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Dynamic Mechanical Analysis of Fly Ash Filled Polyurea Elastomer

In this work, the material properties of a series of fly ash/polyurea composites were studied. Dynamic mechanical analysis was conducted to study the effect of the fly ash volume fraction on the composite's mechanical properties, i.e., on the material's frequency- and temperature-dependent storage and loss moduli. It was found that the storage and loss moduli of the composite both increase as the fly ash volume fraction is increased. The storage and loss moduli of the composites relative to those of pure polyurea initially increase significantly with temperature and then slightly decrease or stay flat, attaining peak values around the glass transition region. The glass transition temperature (measured as the temperature at the maximum value of the loss modulus) shifted toward higher temperatures as the fly ash volume fraction increased. Additionally, we present the storage and loss moduli master curves for these materials obtained through application of the time-temperature superposition on measurements taken at a series of temperatures. [DOI: 10.1115/1.4002650]

Keywords: dynamic mechanical properties, polyurea elastomer, fly ash, time-temperature superposition

1 Introduction

Polyurea is the generic name for a block copolymer formed from the chemical reaction of diisocyanates with polyamines [1]. This reaction is generally very fast and not sensitive to humidity and low temperature [2]. The elastomer is stable and could be a 100% solid polymer system. Because of these advantages, polyurea has become an excellent candidate for coating applications. Its use has expanded rapidly since being commercialized in 1989 [1,3]. Over the last 20 yrs, it has been used in numerous high-profile projects such as the Boston Tunnel Project, the Incheon Airport in South Korea, and most recently, the San Mateo Bridge in California [4].

Polyurea has been studied by a number of researchers [2–5], revealing its many interesting properties. This has led to the polyurea's use beyond coating applications and in impact-resistant steel structures [6–9]. It has been demonstrated that the polyurea coating is able to enhance the energy absorption and dynamic performance of structures.

Mock and Balizer [6] applied a layer of polyurea to the back of steel plates. They have shown that under a blast energy level that catastrophically fractures the steel plate, the steel/polyurea (PU) bilayer plate withstands the blast without any fracturing. Amini et al. [7] also addressed the effect of polyurea on the dynamic response of steel plates. They studied the effect of the relative location of steel and polyurea layers with respect to the blast location. When polyurea is cast on the back face, the authors achieved similar results to Mock and Balizer [6]. Conversely, when polyurea is placed on the front face of the plate, it may actually enhance the destructive effect of the blast, promoting the failure of steel plate. Bahei-El-Din et al. [8] modified the conventional sandwich plate designs by inserting a polyurea interlayer between the outer face-sheet and the foam core. The damage is significantly reduced in the modified design because of the stiffening of the polyurea interlayer under shock compression. This stiffening provides support to the outer face-sheet and alters propagation of stress waves into the foam core. Blast resistance and damage behavior of layered and sandwich polyurea/glass fiber composites (E-glass vinyl ester) were reported by Tekalur et al. [9]. They observed substantial reduction in the maximum deformation, increase in energy absorption, and delay of fracture in the bilayers and sandwiches.

In light of the growing application of polyurea for improved impact resistance, a thorough understanding of its viscoelastic behavior is needed. The stress-strain behavior of polyurea in uniaxial tension or compression over a range of strain rates from 10^{-3} s^{-1} to 10^4 s^{-1} has been studied by many researchers [10–12]. It has been shown that polyurea demonstrated strong hysteresis, cyclic softening, and rate-dependence. Chakkarapani et al. [13] measured the bulk and shear responses of cast and sprayed polyurea and suggested a fluidlike model to describe the high strain-rate response of polyurea. Roland and Casalini [1] measured the local segmental relaxation times for the soft segments of polyurea as a function of temperature and pressure. Amirkhizi et al. [14] produced a viscoelastic constitutive model for polyurea, including pressure and temperature effects, based on experimental relaxation tests and confined and unconfined high strain-rate Hopkinson-bar experiments.

