs (SAI, MAI, PhAI) in composite of PS/MPS.

Fig. 16) and ranged from 2.497 to 2.527 $\times$ 10^6 kg m^{-2} s^{-1} for PS/MPS (MPS—SAII, MAII, PhAII) composites (Table III and Fig. 17). These values of acoustic impedance of pure PS are aproximately close to the related literature result.[74]

One of the reason of different values of elastic parameters of PS/MPS_{500} and PS/MPS_{350} composites is that difference polyfunctional groups were bound to aromatic ring of pure PSs while modifiying PS with SA, MA, and PhA. It can be stated that different functional groups may affect mechanical properties of composites in different ways. To understand the effect of molecular structure, three various carboxylic (—COOH) functional groups with aromatic, saturated aliphatic and unsaturated aliphatic parts in case of PhA, SA, and MA, respectively are specifically studied.[60] As seen from Figure 1, when pure PS modified with SA, —CO—CH_2—CH_2—COOH polyfunctional group was bound to aromatic ring of pure PS, when pure PS modified with MA, —CO—CH=CH—COOH polyfunctional group was bound to aromatic ring of pure PS and when pure PS modified with PhA, —CO—C_6H_4—COOH polyfunctional group was bound to aromatic ring of pure PS. So it is seen that different polyfunctional groups were bound to PS's aromatic ring. So it can be stated that these different groups effect the velocities and elastic constants of CPSs (Fig. 1). It have been stated that the concentration of the functional groups connected to the structure of the PS, changes with the molecular weight of PS, and more functional groups connect to low molecular weight PS.[75] Because of this reason, two kind of CPSs (PS/MPS_{500} and PS/MPS_{350}) were produced and it was researched that which composite will give the best values of elastic constants by ultrasonic velocity measurement.

Many researchers[66,71,72,76–83] have reported that ultrasonic velocity measurements might show the extent of compatibility in highly viscous or solid forms of polymer blends. Singh and coworkers[80–83] studied the ultrasonic velocity for compatible, semicompatible, and incompatible polymeric blends, and

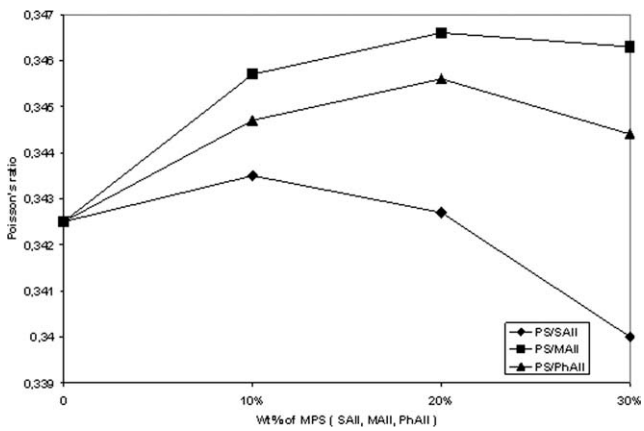

Figure 15 Variation of Poisson's ratio with weight percent of MPSs (SAII, MAII, PhAII) in composite of PS/MPS.

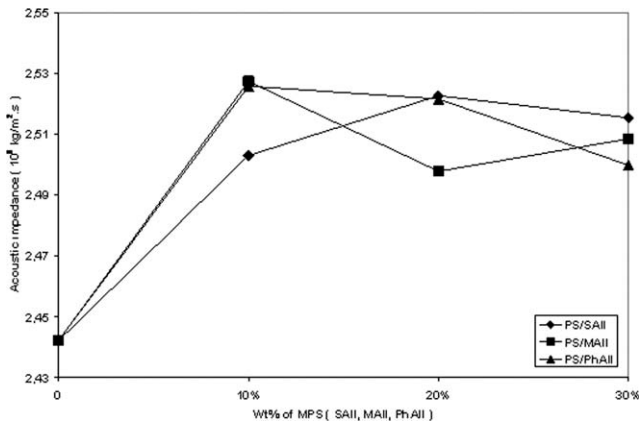

Figure 17 Variation of acoustic impedance with weight percent of MPSs (SAII, MAII, PhAII) in composite of PS/MPS.

