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Dynamic properties of polyurea-milled glass composites Part I: Experimental characterization

Wiroj Nantasetphong[a,*], Zhanzhan Jia[a], Alireza V. Amirkhizi[b], Sia Nemat-Nasser[a]

[a] Center of Excellence for Advanced Materials, Department of Mechanical and Aerospace Engineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0416, United States

[b] Department of Mechanical Engineering, University of Massachusetts, Lowell, 1 University Ave, Lowell, MA 01854, United States

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ABSTRACT

Polyurea (PU) is an elastomer, which exhibits unique thermo-mechanical properties. It is synthesized from a di-functional amine, e.g. Versalink P-1000 and a diisocyanate, e.g. Isonate143L. In this study, various volume fractions milled glass (MG) was added to create polyuria-milled glass composites (PU-MG). Milled glass is a micro fiber with cylindrical shape. The distribution of the milled glass in the polyurea matrix was observed under the scanning electron microscope. The dynamic properties of pure polyurea and the PU-MG composites were measured by dynamic mechanical analysis (DMA) in the low frequency range (1–20 Hz) and by ultrasonic wave measurement in the high frequency range (0.5–1.5 MHz). Both experiments show that increasing the milled glass volume fraction drastically increases both the storage and loss moduli of the composites. DMA results show that dynamic Young's modulus increases with increasing frequency. However, longitudinal and shear moduli from ultrasonic wave measurement appears to be insensitive to frequency within the range of 0.5–1.5 MHz. The experimental dynamic moduli master curves of PU and PU-MG composites were constructed and compared. The relaxation function or creep compliance are generally useful than dynamic moduli for modeling of material response under complex histories. It is of practical use to convert dynamic mechanical data from the frequency domain into the time domain. The discrete relaxation spectra of the composites were calculated by fitting Prony series to the master curves, using least square nonlinear regression. Retardation spectra were then calculated using the interrelation between relaxation modulus and creep compliance in Laplace domain. Finally, the time domain relaxation modulus and creep compliance for each composite were obtained from the two spectra. In order to extend our understanding of the dynamic behavior of the PU-MG composite, micromechanical models have been created and are discussed in the accompanying paper Nantasetphong (2016a).

1. Introduction

Polyurea (PU) is a segmented block copolymer derived by the reaction of a diisocyanate component and a diamine component. Generally, polyurea is formulated to have hard segments with a high glass transition temperature (T_g) and soft segments with a low T_g. The soft phase is primarily constituted of long chain diamine, which confers flexibility to the material, and the hard phase consists of diisocyanate typically in a semi-crystalline ordered state created by hydrogen bonding, which gives an enhanced initial stiffness often followed by a yield-like event. The hard and soft domain phase separation is due to the thermodynamic incompatibility of the segmented chain blocks of polyurea (Rinaldi et al., 2011). Therefore, the microstructure of polyurea has nano-scale hard domains dispersed in the soft domain. The microstructure mechanical properties of polyurea may be tuned by using different isocyanates and amines (Rinaldi et al., 2011). Holzworth et al. also showed that even for the same chemistry, the stoichiometric ratio affects the mechanical properties of polyurea (Holzworth et al., 2013). In this study, molar ratio of isocyanate to amine groups is chosen to be 1.05 as recommended by the manufacturer (Air products chemicals inc , 2003).

Previous researches have shown that the mechanical properties of polyurea depend strongly on the strain rate, temperature and pressure (Amirkhizi et al., 2006; Roland et al., 2007; Qiao et al., 2011b; Nantasetphong et al., 2016b). It also shows strong hysteresis and cyclic softening (Yi et al., 2006). For the polyurea-based composites, not much data is available. Mihut et al. mixed silica-coated hematite hybrid nanoparticles with functionalized surfaces into polyurea and studied its mechanical properties for small and large

* Corresponding author.
E-mail address: w.nantasetphong@gmail.com (W. Nantasetphong).

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deformations as a function of the particle weight fraction. Their results indicate that significant reinforcement of the polyurea-based hybrid nanocomposite is achieved even at very low nanoparticle content with respect to the pure elastomeric matrix, due to the dual effects from multifunctional crosslinkers and reinforcing fillers (Mihut et al., 2013). Qian et al. studied mechanical behaviors of graphite-oxide/polyurea and graphene/polyurea nanocomposites. They found that the aggregation of graphite-oxide in polyurea matrix weakens the hydrogen bonds among polyurea molecules, leading to reduction in mechanical properties of polyurea, while better dispersion of graphene sheets and their larger mechanical strength improve the mechanical properties of the graphene/polyurea composite (Qian et al., 2013). Qiao et al studied polyurea with fly ash composites (Qiao et al., 2011a; Amirkhizi et al., 2011). They showed that by mixing polyurea with fly ash, the strength of polyurea increases along with decrease in density. Alternatively, glass fibers can be blended with a polymer to improve the strength of the polymer. Experiments on milled-glass-fiber-filled polyethylene terephthalate-co-isophthalate composites were conducted by Velasco et al. (2003). Their results showed a trend of increasing composite Young's modulus and tensile strength with increasing fiber volume fraction. Increasing wear and impact resistances is another advantage of polymeric composites containing milled glass fibers (Vasconcelos et al., 2005).