Although numerous studies have been conducted involving polyurea, only a few dynamic mechanical analysis (DMA) results were published [5,10]. Composite materials with polyurea as the matrix have not been addressed in literature either. Hence, the main goal of the present work is to develop polyurea matrix composites and study the dynamic mechanical properties of both the matrix and the composites. The filler used here is fly ash. Fly ash is the by-product of coal burning or heavy oil combustion. The use of fly ash as filler is attractive because it is inexpensive. Furthermore, it possesses low density and a porous structure. In this work, fly ash/polyurea (FA/PU) composites with various volume fractions were prepared and their dynamic mechanical properties, determined as the dynamic storage and loss moduli, were compared with those of neat polyurea elastomer. The purpose of this work is to investigate the effect of the fly ash volume fraction on the dynamic mechanical behavior of the composites. In addition, master curves of the storage and loss moduli of these materials were created using time-temperature superposition (TTS).

Table 1 Chemical composition of fly ash [15]

Chemical composition	Content (wt %)
Al_2O_3	26.07
SiO_2	58.83
K_2O	6.26
Fe_2O_3	3.64
MgO	1.57
TiO_2	1.03
Na_2O	1.16
CaO	0.74
Other	0.70

2 Experimental Details

2.1 Materials. Composites are fabricated using polyurea as the matrix material and fly ash as inclusions. The fly ash was collected from Harbin Thermal Power Station in China. It was sieved with a standard mesh sieve column on a mechanical shaker and the particle sizes in the range of 109–150 μm in diameter were selected. Generally, fly ash is composed mainly of Al_2O_3 and SiO_2. The constituents of fly ash used in this work, which were experimentally determined through X-Ray fluorescence spectrometer [15], are listed in Table 1. Figure 1 shows the scanning electron microscopy (SEM) images of fly ash particles, illustrating their spherical shape, clean surfaces, and porous walls.

The polyurea matrix is obtained from the reaction of an isocyanate and a resin blend component. The isocyanate component used is Isonate 2143L, which is a polycarbodiimide-modified diphenylmethane diisocyanate [16], and the resin blend is Versalink P1000, an oligomeric diamine [17]. It is known that in the resulting polymer, the isocyanate chains arrange into semicrystalline domains through H-bonding [18]. These hard domains are embedded within the soft domain of long flexible diamine chains.
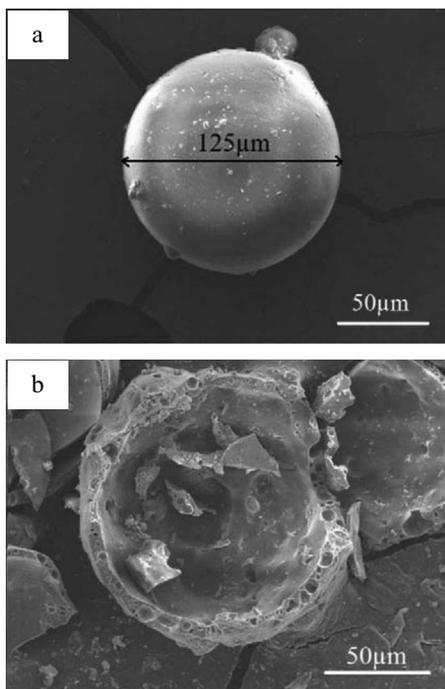

Fig. 1 SEM images of fly ash: (*a*) intact and (*b*) broken particles. Note the porous nature of the shell (the thickness of the shell is about 7 μm in image (*b*); usually, there is one layer of pores in the shell).

In theory, Isonate and Versalink must be mixed in a stoichiometric ratio of 1:1 that is the total number of isocyanate groups equals the total number of amine groups in order to avoid a product with undesirable physical or chemical properties. In order to ensure that the reaction is completed and has produced some cross-linking among the hard domains, around 10% excess Isonate 2143L is used. The amount of excess Isonate 2143L may be estimated through weight measurements of containers before and after the processing. The effect of the excess material on the mechanical properties has been discussed in literature [11,19].

2.2 Preparation of Composites. The two monomers and fly ash particles are mixed using a magnetic stirrer. Samples are cast directly in suitable Teflon molds to produce standard test specimens for the characterization of the composites.

