Ultrasonic Properties of Fly Ash/Polyurea Composites

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Abstract

An experimental study has been conducted to determine the mechanical properties of fly-ash/polyurea composites by measuring their longitudinal and shear wave velocities, and attenuations at various fly ash volume fractions, using ultrasonic. The complex-valued longitudinal and shear moduli were computed from these measurements at various temperatures. It was observed that a 30% volume fraction addition of fly ash has increased the longitudinal storage and loss moduli and shear storage and loss moduli by up to 22%, 141%, 298% and 125%, respectively. The complex bulk modulus and Poisson's ratio of the composites at 1MHz were also estimated. Additionally, a computational model based on the method of dilute-randomly-distributed inclusions was created to estimate the dynamic mechanical properties of the composites. The experimental and computational results were compared and showed good agreement.

Keywords

Particle-reinforcement; Mechanical properties; Ultrasonics; Micro-mechanics

1. Introduction

Polyurea is a crosslinked thermoset elastomeric polymer derived from the chemical reaction between a diisocyanate (NCO-R-NCO) and a diamine (NH₂-R-NH₂), without the aid of a catalyst or an additional cross linker. It is formulated to be flexible under normal conditions yet extremely tough at large deformations. It could be rendered non-flammable, and contains very small to none volatile organic compounds or hazardous air pollutants. As a result, it was regarded as

an amazingly versatile protective coating candidate that can be used in a myriad of applications, such as concrete coating, truck-bed liners, marine coatings, railcar linings, water well protection, enhanced construction joints and much more since it was introduced in 1989 by Texaco Chemical Company [1, 2]. However, its true benefits and advantages were not fully appreciated until it was involved in the critical applications under blast and impact loading [3]. Many researchers have demonstrated its effectiveness in such applications experimentally and numerically [4-9]. Consequently, modifying the properties of polyurea by integrating micro- and nano-particles with polyurea became a new research direction. Carey [10] mixed chopped E-glass fiber into polyurea and studied the effect of discrete E-glass fiber length and volume fraction on the strength and ductility of polyurea under tensile testing. Mihut et al [11] incorporated hematite nanoparticles into polyurea and investigated its mechanical and thermo-mechanical properties for small and large deformations as a function of the particle concentration. Qian et al [12] investigated the properties reinforcements and mechanism of graphite oxide/polyurea and graphene/polyurea nanocomposites through evaluating molecular weights, dispersion and interface interactions. Cai and Song [13] reported the intercalation of C20 organoclay into polyurea and significant reinforcements of Young's modulus, stress and elongation at break were observed in highly crosslinked polyurea.

Under certain conditions, the overall density of the material is also an important parameter and needs to be considered. Hence, hollow spheres with low density become an excellent option to improve the properties of polyurea while reducing the overall density. In our previous studies, polyurea based composites with low density were developed using coal combustion residue, fly ash (FA) [14]. The measurement results demonstrate that the density of the composites with 30% FA volume fraction is up to 12% lower than that of the polyurea matrix, while the mechanical properties at low frequency (1Hz) increase by more than 200%. However, for the applications discussed above, the dynamic mechanical properties of the composites at high strain rates or frequencies are of greater significance. Under such situations, the ultrasonic technique, which has been employed by many researchers to determine the properties of composite material [15, 16], appears to be a valuable method to measure response in high frequency regions.

Characterizing the mechanical properties of polymer materials using acoustic and ultrasonic waves dates back to the late 1940's [17] and then it has been well documented by Ferry [18, 19] and Papadakis [20] that the corresponding complex modulus of polymers may be determined by using longitudinal and shear wave propagation techniques. A renewed interest in this field has resulted from the advancements in sensors, hardware and evaluation technologies over the last decade. Most recently, Hugh [17] demonstrated the practical application and the sensitivity of this technique as a high frequency Dynamic Mechanical Analysis DMA technique for the characterization of polymers.

In the present investigation, the dynamic mechanical properties of fly ash/polyurea (FA/PU) composites are systematically studied by transmission ultrasonic technique while varying the FA concentration. Furthermore, a micromechanical model based on the method of dilute-randomly-distributed inclusions was created to estimate the corresponding dynamic properties. Our main new contributions in this paper are: (1) To reveal the anomalous longitudinal wave dissipation behavior of FA/PU composites; (2) To calculate the complex longitudinal, shear and bulk moduli and Poisson's ratio at 1MHz of the FA/PU composites and their variation with temperature and the FA volume fraction; (3) To create a computational model which can predict the properties of FA/PU composites.

