

Milled Carbon Fiber Polyurea Elastomeric Composites



V. Alizadeh and A. V. Amirkhizi

Abstract Polyurea is one of the widely used materials in the coating industry and is well known to form a mechanically robust elastomeric network. Due to its toughness and ease of application, it has been studied as a potential protective coating in cavitation erosion conditions. The temperature rise within the polyurea under such harsh loading conditions can lead to significant softening and rapid failure of the coating, while in slightly lower intensity situations the coating may not show any signs of damage. Therefore, controlling the temperature rise due to dissipative heating may lead to better and more reliable coatings. Reinforcing the polyurea with milled carbon fibers not only has the benefit of increasing its thermal conductivity (hence distributing localized heating to larger volumes), it could also increase its stiffness, while maintaining its elastomeric nature (in contrast with continuous fiber composites). The milled fibers may be dispersed within the polyurea matrix in 3D randomly oriented arrangements or may be aligned parallel to the coated surface in very thin layers. The aim of this study is to investigate the thermal and mechanical behavior of such composites. The matrix polyurea specimen is synthesized by reacting a mixture of medium length diamine (Versalink P-650) with isocyanate 143 L. Thermal phase transition (DSC) and thermal conductivity measurements (using MDSC) are performed to accurately measure the thermal properties of such composites. DMA tests are conducted to construct the storage and loss moduli master curves. Stress-strain curves under uniaxial loading at high strain rates are obtained using split Hopkinson pressure bar (SHPB). Results show a significant increase in thermal conductivity and stiffness. The presented study assesses the feasibility of improving elastomer-based coatings for protection against harsh cavitation erosion conditions.

Keywords Polyurea · Carbon fibers · Split Hopkinson Pressure Bar · Thermal conductivity · Dynamic properties

Introduction

Polyurea (PU) is currently used as one of the robust material choices in the coating industry, owing to its fast curing in the absence of catalyst at a wide range of temperature and humidity conditions and without significantly affecting its microstructure and properties. Application of polyurea elastomeric coating to the interior of the walls of retrofitted buildings was able to prevent the failure, collapse, and fragmentation of the structure [1]. Further use of polyurea with fabrics like carbon woven materials, Kevlar, and E-glass demonstrated the improved energy dissipation and shock resistance properties under dynamic and impulsive loadings both in air and water [2, 3]. Experimental studies showed that the polyurea coating temperature is increasing under repetitive loads such as those induced by bubble collapse observed in cavitation erosion phenomenon [4]. Introducing carbon fibers within the polyurea matrix can enhance its thermal conductivity which may lead to better performance under the aforementioned loading conditions [5]. Moreover, increase in stiffness while maintaining the elastomeric nature of the composite is another advantage of such approach, which are expected to improve shock resistivity of these particulate composites.

The goal of this study is to investigate thermo-mechanical properties of the reinforced polyurea with milled carbon fiber particulates. Two different volume ratios for carbon fibers, 10% and 30%, are studied and results are discussed. Experimental methods used to determine the thermal properties of the reinforced polyurea are differential scanning calorimetry (DSC) and modulated DSC (MDSC) and provide glass transition temperature, specific heat capacity, and thermal conductivity. Extraction of mechanical properties involves quasi-static and high strain-rate tests using DMA and SHPB, respectively. SHPB tests includes both uniaxial stress and uniaxial strain configurations.