Since the gelation time of polyurea at room temperature is very short, the working time, including mixing time, must be kept below 20 min for pure polyurea. As the volume fraction of fly ash is increased, the working time becomes shorter. Fly ash was added to Versalink P1000 (the more viscous component) prior to the polymerization process of polyurea in order to achieve a homogenous distribution throughout the matrix. The procedure was designed as follows: First, the Versalink P1000 and fly ash were mixed thoroughly to ensure the fly ash would not be removed by air in the subsequent degassing process. Second, the above blend and Isonate 2143L were degassed separately until most of entrapped air bubbles were removed. Third, Isonate 2143L was poured into the above blend and mixed with a magnetic stir bar for 5 min while also being degassed. Finally, the mixture was poured (either directly from the container or using a syringe) into the mold to obtain the test specimens. The container or syringe was positioned as close to the bottom of the mold as possible and the mixture was transferred to flow slowly and freely in the mold in order to avoid inducing air bubbles. Then the two parts of the mold were held tightly together by applying a 1 kg load externally and were placed in an environmental chamber to control the moisture (less than 10% humidity). The specimens were cured in the mold at room temperature for 1 week.

The fly ash volume fractions in the final composite were 5%, 10%, 20%, and 30%. (The corresponding mass fractions are 3.6%, 7.3%, 15.1%, and 23.4%, respectively. These fractions are calculated according to

$$m(\%) = \frac{m_{FA}}{m_V + m_I + m_{FA}} \times 100(\%) \tag{1}$$

where $m(\%)$ is the mass fraction of fly ash and m_{FA}, m_V, and m_I are the masses of fly ash, Versalink P1000, and Isonate 2143L used to make composites, respectively). At least two batches of each composite were prepared. The stoichiometric ratios of Isonate and Versalink for all these composites were within 1.08–1.13.

2.3 Tests

2.3.1 Density Characterization. The density of the material was determined through the application of Archimedes' principle by measurement of the weight of the specimen in air and in water, respectively

$$\rho = \frac{m_{air}}{m_{air} - m_{water}} \times \rho_{water} \tag{2}$$

Here, m_{air} and m_{water} are the mass of composites in air and in water, respectively, and ρ_{water} is the density of water. At least five samples were measured for each category. The average values are given in Table 2.

2.3.2 Dynamic Mechanical Properties Characterization. Dynamic mechanical analysis was conducted using a TA Instruments DMA 2980 using the corresponding software to collect and analyze the experimental data. The specimens measured approxi-

Table 2 Density of neat polyurea and fly ash/polyurea composites

Volume fraction of fly ash (%)	Density (g/cm³)
0	1.10
5	1.07
10	1.05
20	1.01
30	0.97

mately 3 mm thick by 10 mm wide and were clamped at a free length of 17.5 mm. Both ends were cantilevered, i.e., they were constrained from rotation at both ends by clamping plates and excited into a sinusoidal transverse displacement at one end at a constant strain amplitude of 15 μm. The experiments were performed over the temperature range from −80°C to 70°C, stepping upwards in increments of 3°C. At each temperature step, five frequencies of 1 Hz, 2 Hz, 5 Hz, 10 Hz, and 20 Hz were tested sequentially. Thermal soaking times of 3 min at the beginning of each step minimized the effects of thermal gradients. Liquid nitrogen was used to cool the system to subambient temperature. For each category, sets of three samples were tested, two from the same batch and the third from a secondary batch.

2.3.3 SEM. SEM was carried out using a Philips Environmental Scanning Electron Microscope (ESEM) XL30. Composite specimens were immersed in liquid nitrogen until thermal equilibrium was achieved at which point they were removed and immediately fractured with a hammer. Fragments of the composite specimens were coated with a thin layer of iridium (75 nm thick) in an automatic sputter coater and then the fracture surfaces were observed. The acceleration potential was 15 kV.

3 Results and Discussion

3.1 Density Characterization. Densities of composite specimens were determined for all volume fractions. Figure 2 shows the variation of density as a function of fly ash volume fraction. As expected, the density of the composite material decreased by increasing the volume fraction of fly ash. At a volume fraction of 30%, the density of the composite material is only 0.97 g/cm³, about 11.3% less than the neat polyurea. The decrease of density is due to the low density of fly ash particles, which is only 0.78 g/cm³, while that of the neat polyurea is 1.10 g/cm³.