2. Sample Fabrication and Experimental Procedure

FA particles used here were collected from Harbin Thermal Power Station in China. They were sieved with a standard mesh sieve column on a mechanical shaker and the particles in the range of 109 μm –150 μm in diameter were selected in this study. The true density of the intact FA particles is around 0.78 g/cm³ and that of the ground ones is about 2.2 g/cm³. The polyurea matrix was prepared by the reaction of a modified diphenylmethane diisocyanate prepolymer (Isonate 143L from Dow Chemical) with an oligomeric diamine curative (Versalink P1000 from Air Product). Stoichiometric ratio of 1.05:1 prepolymer to curative was used to ensure that the reaction was completed and produced some light chemical cross-linking among the hard blocks. The FA/PU composites were fabricated by magnetically stirring the FA particles in the diamine curative, Versalink P1000 and then mixing with the diisocyanate prepolymer, Isonate 143L. The mixture was cast directly in suitable

Teflon molds to produce test specimens (13mm×13mm×6mm for the longitudinal wave measurements and $\phi 76.2\text{mm} \times 0.7 \sim 1.3\text{mm}$ for the shear wave measurements) and cured in the environmental chamber with humidity under 10%RH. The specimens were fully cured at room temperature for two weeks before testing. A more detailed description on the fabrication procedure may be found in [14]. Five material configurations were prepared, i.e., pure PU and composites containing 5%, 10%, 20% and 30% FA by volume. They were labeled as PU, M5, M10, M20, and M30, respectively. A homogeneous distribution of fly ash particles in the polyurea matrix was confirmed by Scanning Electron Microscopy (SEM) observation. No signs of agglomerates or holes were observed. Moreover, the fly ash particles seemed to have good interfacial adhesion with the matrix as there were no discernible cracks or voids at the interface. Microscopic photos of the composites can also be found in [14].

Ultrasonic measurements were carried out using a modified two-sample technique [21]. The advantage of this technique is that the possible differences of the reflectivity with temperature between transducer and sample during the experiment will be procedurally calibrated out. All samples were tested using the same transmission path, instead of testing two thicknesses simultaneously as described by others researchers [22]. The setup of the experiment system is illustrated in Fig.1. The longitudinal wave measurements were performed in the 0.6-2MHz frequency range between -60°C to 30°C temperatures and the shear wave measurements were done in the temperature range from -50°C to 30°C at 1MHz. In order to guarantee relatively constant contact pressure between the transducers and the sample to ensure good reproducibility even when the setup shortens due to the significant reduction in temperature, a measuring cell was designed; see Fig.2. Four identical springs and aluminum columns were employed. When the sample was clamped, the wing nuts were finger tightened. The measuring cell was placed in a temperature chamber and its temperature was varied by 10°C decrement steps from 30°C to -60°C or -50°C. At each step it was held for 10min (for longitudinal wave measurement) or 20min (for shear wave measurement) prior to the measurement. A 76.2mm diameter and 50.8mm long aluminum rod was inserted in the wave path between the generating transducer and the sample for the shear wave measurement to temporally separate the shear waves and the longitudinal waves which are inevitably generated together with the

shear waves by the transmitting crystals [23]. More details of the measurement were described in our previous works [21].

The longitudinal wave and shear wave velocities and attenuations were obtained, and then the complex longitudinal and shear moduli were determined using these results and the density of the samples [21],

$$M^* = M' + iM'' , \quad (1)$$

$$M' = \frac{\rho c^2 (1 - r^2)}{(1 + r^2)^2} , \quad (2)$$

$$M'' = \frac{2\rho c^2 r}{(1 + r^2)^2} , \quad (3)$$

where M^* represents the complex longitudinal or shear modulus; ρ is the density of the composites; c is the velocity of the ultrasonic wave; r is a dimensionless parameter given by $r = \alpha c / \omega$, where α is the attenuation constant and ω is the angular frequency.

Fig.1. Block diagrams of longitudinal (a) and shear ultrasonic experiment setups (b).

The dashed rectangle indicates the temperature control chamber, which contains the sample and transducers.

Fig.2 Measuring cell used in the longitudinal ultrasonic measurement

3. Results and discussion

3.1 Longitudinal wave

The measured longitudinal wave velocity in the FA/PU composites is shown in Fig.3. Fig.3 (a) presents its dependence on the temperature at 1.6MHz. It can be seen that the longitudinal wave velocity in the composites is in the range from 1700m/s to 2800m/s, and it is sensitive to both temperature and FA volume fraction, i.e. it increases as the temperature decreasing and the FA volume fraction increases. The effect of FA concentration is more pronounced when it is higher than 10%. Moreover, increased sensitivity to FA concentration at higher temperature is observed. For instance, the longitudinal wave velocity in M30 is 9.8% higher than that in pure polyurea at -60°C , and 19.4% higher at 30°C . Fig.3 (b) shows this velocity as a function of frequency at 20°C , indicating that the longitudinal wave velocity in this composites is relatively insensitive to frequency in the considered range.

Fig. 3 Longitudinal wave velocity of FA/PU composites as a function of temperature at 1.6MHz (a) and as a function of frequency at 20°C (b).

Fig.4 (a) shows the attenuation per wavelength of the longitudinal wave as a function of temperature at 1.6MHz. It indicates that, the temperature increases from -60°C to 30°C, the attenuation in pure polyurea initially increases, and then decreases almost linearly to a peak at -50°C. The trend is seen in the composites in the range of -60°C to -20°C, but the peak value varies with the FA volume fraction. M10 possesses a little higher peak value than pure polyurea. Then the peak value decreases significantly with increasing FA volume fraction. On the other hand, when the temperature is varied from -20°C to 30°C, there is a highly significant increase in the attenuation per wavelength of the composites relative to pure polyurea. More importantly, for the composites with high FA volume fraction, i.e. M20 and M30, the temperature dependence of attenuation changes. The attenuation per wavelength of M20 is insensitive to temperature, while that of M30 increases with temperature.

