Characterization and Damping Property of a Modified Polyurea Material

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ABSTRACT: Polyurea material has been used extensively as protective material in military, civil, marine engineering and other industries. The mechanical properties, thermal stability, damping performance and morphology of a modified polyurea material were investigated in this paper. Its properties were characterized by tensile testing, thermo gravimetric analysis (TGA), differential scanning calorimeter (DSC), scanning electron microscope (SEM), dynamic mechanical analyzer (DMA) and so forth. The thermal stabilities of this material were studied by means of TGA. The results of differential scanning calorimeter (DSC) and dynamic mechanical analysis (DMA) were used to identify the glass transitions region of the material. The temperature and frequency dependent storage modulus, loss modulus and loss factors were measured. The glass transition temperature of the material obtained through the DSC was -44.5 ℃ and 33.7 ℃ for $T_{gs}$ and $T_{gh}$, respectively. The internal structural morphology was obtained by SEM images and analyzed to explain the damping performance in regard to the structure aspect. The results of this study showed that the modified polyurea material has excellent damping performance and can be used as a damping material to control vibration.

KEYWORDS: Polyurea, Damping performance, Viscoelasticity, Dynamic mechanical analysis

1. INTRODUCTION

Polyurea has been widely used in structural protection for military purposes to mitigate natural disasters, collisions, blasts and explosives due to its excellent performance, such as good adhesion, high thermal stability, corrosion resistance, high ductility and great mechanical properties (Qiao et al., 2011; Roland and Casalini 2007; Shim and Mohr 2009). The properties of polyurea has been investigated by numerous researchers, including high and low strain rate behavior and viscoelastic behavior of polyurea (Grujicic et al. 2012; Qiao et al. 2011; Raman et al. 2013; Roland et al. 2007; Sarva et al. 2007; Yi et al. 2006; Zhao et al. 2007). As a viscoelastic material, the properties of polyurea are strongly strain rate-dependent. Typical dynamic mechanical analyzer are limited to frequencies below 100 Hz, although the high strain rates can be obtained by
using custom-built instruments (split Hopkinson pressure bar, SHPB) and time-temperature superposition (TTS) principle (Qiao et al. 2011; Roland et al. 2007). A lot of works have been done over the strain rate range from $10^{-3}$ s$^{-1}$ to $10^{4}$ s$^{-1}$ by means of SHPB system and the high frequency even to $10^{7}$ s$^{-1}$ based on the TTS principle has been carried out (Roland et al. 2007; Zhao et al. 2007). More recently, it has been validated that the polyurea coating has potential to absorb energy as a damping material when used in metallic structure systems or used as an inserted layer in a blast-tolerant sandwich structure to resist transient impacts. Mock and Balizer (2005) investigated a composite structure system of polyurea and steel plates under a blast energy. No fracture can be found on the steel/polyurea composite plate structure. Recently, the behavior of the steel/polyurea bilayer plate subjected to high velocity impacts was investigated and a reducing damaging effect of polyurea was found (Mohotti et al. 2013; Roland et al. 2010; Xue et al. 2010). Furthermore, Mohotti et al. (2014) also investigated the capability of polyurea to absorb the impact energy and protect the plates with respect thickness of polyurea layer on rigid blunt-nosed projectile impacts and low velocity impacts (5–15 m/s). Amini et al. (2006; 2010) studied the transient response of polyurea coated steel plates by numerical analysis and experiment, analyzing the impact direction, the thickness of polyurea layer, and the bonding strength between the two materials.

Numerous studies have been conducted involving polyurea, however, only a few dynamic mechanical analysis (DMA) results were published (Qiao et al. 2011). Moreover, the composite systems were most focus on the study of impact direction thickness of polyurea layer and the impact velocity rather than the damping performance of polyuria, which is equally important to the system. In this paper, a modified polyurea was investigated, including the mechanical properties, thermal stability, microstructure and dynamic mechanical behavior, especially.