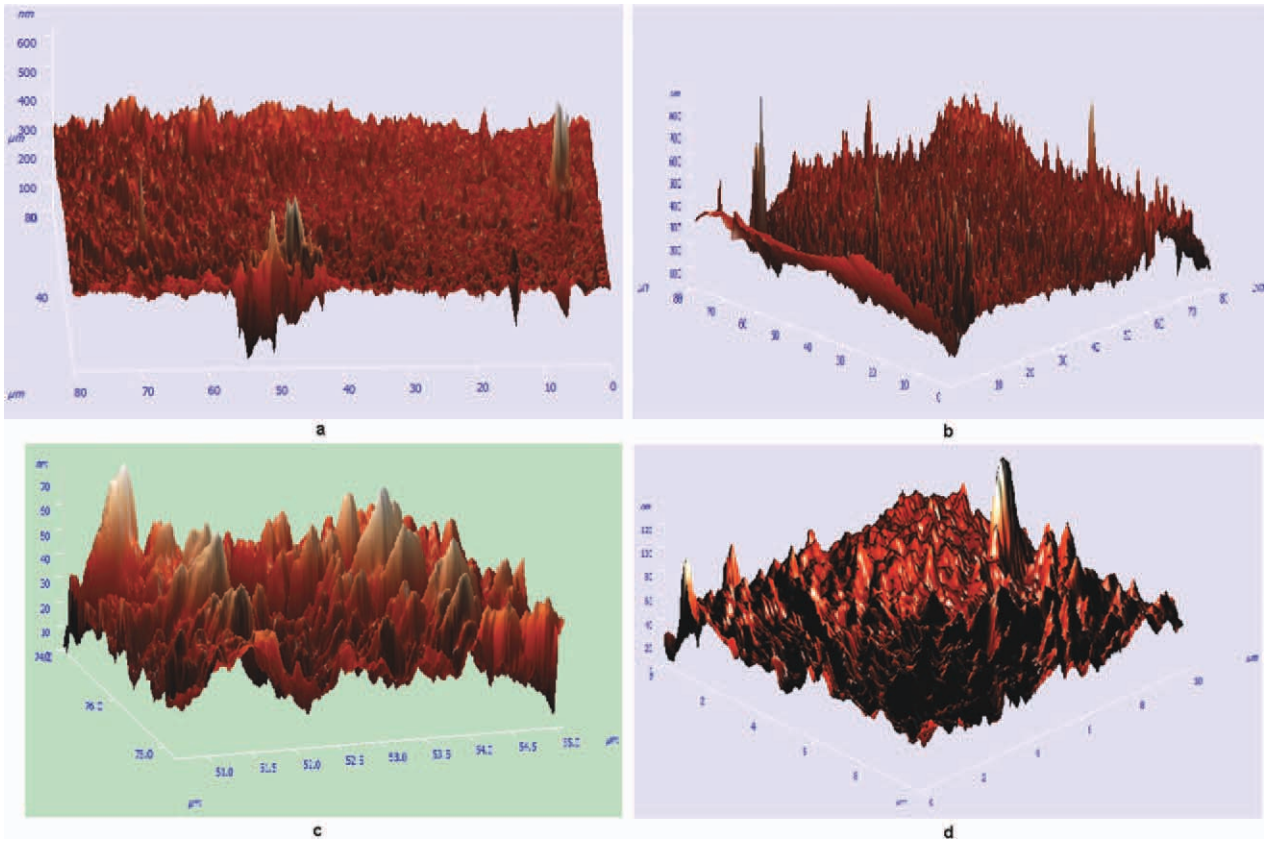

Figure 18 Three-dimensional AFM image of pure PS (a) and composite sample; (b) PS/SAII (70 : 30); (c) PS/PhAII (90 : 10); (d) PS/MAII (90 : 10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

they found that in compatible blends, the ultrasonic velocity varied linearly with composition. From the results of Tables II and III, it can be stated that the high velocity, elasticity parameters and acoustic impedance values and low Poisson's ratio values of the composites shows the good degree compatibility of PS and MPSs. Therefore the degree of compatibility or incompatibility of the components of CPSs may be the second reason of difference values of elastic parameters of PS/MPS_{500} and PS/MPS_{350} composites.