The parameter k defined by,

$$k = \frac{\alpha_c}{\alpha_m(1 - V_f)} , \quad (4)$$

where α_c , α_m are the attenuation of longitudinal wave in FA/PU composites and pure polyurea respectively, and V_f is the FA volume fraction, can be used as a measure of enhanced dissipation in the material due to the presence of the inclusions; see Fig.5. It can be observed that k is relatively insensitive to temperature variations, increasing lightly for temperatures less than or equals to -30°C. When FA volume fraction is 5%, k is approximately equal to 1, attaining higher values for higher FA concentration. However, there is only a minimal incremental change in k with the change in FA volume fraction. Starting at -20°C, k of all FA/PU composites is larger than 1 and increases remarkably as the temperature increases. The increment of k with FA volume fraction also increases. These phenomena indicate that new energy dissipation mechanisms are introduced by adding FA particles, attaining a greater importance as temperature is increased, i.e., as the contrast in the stiffness of the inclusion and matrix is increased.

Fig. 4 (a): Attenuation per wavelength of longitudinal wave in FA/PU composites as a function of temperature at 1.6MHz; and (b) attenuation coefficient per unit thickness as a function of frequency at 20°C.

Fig. 5 Parameter k of FA/PU composites as a function of temperature

Attenuation of ultrasonic wave in a composite material results from two major mechanisms: scattering and absorption [24, 25]. The scattering is the redirection of ultrasonic wave energy by inclusions in the matrix. The absorption mechanism can be classified into two types, intrinsic and structural. The intrinsic mechanism refers to the absorption in the inclusion material and the viscoelastic loss in the polymeric matrix. The structural mechanism is related to the ultrasonic wave energy dissipation caused by the oscillation of the inclusions that are embedded in the network of the polymeric matrix. Here, the intrinsic attenuation from the FA material is expected to be very small compared with the other mechanisms because the material is essentially elastic. Biwa et al [26] suggests that only the intrinsic mechanism of the matrix and the

scattering mechanism contribute to the attenuation of longitudinal wave in polymer based composites filled with elastic particles. As a result, the attenuation coefficient of the composites can be obtained from

$$\alpha_c = (1 - V_f)\alpha_m + \frac{3}{8\pi a^3} V_f r^{sca} , \quad (5)$$

where a and r^{sca} are the radius and scattering cross-section of the particle respectively. Substitution of Eq.(5) into Eq.(4) yields

$$k = 1 + \frac{3r^{sca}}{8\pi a^3 \alpha_m} \cdot \frac{V_f}{1 - V_f} . \quad (6)$$

Thus k increases with FA volume fraction. However, whether such dependency is pronounced or not depends on $3r^{sca}/8\pi a^3 \alpha_m$. According to the calculation by Biwa et al [26], r^{sca}/a^2 increases with the normalized frequency which is equal to $(a/c_{LI})f$. Here, c_{LI} is the longitudinal wave velocity in the matrix and decreases significantly with temperature as shown in Fig.3 (a). So r^{sca}/a^2 should increase with temperature. As α_m also increases with temperature, $3r^{sca}/8\pi a^3 \alpha_m$ increases when temperature increases. Hence k would increase and its dependency on the FA volume fraction would be more significant as the temperature increases, in agreement with trends seen in Fig.5 for k . On the other hand, at low temperatures the polyurea chains cannot move easily and they also restrict the movement of the FA particles. Thereby, the effect of the structural mechanism may be ignored. The mobility of the polyurea chains and hence the structural mechanism increase with temperature. Based on the above analysis, we may conclude that the viscoelastic losses in the polyurea matrix are the major contributor to the total attenuation at low temperatures ($T \leq -30^\circ\text{C}$). In this region, the scattering mechanism may play a small role. As the temperature increases, the structural mechanism begins to work and the scattering mechanism becomes more significant.

Fig.4 (b) shows the dependence of attenuation coefficient per unit thickness of longitudinal wave on frequency. The measured attenuation coefficient per unit thickness is a nearly linear function of frequency. This is consistent with the observation of Mott et al [27] on polyurethane.

From data on longitudinal wave velocity and attenuation coefficient, the longitudinal storage modulus (L') and longitudinal loss modulus (L'') of FA/PU

composites are calculated. The results at 1.6MHz are shown in Fig.6. It can be seen that the longitudinal storage modulus of FA/PU composites decreases as temperature increases, while it increases monotonically with FA volume fraction in the region studied. For example, M30 composites shows a 10%~22% increase. As expected, the effect of FA volume fraction becomes more significant at higher temperatures, similar to the behavior of Young's storage modulus at low frequencies [14]. However, the longitudinal loss modulus of the composites decreases monotonically with temperature in the region studied. In addition, the loss modulus increases with FA volume fraction at high temperatures, reaching a 141% higher value than that of pure polyurea, as already pointed out based on the k -value. Furthermore, introducing FA particles into polyureas lightly reduces the overall composite's longitudinal loss modulus at low temperatures.