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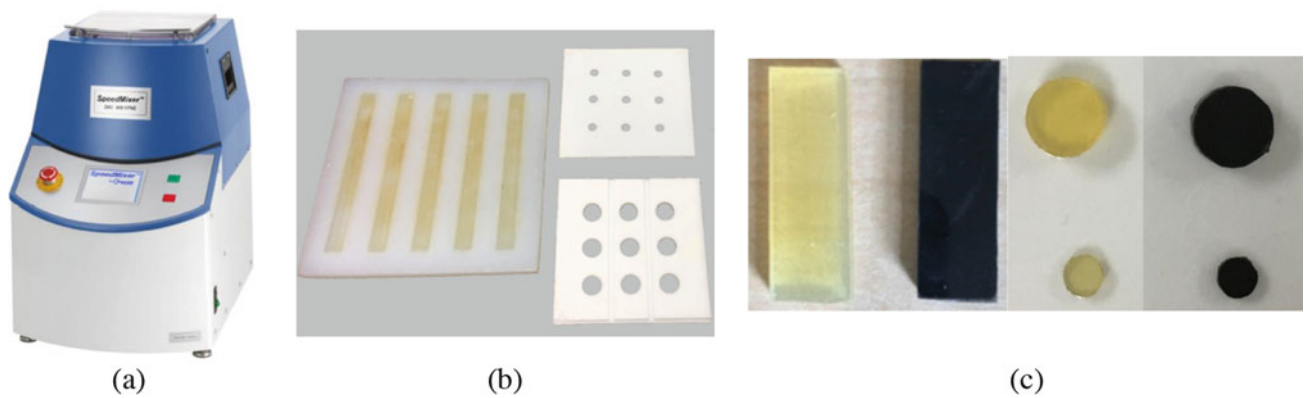


Fig. 1 (a) FlackTek DAC-600.1 VAC-P speed mixer, (b) Teflon molds for DMA and SHPB tests, (c) Polyurea samples for DMA and SHPB tests (the black samples have milled carbon fiber inclusions)

Fig. 2 Differential scanning calorimetry (DSC) instrument



Sample Fabrication

The matrix polyurea specimen is synthesized by reacting a mixture of medium length diamine Versalink P-650 (VP-650) (Air Products) and isocyanate 143 L (Dow Chemicals) at room temperature. Versalink amine was preheated for 5 h to dry and remove water then stored with molecular sieves to maintain low level of moisture. First the VP-650 is mixed with carbon fibers (Zoltek PX30) at 1000 rpm for 2 min and degassed under vacuum (-900 mbar) at room temperature using FlackTek DAC-600.1 VAC-P speed mixer. Then the homogeneous VP-650 and carbon fibers compound was mixed with isocyanate. The mixture was cast in Teflon molds and kept in desiccator for 24 h. Samples were then heat cured at 80 °C under vacuum for 24 h to achieve complete cure and network formation. Figure 1 depicts the speed mixer used along with the Teflon molds and polyurea samples.

Differential Scanning Calorimetry (DSC)

Thermal phase transition of polyurea was investigated using TA-Q800 DSC instrument. The heat flow was measured over the temperature range of -80 to 200 °C. The operation was performed in heating and cooling cycles at 10 °C/min rate. This test method was used to determine polyurea glass transition temperatures and enthalpies of fusion. Transitions were investigated using midpoint inflection method to calculate T_g . Figure 2 shows the DSC instrument used for this study.

Thermal Conductivity Measurements

Thermal conductivity is a crucial factor in energy dissipation applications. Modulated DSC (MDSC) approach is suitable for the determination of thermal conductivity (k) of polyurea samples if k lies in the range of 0.1–1 W/mK. In MDSC tests samples are exposed to a cyclic (sinusoidal modulation) thermal profile superposed on a linear ramp. The resultant experimental data after deconvolution gives reversing (heat capacity) and non-reversing components of the heat flow. For small samples, whose temperatures are uniform throughout the test, this provides a very good partition of the two components. However, for a large sample the assumption of temperature uniformity is not reasonable, and the heat flow is affected by the thermal conductivity within the material. After determining the specific heat capacity, C_p , using a small sample, a much taller cylindrical sample is tested similarly to measure its apparent heat capacity C . The cylindrical sample is exposed to a temperature modulation at one end, while the other end can only be heated by the conduction through its height. Therefore, the measured apparent heat capacity is lower in comparison with the specific value. The observed thermal conductivity of the sample k_o may be estimated as [6],

$$k_o = \frac{8lC^2}{C_p m d^2 p}, \quad (1)$$

where, C_p is the specific heat capacity of the material, p is the modulation period, and l, d, m, C , are the cylindrical sample's length, diameter, mass, and apparent heat capacity, respectively. To account for the heat loss through the material (from the sides) a correction (calibration) factor D need to be defined. The corrected thermal conductivity can be calculated as,