2. EXPERIMENTAL

2.1. Materials

The modified polyurea was obtained from the reaction of a polycarbodiimide-modified diphenylmethane diisocyanate and amine terminated polyether (Qtech-413, Qingdao Shamu International Trade Co., Ltd). The stoichiometric ratio of 1.05:1 isocyanate to amine was used to ensure that the reaction is completed. First, the two components were degassed separately under 1 torr vacuum until most of the entrapped air bubbles were removed. Then, they were mixed for a few seconds sprayed on a Teflon mold by PHX-40 machine (PMC instrument) to get the test samples. Prior to measurements, the samples were cured at room temperature (25°C) for two weeks under an environmental condition.
2.2 Mechanical properties

The basic properties, especially mechanical performance of the material was characterized by solid content, hardness, tensile strength ($\sigma_{\text{max}}$) and elongation at break ($\varepsilon_b$). Three standard dumbbell-shaped specimens made by model MZ-4102 were used for each test. The hardness of the material samples was determined using Shore-A durometer, MZHU Model LX-A. The tensile tests were performed by MZ-400 tester with a strain rate of 5 mm/min at room temperature. The average of tensile strength [$\sigma$] and elongation at break ($\varepsilon$) were calculated from three samples.

2.3 Procedure and sample preparation for TGA

The thermal stability was determined by thermogravimetric analysis (TGA) with TGA/DSC 1 series apparatus, model SDT-Q600 of TA instruments. Samples in an alumina crucible with approximately 5mg mass were heated from 50 to 700 $^\circ$C at a heating rate of 10 $^\circ$C/min under nitrogen atmosphere (flow of 100mL/min).

2.4 Procedure and sample preparation for DSC

Model DSC. 204 F1 (NETZSCH, Germany) was employed by the differential scanning calorimeter (DSC) analyses. The samples were heated at a rate of 10 $^\circ$C /min under nitrogen from -90 to 100 $^\circ$C to study glass transition temperature ($T_g$) of the material.

2.5 Procedure and sample preparation for DMA

Dynamic mechanical analysis (DMA) were conducted on model DMA. 242 (NETZSCH, Germany) to analyze the glass transition temperature and dynamic mechanical properties of the samples. Rectangular samples with the dimensions of 10.00x4.00x2.26 mm$^3$ were prepared. The measurements were taken in double-cantilever mode and the displacement amplitude was set as 30$\mu$m. Six excitation frequencies of 1, 5, 10, 25, 50 and 100 Hz were tested sequentially. The experiment covered the temperature range of -80 to 100 $^\circ$C at a scanning rate of 3 $^\circ$C/min. The storage modulus (E’), loss modulus (E’’), and loss factors (tan$\delta$) of the samples were measured as a function of temperature and frequency.

2.7 Procedure and sample preparation for SEM

Scanning electron microscope (SEM) equipment JSM-5600 (JEOL instrument, Japan) was used to examine the surface morphology of the cut section of the sample. The samples were placed on top of a circular platform and then plated with gold base. The samples were examined at 35x and 100x magnifications using an accelerating voltage of 20 kV.
3. RESULTS AND DISCUSSION

3.1 Mechanical properties

The solid content of the material was 95.09%, signifying it offers a high solid content and is an environmentally friendly material. The hardness of the samples was 85±1 Shore A. It can be read from the stress–strain curve (Fig. 1) the tensile strength \( \sigma_{\text{max}} \) was 6.2 MPa, and elongation at break \( \varepsilon_{\text{b}} \) was 340.4%, indicating that the modified polyurea material behaved as thermoset polyesters and exhibited satisfactory mechanical performance.

![Stress–strain curves of the modified polyurea.](image1)

**Figure 1. Stress–strain curves of the modified polyurea.**

3.2 Thermal studies

The thermal behavior of the new polyurea material was studied by TGA and the thermal gravimetrical trace is shown in Fig. 2. Within the experimental temperature range, it can be found the thermograms exhibited a single-step decomposition profile with an initial decomposition temperature \( T_{\text{initial}} \) starting 215.2 °C, which can be tentatively used to evaluate the stabilities. The 50 wt% loss temperature \( T_{50\%} \) and final decomposition temperature \( T_{\text{end}} \) are 382.8 °C and 529.2 °C, respectively. The mass loss was attributed to the decomposition of the material and the residue at last is approximately 6.6%.