Fig. 6 (a): Longitudinal storage; and (b) loss moduli of FA/PU composites as a function of temperature at 1.6MHz

3.2 Shear wave

Fig.7 shows the dependence of the shear wave velocity of FA/PU composites on temperature. The maximum temperature which could be investigated for a particular specimen was restricted by the attenuation of signals at higher temperatures. The attenuation in the FA/PU composites with lower FA concentration increases significantly with temperature, so that the velocity could not be measured for these specimens at high temperatures. It should be noted that the results for pure polyurea presented here were obtained using thin specimens (around 0.6 mm and 1 mm). Fig.7 shows that the shear wave velocity of the composites decreases as temperature is increased, consistent with the variation in the pure polyurea. This velocity increases as

the FA volume fraction is increased. For the composites with 30% FA by volume, the shear wave velocity of the composites is in the range of 680~1285m/s, about 112%~37% higher than that of pure polyurea.

Fig. 7 Shear wave velocity of FA/PU composites as a function of temperature at 1.0MHz

The temperature dependence of the attenuation coefficient per unit thickness of shear wave in FA/PU composites at 1MHz is shown in Fig.8. The attenuation coefficient per unit thickness of the shear wave increases with temperature. However, such temperature sensitivity decreases as the FA volume fraction increases. The attenuation per wavelength, which indicates the normalized dissipation capability of the composites, is proportional to the product of attenuation coefficient per unit thickness and velocity. Since these two parameters have opposite temperature dependencies and the shear wave attenuation data shows fluctuations, no significant temperature dependence of the attenuation per wavelength may be deduced. Yet in the considered temperature range, attenuation per wavelength decreases remarkably with FA volume fraction. As a result, the average of the maximum and the minimum attenuation per wavelength of each composite in the considered temperature range was used to determine k according to Eq. (4). The attenuation per wavelength and k values can be found in Table 1. It can be seen that all of the k values are less than 1 which suggests that the viscoelastic loss of shear wave in polyurea matrix is the dominant attenuation mechanism in FA/PU composites. Furthermore, the FA particles embedded in the polyurea matrix reduce the attenuation ability of the polyurea matrix, perhaps by restricting the motion of the matrix.

Fig. 8 Attenuation coefficient per unit thickness of shear wave in FA/PU composites as a function of temperature at 1.0MHz.

Table 1 Range of attenuation per wavelength of shear wave in FA/PU composites and values of parameter k

	PU	M5	M10	M20	M30
Maximum (dB)	6.95	6.03	4.82	5.36	4.54
Minimum (dB)	5.75	5.09	4.30	3.10	3.06
k	—	0.944	0.807	0.828	0.833

The shear storage (G') and loss (G'') moduli were also calculated from the velocity and attenuation. Instead of using the actual attenuation per wavelength at each temperature, the maximum and minimum values of the attenuation per wavelength over the temperature range studied were used. The maximum and minimum shear storage and loss moduli and their average values at various temperatures were obtained. The effect of the variation of attenuation per wavelength on G' is negligible. The differences are less than 2% between the G' 's calculated from the maximum and minimum attenuation per wavelength. However, this variation affects the G'' of the composites significantly, especially at low temperatures. Fig.9 shows the average shear storage and loss moduli of FA/PU composites as a function of temperature at 1MHz. A typical example which shows the effect of the variation of attenuation per wavelength on the G'' is also given as an inset in Fig.9 (b). The error

bars indicate the range calculated from the maximum and minimum attenuation per wavelength. Note that the error bars represent the variation in attenuation per wavelength for the entire temperature range and hence are the most conservative choice, which appears particularly wide in low temperatures. Fig.9 reveals that both the shear storage and loss moduli of FA/PU composites decrease monotonically with increasing temperature. The FA volume fraction considerably affects the shear storage modulus of the composites, whereas it has far less effect on the corresponding shear loss modulus. When FA volume fraction increases up to 30%, the shear storage modulus of the composites increases by 60%~298% compared to that of pure polyurea in the tested temperature range. However, the loss modulus of the composites only shows significant increase at high temperatures and the maximum increment is 125%.

Fig. 9(a): Average shear storage; and (b): loss moduli of FA/PU composites as functions of temperature at 1.0MHz; the inset shows the shear loss modulus of M30 composites as a function of temperature at 1.0MHz; the error bars indicate the range calculated from the maximum and minimum values of the attenuation per wavelength over the entire temperature range.