In this study, the micron-scale cylindrical glass fibers were introduced as the filler material into polyurea. Pure polyurea and polyurea with milled glass (PU-MG) composites with 5%, 10%, 15%, and 20% volume fractions of inclusions were created. The main contributions of this study are the following:

1. The effect of milled glass volume fraction, frequency, and temperature on dynamic mechanical properties of PU-MG composites was experimentally measured. The composites were studied using dynamic mechanical analysis (DMA) in the low frequency range of 1–20 Hz and –80–50 °C and through ultrasonic wave measurements in the high frequency range of 0.5–1.5 MHz and –50 to 30 °C.
2. The energy dissipation behavior of PU and PU-MG composites were studied, considering volume fraction, frequency, and temperature.
3. The master curves of PU and PU-MG composites were constructed with the assumption that PU and PU-MG composites are thermorheologically simple. These curves contain the material information over wider ranges of frequency than can be obtained from a single standard experimental technique. These master curves and their parameterization in selected ranges of strain rates/frequencies and temperatures may be used for robust computational modeling of complex structures that include these composites as layers, dampers, or high strain-rate stiffeners and stabilizers (Barsoum, 2015; Zhao et al., 2007; Agrawal et al., 2016). While, the comparison of the master curves obtained from DMA with the ultrasonic results show that this assumption is justified for use in storage modulus, it was observed that the loss modulus at higher frequencies is consistently higher than what is predicted from DMA master curves. This indicates the presence of enhanced dynamic loss mechanisms at ultrasonic frequencies and underlines the need for further modeling that can capture these effects.
4. Discrete relaxation and retardation spectra, as well as uniaxial relaxation function and creep compliance of the composites were calculated. The discrete relaxation and retardation spectra can be used with finite element programs for designing and analysis of the composites, under dynamic and unsteady load histories. A small modification to the formulation previously presented in Baumgaertel and Winter (1989) was realized for the solid viscoelastic cases. The effect of volume fraction of milled glass on the profiles of the relaxation and compliance were studied.

Additionally, in our accompanying paper, micromechanical models will be discussed and used as a computational tool to estimate mechanical properties of the composite and to extend our understanding of their dynamic behavior (Nantasetphong et al., 2016a). These models are not limited to PU-MG composite and can be directly used for other composites with similar particulate microstructure; see for example Qiao et al. (2016).

2. Material fabrication

In this study, Isonate 143L (The dow chemical company, 2001), which is a polycarbodiimide modified diphenylmethane diisocyanate, was used with the diamine Versalink P-1000 (Air products chemicals inc, 2003), which is a poly(tetramethyleneoxide-di-p-aminobenzoate). The milled glass was purchased from Fibertec, Inc. (product number 3032). The fibers have an average diameter of 16 μm, average length of 200 μm, and average density of 2.5 g cm^3. PU-MG composites of volume fractions of 5%, 10%, 15%, and 20% were fabricated, as well as PU with no MG (PU-0%MG). The composite fabrication procedure is shown elsewhere (Jia et al., 2016). The nominal dimension of the DMA samples was 3 mm × 10 mm × 20 mm. Two DMA samples from the same batch were fabricated for each milled glass volume fraction. The nominal dimension of the ultrasonic test samples were 25.4 mm (1 inch) in diameter and 6mm in thickness for longitudinal waves, and 76.2 mm in diameter (3 inch) and 0.7 mm (hereafter referred to as thin) or 1.2 mm (thick) in thickness for shear waves. Two longitudinal-, one thick and one thin shear-wave-test samples were fabricated for each volume fraction.

3. Characterization

3.1. Dynamic mechanical analysis

Dynamic mechanical analysis was conducted on a TA Instrument Dynamic Mechanical Analyzer 2980. The experimental data was collected and analyzed using the Universal Analysis software to obtain storage modulus E', loss modulus E'', and $\tan\delta$. During the test, the sample was cantilevered at both ends with a free length of 17.5 mm between the clamps. One end of the sample was fixed, and the other end was attached to the movable clamp, which oscillated harmonically with amplitude of 15 μm. The temperature range of the test was –80 to 50° with 3 °C increments for each step. The sample was equilibrated at each temperature point for 3 min before the frequency sweep. The tested frequencies were 20 Hz, 10 Hz, 5 Hz, 2 Hz, and 1 Hz, stepping down sequentially for each sweep. Liquid nitrogen was used to cool the system down to subambient temperatures.

3.2. Scanning electron microscopy

The fractured surfaces of polyurea with milled glass composites were observed using a Philips Environmental Scanning Electron Microscope XL30 scanning electron microscopy (SEM).

The fractured surface was coated with 75 nm of iridium in an automatic sputter. DMA and longitudinal-wave-test samples were cross-sectioned, fractured, and observed under SEM. It shows that the milled glass fibers are randomly dispersed in the polyurea matrix as shown in Fig. 1. The milled glass fibers in shear-wave-test samples, as shown in Fig. 2, tend to lie parallel to the surface of the samples due to fabrication process needed to achieve such thin samples. The mixture has to flow parallel to the surface of the top and bottom glass plate molds and this will naturally push the fibers to rearrange themselves parallel to the two plates as well.