3.2 Fracture Surface. Fly ash distribution and presence of agglomerates and holes were determined in all specimens by fractographs obtained by SEM. Figure 3 shows fractographs of 20% fly ash/polyurea composites. As can be seen from Fig. 3(*a*), fly ash particles are distributed in the matrix homogeneously with no signs of agglomerates or holes. As shown in Fig. 3(*b*), there are no
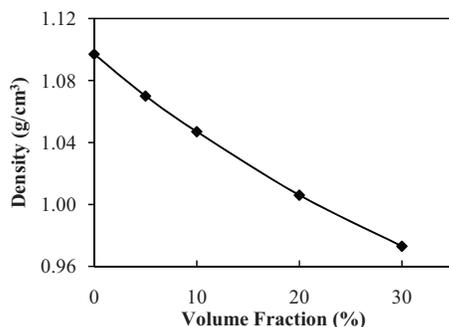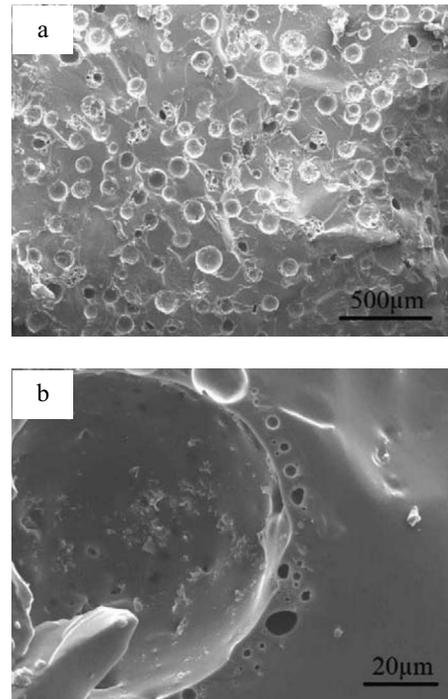
Fig. 3 SEM fractographs of 20% fly ash/polyurea composites

observable cracks or voids between the remaining fly ash and the matrix, indicating that the fly ash particles have very good interfacial adhesion with the matrix.

3.3 Dynamic Mechanical Analysis. Dynamic mechanical properties of pure polyurea and fly ash/polyurea composites are determined as the dynamic storage and loss moduli. Dynamic storage modulus is defined as the stress in phase with the strain in a sinusoidal deformation divided by the strain; it is a measure of the energy stored and recovered per cycle when different systems are compared at the same strain amplitude. The loss modulus is defined as the stress 90 deg out of phase with the strain divided by the strain; it is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation when different systems are compared at the same strain amplitude [20]. The complex dynamic modulus (E^*) is generally expressed as

$$E^* = E' + iE'' \tag{3}$$

where E' and E'' are the storage and loss moduli, respectively.

The storage and loss moduli of each specimen were obtained as functions of temperature at five different frequencies. The representative 1 Hz results are shown in Figs. 4 and 5.