3.3 Bulk Modulus and Poisson's ratio

The relationship between the complex longitudinal, shear, and bulk moduli is,

$$L^* = K^* + \frac{4}{3} G^* . \quad (7)$$

Separating the real and imaginary parts of Eq.(7) and rearranging, it gives,

$$K' = L' - \frac{4}{3} G' , \quad (8)$$

$$K'' = L'' - \frac{4}{3} G'' . \quad (9)$$

The values calculated from Eqs.(8) and (9) are graphed in Fig.10. Maximum and minimum shear storage and loss moduli based on the maximum and minimum attenuation per wavelength were used. Here again, the effect of the variation of attenuation per wavelength of shear wave is negligible on K' and significant on K'' , especially at low temperatures as shown in the inset of Fig.10 (b). The differences are less than 1% between the K' 's calculated from the maximum and minimum G' 's. Fig.10 (a) indicates that the bulk storage modulus of FA/PU composites decreases with the increasing temperature, its variation being much smaller than that of the shear storage modulus. Generally, the average distance between the molecules is expected to increase with increasing temperature. As a result, the decrease in the bulk storage modulus may be attributed to the consequent decrease in the slope of the interatomic potential [28]. Since the results for G'' are somewhat noisy, it is difficult to obtain accurate values for K'' . Nevertheless, it still can be seen that the bulk loss modulus of the composites is non-zero at all temperatures and is comparable in magnitude with the shear loss modulus. A trend that the bulk loss modulus decreases with temperature is also apparent, except for higher temperature response of the 30% volume fraction samples. According to the classical Stokes assumption, there are no losses associated with a pure compression ($K''=0$). In other words, the bulk loss modulus should be negligible in comparison to the shear loss modulus [29]. Given the measured values of K'' and G'' for pure polyurea, it appears that a considerable portion of the energy losses are due to a pure bulk viscosity and the Stokes assumption does not hold here. Similar behavior has been observed by Cunningham and Ivey [29] for Butyl. Furthermore, it is noteworthy that the FA concentration has little influence on both the bulk storage and loss moduli of the composites.

Fig.10 (a): Average Bulk storage; and (b): loss moduli of FA/PU composites as functions of temperature at 1.0MHz; the inset shows the bulk loss modulus of M30 composites as a function of temperature at 1.0MHz; the error bars indicate the range calculated from the maximum and minimum shear loss modulus

Using the theory of linear viscoelasticity [30], the complex Poisson's ratio ν^* can be written in the same form as for the elastic case, namely

$$\nu^* = \frac{L^* - 2G^*}{2L^* - 2G^*}. \quad (10)$$

Separating the real and imaginary parts of Eq.(10) results in quite complicated expressions. Pritz [31] suggested some simplified relations between these viscoelastic constants, as shown below,

$$\nu' = \frac{L' - 2G'}{2L' - 2G'}, \quad (11)$$

$$\nu'' = \left(\frac{G''}{G'} - \frac{L''}{L'} \right) (1 - \nu') (1 - 2\nu'). \quad (12)$$

These relations were derived under the conditions that the square of the loss factors (loss modulus divided by the storage modulus) and the multiplication of the two loss factors are much smaller than unity, which are satisfied if the loss factors are smaller than 0.3. Here, both pure polyurea and FA/PU composites satisfy these conditions. Hence, the complex Poisson's ratio was calculated from Eqs. (11) and (12). Here again, maximum and minimum shear storage and loss moduli were used. All of the resulting values of ν'' are smaller than 0.02 and there is no obvious correlation between it and the temperature or the FA volume fraction. The temperature dependence of ν' (average of the two extrema) is shown in Fig.11.

Fig. 11 The real part of complex Poisson's ratio of FA/PU composites as functions of temperature at 1.0MHz

On inspecting the Poisson's ratio curves of Fig.11, it is apparent that Poisson's ratio is not constant for pure polyurea and FA/PU composites at 1MHz in the tested temperature regime. As the temperature increases, the Poisson's ratio of pure polyurea increases and approaches 1/2 which means that pure polyurea tending to become "incompressible". However, it is interesting to note that the bulk modulus of pure polyurea (Fig.10 (a)) decreases as the Poisson's ratio approaching 1/2. This is consistent with the observation of Mott et al [27] on polyurethane. Adding FA particles decreases the Poisson's ratio of the system significantly. As the Poisson's ratio of the shell of FA particles is only about 0.21 [32], much smaller than that of pure polyurea, this observation is easily understood.

3.4 Computational results

The properties of the FA/PU composites are estimated using micromechanical modeling. In this work, the FA/PU composites are modeled as composites with dilute randomly distributed hollow spherical inclusions. The major theoretical framework of this model was first developed by Hashin [33] for estimating the elastic moduli of heterogeneous material. Later Lee and Westman extended Hashin's work and developed models to determine the elastic properties of hollow-sphere-reinforced composites [34]. Replacing the elastic moduli by complex moduli in the elastic model with identical phase geometry, the model could be modified and applied to predict viscoelastic properties of polymeric material [35]. This way, the model in the present study was developed. Instead of finding an exact formula for the moduli of the

composites, we sought to obtain approximate upper and lower values for complex bulk and shear moduli based on the minimum complementary energy and minimum potential energy theorems.

The inclusion and matrix in the model are both considered as homogeneous and isotropic materials with known moduli. Furthermore, three assumptions are made for the actual FA/PU system such that it can be treated as a composite with dilute randomly distributed hollow spherical inclusions: (1) FA particles do not interact with other adjacent particles; (2) they are small, symmetric, and assumed to be spherical; and (3) they have a uniform distribution throughout the polyurea matrix. The assumed representative volume element (RVE) is a spherical body containing one hollow spherical inclusion (three concentric spheroids with suitable diameters; see Figure 12). The outer spheroid is labeled as phase 0. It represents the matrix phase. The next inner one is marked as phase 1. It represents the shell of the FA particle. The smallest one is the hollow core of the particle and is labeled 2. The volume fraction of inclusion is the same as the volume fraction of the actual FA/PU composites.