It is known that all the elastic constants are related with strong and weak internal forces (covalent bonds, Van der Waal's force, hydrogen bond) between atoms and molecules of materials. These forces are inversely proportional to the sixth power of the distance which is between molecular chains. The smaller distance between the molecular chains are increasing the gravitational force between molecular chains.[84] Therefore it can be stated that the main factor of effecting the differences in results of velocity and elastic constants of the PS/MPS_{500} and PS/MPS_{350} composites are these internal forces. Because interatomic bonding forces holding atoms together form the internal structure. Strength of materials, electrical, and thermal properties greatly depend on the internal structure. If bonds strong elasticity modulus, strength and high melting temperature, thermal expansion is low. The properties of materials on the type of bond and bond energy depend largely on the arrangement of atoms. Interatomic bond forces applied against the resistance forces, the shape change and try to prevent breakage.

From the related literature it can be stated that the Poisson's ratio, shear wave velocity and Young's modulus are the best parameters provides more information about the character of the bonding forces than any of the other wave velocities (longitudinal waves, surface waves, plate waves, Love waves, Stonely waves, Bulk guided waves etc.) and elastic constants (L, G, K). As the smaller value of the Poisson's ratio, indicates that this material is so durable. The bigger value of shear velocity and Young's modulus indicates that this material is so durable too.

Morphological results

The AFM images showed the representative 3D surface morphologies of the pure PS and three composites. As expected, the surface morphologies were quite different because of bumpy surfaces. As seen from Figure 18, in comparison to the pure PS with a relatively smooth surface [Fig. 18(a)], the composites surfaces exhibited increased roughness [Fig. 18(b–d)]. The ability of additives to migrate to the surface

is defined by several factors such as size, mobility, end-group functionalities, relative composition, and molecular architecture. The existence of MPS with various anhydrides made the composite surface rougher. This is due to the generation of functional groups onto the PS by chemical modification. It can be clearly seen that MPSs are well distributed throughout the pure PS. In Figure 18(b), for composite containing MPS with SA more rougher surface is observed, thus a greater energy is needed to break this sample. Therefore the biggest value of Young's modulus (3.934 GPa) were seen at the PS/SAII composite at 70 : 30 composition wt. ratio. It can be clearly seen that the most of heights on the surface of PS/MAII composite [Fig. 18(d)] are aligned in different directions indicating more brittle fracture. In accordance with the Young's modulus is lower than other composites.

CONCLUSIONS

Summarizing the above measurement results, it can be conclude that the ultrasonic velocities, Poisson's ratio and elastic constants are quite important parameters in order to understand the physical properties of polymers. One of the important results of this study is that showed that the best way for improving the mechanical properties of pure PS is to producing CPSs. In fact the researches[60,85,86] made before had shown that modifying PS with various organic anhydrides, increases the elasticity properties of PS. But modifying PS by various anhydrides is an expensive way. Producing composites is a cheaper way then modfiying PS. Therefore it can be stated that improving the mechanical properties of PS by producing CPSs, is the best way.

The densities, ultrasonic wave velocities, AFM images and elastic properties of pure PS and PS based composites have revealed the following conclusions:

1. According to the values of wave velocities, AFM images and elastic constants, the most appropriate wt % ratios for PS/MPS composites were determined as 70 : 30 ratio for PS/SAI and PS/SAII, as 90 : 10 wt. ratio for PS/MAI, PS/MAII, PS/PhAI, and PS/PhAII.
2. The pulse echo method has the ability to evaluate the mechanical properties and the degree of compatibility of polymer blends.
3. The smallest value of Poisson's ratio (0.3400), the biggest value of shear wave velocity (1185 m s^{-1}) and the biggest value of Young's modulus (3.934 GPa) were seen at the PS/SAII composite at 70 : 30 composition wt. ratio. This behavior is attributed to the fact that the addition of SAII improved the mechanical properties of the studied CPS.
4. The addition of MPS_{500} to pure PS has been demonstrated to increase of an average value for the elastic constants by 4.1% approximately, in comparison to pure PS.
5. The addition of MPS_{350} to pure PS has been demonstrated to increase of an average value for the elastic constants by 4.5% approximately, in comparison to pure PS.
6. Instead of using polystyrene alone where polystyrene is used, using as PS/SAII at wt. ratio of 70 : 30, PS/PhAI or PS/PhAII at wt. ratio of 90 : 10 will allow to obtain more reliable, durable, robust, as well as more economical materials to use.

Finally, it can be concluded that the results of this study has also showed that the elastic constants increase with increasing SAI and SAII weight percentage content in PS/MPS from 10 to 30. So it can be recommended to research variation of the elastic constants with increasing SAI and SAII weight percentage content in PS/MPS from 30 to 70.

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