3.3.1 Effect of Filler Concentration. The temperature dependence of the storage and loss moduli for the polyurea matrix and FA/PU composites with various fly ash volume fractions are plotted in logarithmic scale in Figs. 4 and 5, respectively. The storage modulus of composites decreases in the temperature region associated with the glass transition temperature as is also the case for the polyurea matrix. However, as the fly ash volume fraction increases, the storage modulus also increases. It is interesting to see that the storage modulus of 5% FA/PU composites is similar to that of the neat polyurea and the properties of 10% FA/PU composites and 20% FA/PU composites are also similar. However, great jumps occur when the fly ash volume fraction increases from 5% to 10% and from 20% to 30%. The increase in the storage modulus may be due to the fact that the addition of fly ash particulates increases the degree of cross-linking in the fly ash/polyurea composites. It is reported in literature that increase in cross-linking can reduce the difference in the values of the modu-
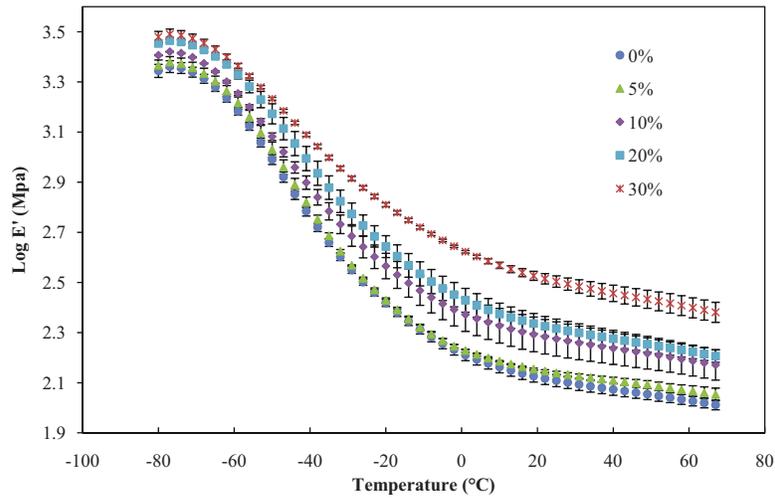
Fig. 2 The density of composites as a function of fly ash volume fraction

Fig. 4 Temperature dependence of log E' for the matrix and the FA/PU composites (the error bars represent the standard deviation and the central points are the average values of three results)

lus between the glassy and rubbery states. Consequently, it can induce a higher modulus in the plateau region [21,22]. Our experimental results in Fig. 4 are consistent with these reports.

It is noteworthy that the increase in modulus due to higher volume fraction of fly ash is more pronounced in the rubbery zone ($T > T_g$) than in the glassy region ($T < T_g$). Figure 6 shows the relative modulus E'_c / E'_m (E'_c and E'_m are the storage moduli of the composites and polyurea matrix, respectively). It can be seen that there is a jump in the relative modulus near T_g and the magnitude of this jump increases as the fly ash volume fraction increases. For the case with 30% fly ash, there is a greater than 50% increase in relative modulus as temperature passes the glass transition temperature. A theory was developed by Lee and Nielsen [23] to explain the above phenomena. Since filled systems are never perfectly dispersed, there are always some particle-particle contacts in doublets and in agglomerates containing a larger number of particles. The modulus of the composite is greater when some of the inclusions are in contact and are restrained from easily moving relative to one another. Above T_g, the polymer modulus is relatively small so the matrix does not exert sufficiently large forces

on the contacting particles to overcome their frictional contact forces or to break up their agglomerates. Then the contacting particles or agglomerates behave as large rigid inclusions. The transformation from relatively flexible agglomerates into rigid agglomerates near the T_g temperature is thought to be the major contributor to the jump in the *relative* modulus. Lee and Nielsen [23] provided an analysis relating this change in the relative modulus to the number of particle-particle contacts that is proportional to the inclusion concentration in a well-dispersed system. A secondary factor may be the change in the ratio of the modulus of the fly ash and that of the polyurea through the glass transition.

The loss modulus changes similarly. There may be two explanations for the high-temperature loss modulus-enhancement by increasing the fly ash volume fraction: First, the characteristics of the spherically hollow structure of fly ash particles can enhance energy dissipation when composites are subjected to external dynamic loads [24]. Second, as suggested by Lee and Nielsen [23], the polymer-filler slippage and particle-particle slippage at lower temperatures are hindered by the mismatch in the coefficient of thermal expansion of polymer matrix and fillers. The polymer
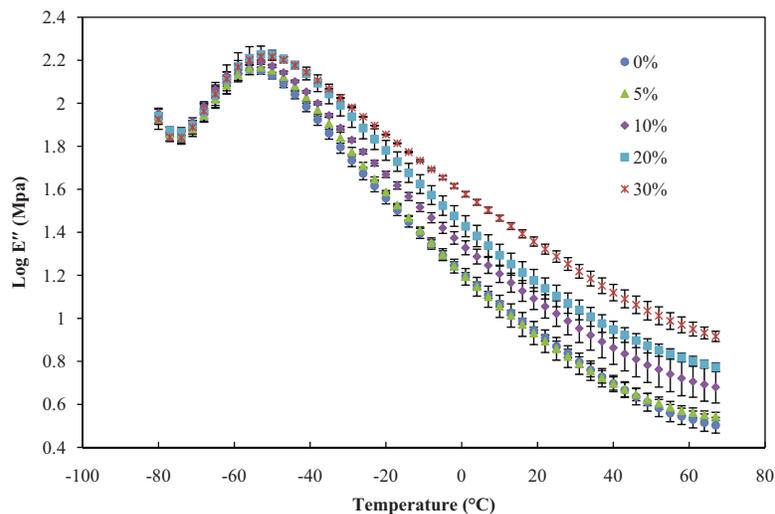