Fig. 12 FA/PU composites model

Since it is an elasticity problem of spherically symmetric body, the strain and stress fields are readily be calculated. The resulting expressions for the overall moduli involve only the stress and strain fields within the inclusion. The calculation is performed by considering the change in strain energy in a loaded homogeneous solid due to the presence of the inclusion. Two estimates (upper and lower values) of the mechanical properties are presented for each composite configuration, one based on prescribed tractions due to uniform stress on the RVE and one based on prescribed linear displacement boundary conditions. The required parameters are as follows:

- (1) Volume fraction of hollow spheres, $c = (r_o/b)^3$; here, $c = 0.05$ (5%), 0.1 (10%),

0.2 (20%) and 0.3 (30%) respectively, where r_o is external radius of FA particles, b represents the radius of a spherical RVE.

(2) Ratio of the internal and external radii of the hollow sphere: $d = r_i/r_o$; here, the densities of intact (ρ_1) and ground (ρ_2) FA particles were measured, and then the ratio was calculated, using $d = r_i/r_o = (1 - \rho_1/\rho_2)^{1/3} = 0.86$.

(3) Two mechanical properties of each phase. Here, shear (G) and bulk (K) moduli of each phase are used. Complex shear and bulk moduli of polyurea (G_0 and K_0), which were obtained experimentally at various temperatures, are used as properties of matrix in the model. Characterizing the moduli of the shell of FA particles experimentally is rather difficult. As a result, the storage moduli were estimated from the crystallinity of FA and the volume fraction of each component using the rule of mixtures and assumed to be constants for all testing temperatures. The crystal phases of FA particles were investigated by XRD analysis, as in [36]. Following the procedure discussed in [32], the upper and lower estimated values for the storage moduli of the shell of FA particles were obtained and are listed in Table 2. Their average values are used for the real parts of G_I and K_I of the shell phase. The loss moduli (imaginary parts of G_I and K_I) were assumed to be zero. The core phase is empty. Thus G_2 and K_2 are zero.

Table 2 Estimated Young's, bulk, and shear moduli of the shell of fly ash particles

	Upper Estimate	Lower Estimate	Average
Young's modulus(GPa)	90.3	79.8	85.05
Bulk modulus(GPa)	51.9	45.9	48.90
Shear modulus(GPa)	37.3	33.0	35.15

Since the model has spherically symmetric geometry, the displacement fields of the model under prescribed uniform stress and linear displacement boundary conditions may be explicitly derived [33, 34]. Once the stress and strain fields are known, the strain energy of the model under the two boundary conditions can be calculated and compared with the strain energy of the homogenized spherical solid with to-be-found effective moduli. With suitable choice of admissible displacement (or traction, respectively) fields, combined with the minimum potential energy

theorem (or minimum complementary energy theorem, respectively), the effective moduli are obtained [34].

The predicted longitudinal storage and loss moduli and shear storage and loss moduli of FA/PU composites are shown in Fig.13. The experimental shear storage and loss moduli shown are the average values based on the maximum and minimum attenuation per wavelength of shear wave. It can be seen that the gap between the two estimates (upper and lower values) of the moduli of the composite increases as the FA volume fraction increases. Nevertheless, the resulting values are still relatively close. Notably, the temperature- and FA concentration-dependence of these estimates are similar to the experimental results, i.e. all of these moduli decrease significantly with increasing temperature, and increase as the FA volume fraction increases. Clearly, the model can be used to describe the trend of the material response. However, by comparing the values of these estimates with the experimental results, we can see that there is a difference between the computation and experiment, and it increases with FA volume fraction. This difference is due to the inaccuracies of the model; especially the assumption that FA particles do not interact with each other. The computational results deviate from the experiment in the following ranges:

(1) The model overestimates the storage longitudinal modulus at high FA volume fraction, particularly in the corresponding volumetric deformation. This could be associated with the interaction of the particles and breakdown of the dilute distribution approximation. Interestingly enough, the shear predictions appear to be much more acceptable. This may be due to the soft shear response of the matrix, which allows for localization of deformation and therefore essentially masking the particles from one another.

(2) The loss moduli, particularly the longitudinal loss modulus, are underestimated at high temperatures. This is also understandable by considering the corresponding softening of matrix may amplify the loss disproportionately by (a) localization and large deformation in between the particles, and/or (b) cooperative or out-of-phase dynamics of particles or particle/matrix regions.

Although the deviation based on the volume fraction could be explained easily by the limitations of the dilute distribution model, it appears that the enhanced loss in longitudinal waves goes beyond that and changes the deviation direction (see Figure

13.b). The physical mechanism responsible for this change appears to be a dynamic effect as it is mostly manifested in loss. With lower wave speeds and consequently lower wave lengths at the range of this deviation, we believe particle scattering may be contributing to this enhanced loss substantially.