$$k = \frac{k_o - 2D + \sqrt{k_o^2 - 4Dk_o}}{2}; \quad D = \sqrt{k_o k_{ro}} - k_r, \quad (2)$$

where, k_{ro} and k_r are the observed and actual thermal conductivities of a reference material. Polystyrene has been used for this reference measurement. In the present work, the reversing heat capacity of samples were estimated between -40 and 40 °C using MDSC with temperature increments of 5 °C, modulation amplitude and period of 1 °C and 80 s, respectively. Thermal conductivity measurements were performed at $-25, 0,$ and 25 °C with modulation on samples of diameter $d = 4 \pm 0.2$ mm and height $l = 4 \pm 0.2$ mm.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical tests were performed in a single cantilever bending configuration (single beam cantilevered at both ends) with beam length of 17 ± 0.25 mm in temperature step mode with a frequency table of 0.5, 1, 2, 5, 10, and 20 Hz at a temperature step of 5 °C/min from -80 to 50 °C. The isothermal time for each step was 3 min and the initial amplitude was set at 15 μm. The width and thickness of the samples used for DMA were 11.7 ± 0.05 and 4 ± 0.25 mm, respectively.

Split Hopkinson Pressure Bar (SHPB)

A quick opening of the compressed gas valve launches the striker bar, which travels down and impacts the incident bar. The impact generates an elastic compression wave, which travel along the incident bar and then loads the sample. Once the wave reaches the sample, a part of wave is transmitted through the specimen to the transmission bar (transmitted wave) and a part is reflected (reflected wave) back to the incident bar. The incidence, transmitted, and reflected waves are recorded by the strain gages mounted at the same distance from the sample on the corresponding bars. The stress and strain rate within the sample are generally estimated as,

$$\sigma(t) = \frac{A_0}{A} E_0 \varepsilon_T(t), \quad \dot{\varepsilon}(t) = -\frac{2c_0}{L} \varepsilon_R(t), \quad (3)$$

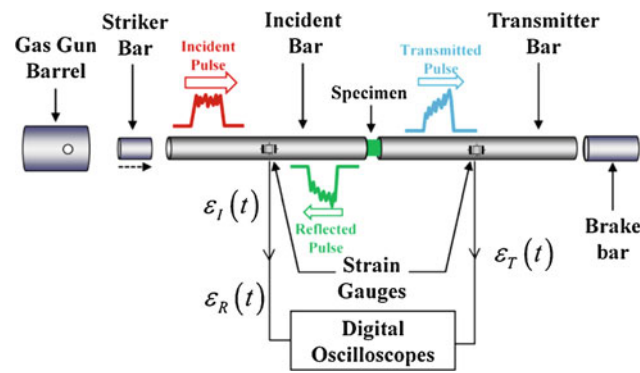


Fig. 3 Schematic view of the SHPB apparatus

where E_0 , A_0 and c_0 are the Young's modulus, cross-sectional area and sound speed of the split-Hopkinson bars, respectively. $\varepsilon_T(t)$ and $\varepsilon_R(t)$ are the measured transmitted and reflected strain signals in the bars and A and L are the cross-sectional area and length of the sample.

Samples were tested under uniaxial stress compression (unconfined) at different strain rates from 3000 to 12,000/s at room temperature. They were also tested under nearly uniaxial strain compression (confined) at strain rate of around 3500/s. The variation in the strain rate is accomplished by varying the striker bar impact velocity. For the nearly uniaxial strain tests, samples have 12.7 ± 0.1 mm diameter with 5 ± 0.1 mm length. The uniaxial stress loading configuration samples have 6.5 ± 0.1 mm diameter and 2 ± 0.1 mm length.

Conclusions and Summary

Results showed that introducing carbon fibers within the polyurea structure can increase heat capacity and thermal conductivity of the polyurea matrix quite substantially. Polyurea having higher volume ratios of carbon fiber inclusions shows more resistance to temperature elevations (higher heat capacity) and higher heat diffusion (higher thermal conductivity). DMA and SHPB results also show much higher stiffness at low and high strain rate loading conditions while the loss is not affected comparatively.

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