Fig. 5 Temperature dependence of log E'' for the matrix and the FA/PU composites (the error bars represent the standard deviation and the central points are the average values of three results)
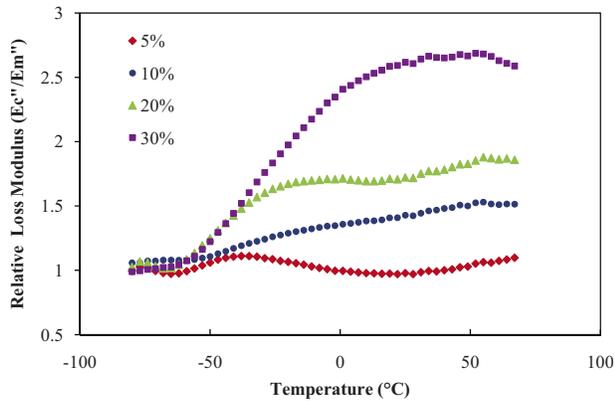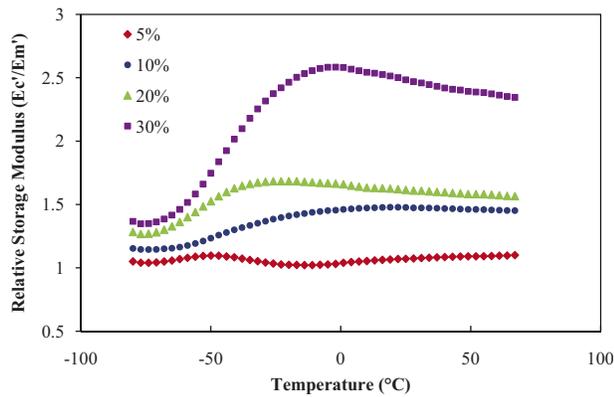
Fig. 6 Temperature dependence of relative storage (top) and loss (bottom) moduli for FA/PU composites (E_c', E_m', E_c'', and E_m'' are the storage ($'$) and loss ($''$) moduli of the composites (*c*) and polyurea matrix (*m*))

shrinks more than the fly ash and therefore the contact forces increase as the temperature is decreased, and the particle-particle slippage process dissipates more energy. Of course, it is difficult to separate direct dissipation enhancement due to localized high strains from that inherent to dissipation due to strain softening.

The material's T_g is measured as the temperature at the peak of the loss modulus is at about 1 Hz, as shown in Table 3. The temperature was stepped upwards in increments of $3\,°$C so the T_g shown here may not be very accurate. However, the increase in T_g is still observed with the increasing fly ash content. This is most likely due to the segmental immobilization of the fly ash surface. These results also suggest that the degree of cross-linking increases as a result of the addition of fly ash.

3.3.2 Time-Temperature Superposition. In order to compare the properties of composites with various fly ash contents, TTS was used as a tool to construct master curves for storage and loss moduli by using multifrequency data at a variety of temperatures (Figs. 7 and 8). Taking neat polyurea as a base-line, the procedure is examined here. An ad hoc reference temperature $T_{ref}=10\,°$C was chosen. Then logarithmic plots of the normalized modulus E^*T_{ref}/T against the angular frequency ω were produced, as shown in Fig. 9, with the normalization being performed using the

Table 3 T_g of polyurea matrix and FA/PU composites as defined by the peak of loss modulus curve at 1 Hz frequency