Fig. 13 Computational results of longitudinal storage (a) and loss moduli (b) and shear storage (c) and loss moduli (d) of FA/PU composites

4. Conclusions

In this work, the dynamic mechanical properties of FA/PU composites with various FA volume fractions were examined by ultrasonic measurements. Velocity and attenuation of both longitudinal and shear ultrasonic waves were measured. The composites exhibit anomalous longitudinal wave dissipation behavior, i.e. the attenuation per wavelength of the composites increases significantly at higher temperature (-20°C to 30°C) compared with that of pure polyurea and its temperature dependence changes. The complex longitudinal, shear, and bulk moduli were computed from the ultrasonic data. All of these moduli of FA/PU composites decrease significantly and monotonically with increasing temperature, except for the high-temperature loss of high-volume-fraction (30%) composites. No peaks occur in the temperature regime studied. The longitudinal storage and loss moduli and shear storage modulus of FA/PU composites increase significantly with increasing FA volume fraction. The increase could be up to 298% compared to those of pure polyurea (for shear storage modulus). Complex Poisson's ratio of the composites was also obtained. Its real part increases with temperature and decreases with FA volume fraction. However, its imaginary part is generally smaller than 0.02 and shows no obvious dependence on temperature or the FA volume fraction. A computational model was developed based on the minimum complementary energy and minimum potential energy theorems. Acceptable agreement between the experimental and computational results was obtained. The deviation between the model and experimental results is due to idealized assumptions used in the computation model.

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Reference

- [1] J.W. Bulluck, Protective coatings for high strength steels, United States Patent, 2012, US8206791B2.

- [2] J. Shime, D. Mohr, Using split hopkinson pressure bars to perform large strain compression tests on polyurea at low, intermediate and high strain rates, *Int. J. Impact Eng.* 36 (2009) 1116-1127.
- [3] A.V. Amirkhizi, J. Isaacs, J. McGee, S. Nemat-Nasser, An experimentally-based viscoelastic constitutive model for polyurea, including pressure and temperature effects, *Philos. Mag.* 86 (2006) 5847-5866.
- [4] D. Mohotti, T. Ngo, P. Mendis, S.N. Raman, Polyurea coated composite aluminium plates subjected to high velocity projectile impact, *Mater. Design* 52 (2013) 1-16.
- [5] D. Mohotti, T. Ngo, S.N. Raman, M. Ali, P. Mendis, Plastic deformation of polyurea coated composite aluminium plates subjected to low velocity impact, *Mater. Design* 56 (2014) 696-713.
- [6] J. LeBlanc, C. Shillings, E. Gauch, F. Livolsi, A. Shukla, Near field underwater explosion response of polyurea coated composite plates, *Exp Mech.* 2015, DOI 10.1007/s11340-015-0071-8.
- [7] D. Mohotti, T. Ngo, S.N. Raman P. Mendis, Analytical and numerical investigation of polyurea layered aluminium plates subjected to high velocity projectile impact, *Mater. Design* 82 (2015) 1-17.
- [8] M. Grujicic, W.C. Bell, B. Pandurangan, T. He, Blast-wave impact-mitigation capability of polyurea when used as helmet suspension-pad material, *Mater. Design* 31 (2010) 4050-4065.
- [9] J. Bonsmann, W.L. Fourny, The effect of polyurea mass ratio on the acceleration mitigation capabilities of dynamically loaded structures, *J. Dynamic Behavior Mater.* 1 (2015) 28-42.
- [10] N.L. Carey. Discrete fiber-reinforced polyurea systems for infrastructure strengthening and blast mitigation. Ph.D. thesis of Missouri University of Science and Technology 2012.
- [11] A.M. Mihut, A. Sánchez-Ferrer, J.J. Crassous, L.A. Hirschi, R. Mezzenga, H. Dietsch, Enhanced properties of polyurea elastomeric nanocomposites with anisotropic functionalized nanofillers, *Polym.* 54 (2013) 4194-4203.
- [12] X. Qian, L. Song, Q. Tai, Y. Hu, R.K.K. Yuen, Graphite oxide/polyurea and graphene/polyurea nanocomposites: a comparative investigation on properties

- reinforcements and mechanism, *Compos. Sci. Technol.* 74 (2013) 228-234.
- [13] D. Cai, M. Song, High mechanical performance polyurea/organoclay nanocomposites, *Compos. Sci. Technol.* 103 (2014) 44-48.
- [14] J. Qiao, A.V. Amirkhizi, K. Schaaf, S. Nemat-Nasser, Dynamic mechanical analysis of fly ash filled polyurea elastomer, *J. Eng. Mater. Technol.* 133 (2011) 011016.
- [15] V. Samulionis, Š. Svirskas, J. Banys, A. Sánchez-ferrer, A. Mrzel, Ultrasonic and dielectric studies of Polyurea elastomer composites with inorganic nanoparticles, *Ferroelectrics*, 479 (2015) 67-75.
- [16] D.J. Wang, Y.J. Huang, L.Z. Wu, J. Shen, Mechanical, acoustic and electrical properties of porous Ti-based metallic glassy/nanocrystalline composites, *Mater. Design* 4 (2013) 69-73.
- [17] J.M. Hugh, Ultrasound technique for the dynamic mechanical analysis (DMA) of polymers, Thesis of Technical University of Berlin 2007.
- [18] E.R. Fitzgerald, J.D. Ferry, Method for determining the dynamic mechanical behavior of gels and solids at audio frequencies: comparison of mechanical and electric properties, *J. Colloid Sci.* 8 (1953) 1-34.
- [19] J.D. Ferry, *Viscoelastic properties of polymers*, John Wiley and Sons Inc., 1980.
- [20] E.P. Papadakis, Monitoring the moduli of polymers with ultrasound, *J. Appl. Phys.* 45 (1974) 1218-1222.
- [21] J. Qiao, A.V. Amirkhizi, K. Schaaf, S. Nemat-Nasser, G.H. Wu, Dynamic mechanical and ultrasonic properties of polyurea, *Mech. Mater.* 43 (2011) 598-607.
- [22] U. Buchholz, M. Jaunich, W. Stark, W. Habel, Acoustic data of cross lined polyethylene (XLPE) and cured liquid silicone rubber (LSR) by means of ultrasonic and low frequency DMTA, *IEEE T. Dielect. El. In.* 19 (2012) 558-566.
- [23] J.R. Cunningham, D.G. Ivey, Dynamic properties of various rubbers at high frequencies, *Appl. Phys.* 27 (1956) 967-974.
- [24] A. Hedayati, A. Arefazar, Effects of filler characteristics on the acoustic absorption of EPDM-based highly filled particulate composite, *J. Reinf. Plast. Compos.* 28 (2008) 2241-2249.