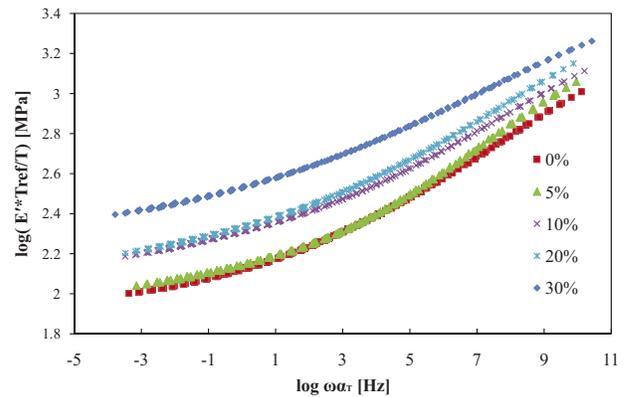| FA volume fraction (%)	0	5	10	20	30
T_g	−55.0	−54.0	−54.0	−52.0	−52.0

Fig. 7 Master curves of storage modulus for polyurea and the FA/PU composites

absolute temperature values. A MATLAB code was used to (horizontally) shift the curves at suitable distances ($\log a_{E',T_{ref}}(T)$), starting with the closest neighbors of T_{ref} and continuing sequentially. The same procedure was repeated for the loss modulus and a $\log a_{E'',T_{ref}}(T)$ table was developed. The shift factor $\log a_{T_{ref}}(T)$ at each temperature was determined as the average value of $\log a_{E',T_{ref}}(T)$ and $\log a_{E'',T_{ref}}(T)$. Finally, master curves for storage and loss moduli were constructed using $\log a_{T_{ref}}$. Note that even though the difference between $\log a_{E',T_{ref}}(T)$ and $\log a_{E'',T_{ref}}(T)$ is greater than what has been noted before, the transition between temperatures as one constructs master curves (using the average value) appears seamless and satisfactory.

The collection of the shifted curves constitutes the master curves shown in Figs. 7 and 8. These master curves represent the expected frequency dependence of dynamic properties of the material over 12 decades of frequency based on the experimental data taken over less than 2. The storage and loss moduli both increase with the increasing volume fraction of the fly ash. There are relatively large jumps in their values as the fly ash volume fraction is increased from 5% to 10% and from 20% to 30%. A similar change occurs in the temperature dependence of these properties at each frequency.

The shift factor $\log a_{T_{ref}}$, which represents the basic effect of temperature on the material's viscoelastic properties, is shown in Fig. 10. It can be seen that the composite response is not very sensitive to the volume fraction of the inclusions. However, the shift factor curve slightly deviates from the empirical curve estab-
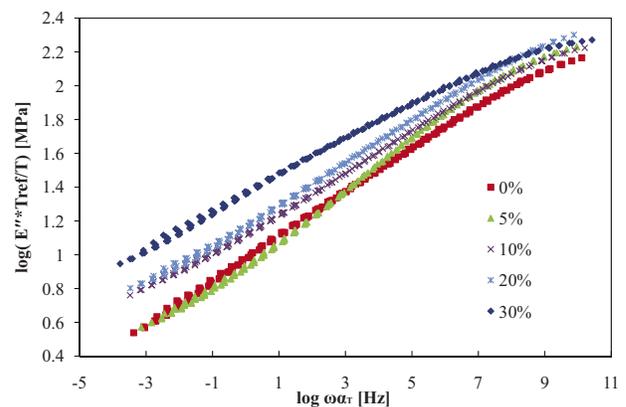