- [25] H.C. Kim, J.M. Park, Ultrasonic wave propagation in carbon fibre-reinforced plastics, *J. Mater. Sci.* 22 (1987) 436-4540.
- [26] S. Biwa, S. Idekoba, N. Ohno, Wave attenuation in particulate polymer composites: independent scattering/absorption analysis and comparison to measurements, *Mech. Mater.* 34 (2002) 671-682.
- [27] P.H. Mott, M. Roland, R.D. Corsaro, Acoustic and dynamic mechanical properties of a polyurethane rubber, *J. Acoust. Soc. Am.* 111 (2002) 1782-1790.
- [28] P.H. Mott, J.R. Dorgan, C.M. Roland, The bulk modulus and poisson's ratio of "incompressible" materials, *J. Sound Vib.* 312 (2008) 572-575.
- [29] J.R. Cunningham, D.G. Ivey, Dynamic properties of various rubbers at high frequencies, *J. Appl. Phys.* 27 (1956) 967-974.
- [30] D.R. Bland, *The theory of linear viscoelasticity*, Pergamon Press, 1960.
- [31] T. Pritz, Measurement methods of complex Poisson's ratio of viscoelastic materials, *Appl. Acoust.* 60 (2000) 279-292.
- [32] T. Matsunaga, J.K. Kim, S. Hardcastle, P.K. Rohatgi. Crystallinity and selected properties of fly ash particles, *Mater. Sci. Eng. A* 325 (2002) 333-343.
- [33] Z. Hashin, The elastic moduli of heterogeneous materials, *J. Appl. Mech.* 29 (1962) 143-150.
- [34] K.J. Lee, R.A. Westmann, Elastic properties of hollow-sphere-reinforced composites, *J. Compo. Mater.* 4 (1970) 242-252.
- [35] Z.V.I. Hashin, Complex moduli of viscoelastic composites—I. general theory and application to particulate composites, *Int. J. Solids Struct.* 6 (1970) 539-552.
- [36] J. Qiao, A.V. Amirkhizi, S. Nemat-Nasser, G.H. Wu. Ultrasonic studies of fly ash/polyurea composites, In: *Proceeding of the SPIE Conference*, San Diego, March, 2013. 86891C.

Figure Captions

Fig.1. Block diagrams of longitudinal (a) and shear ultrasonic experiment setups (b). The dashed rectangle indicates the temperature control chamber, which contains the sample and transducers.

Fig. 2 Measuring cell used in the longitudinal ultrasonic measurement

Fig.3 Longitudinal wave velocity of FA/PU composites as a function of temperature at 1.6MHz (a) and as a function of frequency at 20°C (b).

Fig. 4 (a): Attenuation per wavelength of longitudinal wave in FA/PU composites as a function of temperature at 1.6MHz; and (b) attenuation coefficient per unit thickness as a function of frequency at 20°C.

Fig. 5 Parameter k of FA/PU composites as a function of temperature

Fig. 6 (a): Longitudinal storage; and (b) loss moduli of FA/PU composites as a function of temperature at 1.6MHz

Fig. 7 Shear wave velocity of FA/PU composites as a function of temperature at 1.0MHz

Fig. 8 Attenuation coefficient per unit thickness of shear wave in FA/PU composites as a function of temperature at 1.0MHz.

Fig. 9(a): Average shear storage; and (b): loss moduli of FA/PU composites as functions of temperature at 1.0MHz; the inset shows the shear loss modulus of M30 composites as a function of temperature at 1.0MHz; the error bars indicate the range calculated from the maximum and minimum values of the attenuation per wavelength over the entire temperature range

Fig.10 (a): Average Bulk storage; and (b): loss moduli of FA/PU composites as functions of temperature at 1.0MHz; the inset shows the bulk loss modulus of M30 composites as a function of temperature at 1.0MHz; the error bars indicate the range calculated from the maximum and minimum shear loss modulus

Fig. 11 The real part of complex Poisson's ratio of FA/PU composites as functions of temperature at 1.0MHz

Fig. 12 FA/PU composites model

Fig. 13 Computational results of longitudinal storage (a) and loss moduli (b) and shear storage (c) and loss moduli (d) of FA/PU composites

Table Captions

Table 1 Range of attenuation per wavelength of shear wave in FA/PU composites and values of parameter k

Table 2 Estimated Young's, bulk, and shear moduli of the shell of fly ash particles