Fig. 8 Master curves of loss modulus for polyurea and the FA/PU composites
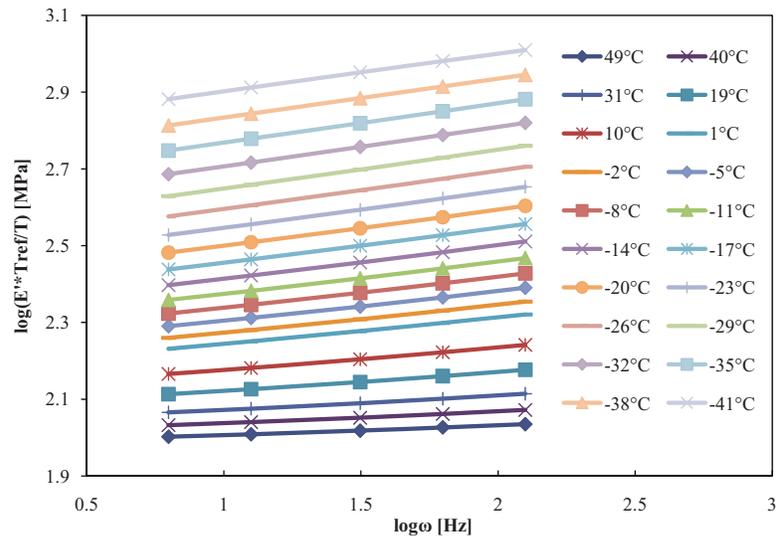
Fig. 9 Normalized storage modulus of polyurea as a function of frequency in logarithmic scale

lished by Williams et al. [25]. To demonstrate this, we calculated two different fits both based on Williams-Landel-Ferry (WLF) equation

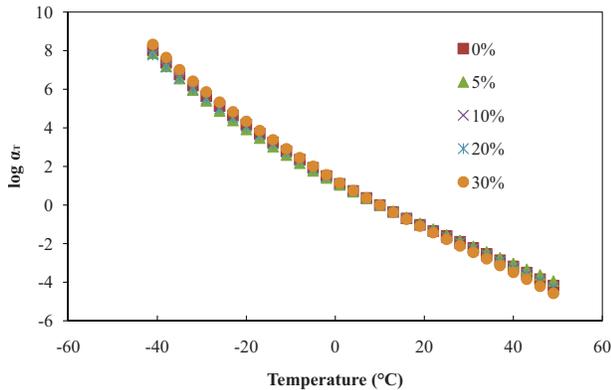$$\log a_{T_0} = \frac{-C_1(T-T_0)}{C_2+(T-T_0)} \tag{4}$$

Fig. 10 Temperature dependence of the shift factor $\log a_{T_{ref}}$ used in plotting Figs. 7 and 8

Table 4 Best fit values for C_1 and C_2 using $T_0 = T_{ref} = 10\,°C$

FA volume fraction (%)	C_1	C_2
0	27.33	226.6
5	24.2	211.7
10	29.59	241.1
20	31.83	263.3
30	34.39	265.6

Table 5 Best fit values for using T_0 using $C_1 = 8.86$ and $C_2 = 101.6$

FA volume fraction	0%	5%	10%	20%	30%
T_0	9.292	8.549	9.278	8.661	9.891

First, we found the best fit for the values of C_1 and C_2 using $T_0 = T_{ref} = 10\,°C$. The results are summarized in Table 4. Second, we started with using the empirical and universal values of $C_1 = 8.86$ and $C_2 = 101.6$ and found the best value of T_0 for each curve. These values are shown in Table 5. For computational purposes, it appears that the results in Table 4 along with the master curves in Figs. 7 and 8 may be more suitable.

4 Conclusion

Fly ash/polyurea composites with various filler contents were prepared. From the SEM photographs, the uniform distribution of fly ash and good interface adhesion between the fillers and the polymer matrix are obtained. When the volume fraction of the inclusions is 30%, the density of the composite is 11.3% lower than that of the polyurea matrix (the composite is then less dense than water).

The dynamic mechanical properties of the composites naturally change with the fly ash volume fraction. The storage modulus increases sharply with the increasing fly ash volume fraction, and a jump in the value of the relative modulus occurs in the glass transition region possibly due to the change of particle-particle contact interaction. The loss modulus also increases as the fly ash volume fraction increases. The T_g, measured as the temperature at the peak value of the loss modulus, shifts to higher temperatures at higher fly ash volume fractions, which might suggest a reduced contribution from the viscoelasticity of the polymer matrix and an elevated degree of cross-linking.

TTS was used to predict the storage and loss moduli over several decades of frequency for all materials that were studied, and the corresponding shift factor $\log a_{T_{ref}}$ was obtained.

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