![TGA traces of modified polyurea with a heating rate of 10 °C/min under nitrogen.](image2)

![DSC traces of modified polyurea at a scanning rate of 10 °C/min.](image3)

**Figure 2.** TGA traces of modified polyurea with a heating rate of 10 °C/min under nitrogen.

**Figure 3.** DSC traces of modified polyurea at a scanning rate of 10 °C/min.
The glass transition temperature, i.e., \( T_g \), marks the transition from the glassy (solid) state to the liquid or rubbery state. For common polymer materials, this glass transition covers a temperature range of about 20-50°C. Fig. 3 displays the DSC traces of the material, in which the glass transition temperature \( T_g \) values can be obtained from the change in the slope of the heat flow vs. temperature curve (Sadeghinia et al., 2012). There are two \( T_g \) values for the material: \( T_{gs} \) and \( T_{gh} \), which are related to the soft segment and hard segment, respectively. The two values indicate micro-phase separation morphology of the material (Das et al. 2007; Fragiadakis et al. 2010; Huang and Lv 2010; Lv et al. 2007). As it can be seen in Fig. 3, \( T_{gs} \) is about \(-42.5^\circ C\) and \( T_{gh} \) is around \(33.7^\circ C\). The hard segment and crystalline structures are typically dispersed in the continuous soft segment matrix providing good mechanical properties. Mechanical properties and glass transition region can be controlled by changing the proportion of the two segments (Pathak et al. 2008).

3.3 Dynamic Mechanical Properties

The glass transition is a kinetic process which depends on both the measurement method and the data evaluation procedure. The \( T_g \) values also can be obtained from DMA data. Fig. 4 and Fig. 5 clearly show the changes of storage modulus (\( E'\)), loss modulus (\( E''\)), and loss factor (\( \tan\delta \)) as increasing the temperature and frequency. The dynamic properties reflect the amount of the energy stored as elastic energy and the amount of energy dissipated during the strain process. \( E' \) can assess the elastic property of the material and represent the modulus in bending of specimens. With the temperature increasing, \( E' \) dropped rapidly and then reached a plateau. At high temperature range, the elongation rubbery modulus keeping a constant value and signifying it is independent of the frequency as showed in Fig. 4.

\( E'' \) can represent the quantity of energy absorbed by the material under the action of alternating stress, signifying the viscous performance of the viscoelastic material. It can be seen from Fig. 4, that \( E'' \) first increased with the temperature increasing and got the maximum value around the temperature of \( T_g \), and then dropped rapidly due to the change in intramolecular friction (Jiang et al. 2012). The peak of \( E'' \) profiles for the material shifted to high temperature in response to the increasing of frequency. Furthermore, the peak value of \( E'' \) tended to be high with increasing frequency.
The tan δ is the ratio between the loss modulus and the storage modulus, representing the so-called loss factor, where $\delta$ equals the phase angle between the stress and the strain. The loss factor is an evaluation index of energy dissipated by the material. It was obviously observed that the peak of the tan δ increased with the increase of the frequency as shown in Fig.5. In this paper, the glass transition temperature $T_g$ was defined as the temperature, where the loss factor reached a extreme value. The higher frequency of excitation, the higher $T_g$ was found for the material as plotted in Fig.6. The maximum loss factor value was located around $T_g$ where the chain segments began to move and the stronger intramolecular friction should be overcome. When the temperature exceeded $T_g$, the tan δ value dropped due to the relatively easier movement of the chain segments at higher temperature.

As can be seen from Fig.4, $E_r$ (Elongation rubbery modulus) is independent of the frequency, but mostly influenced by temperature. However, in the glass transition region, the frequency dependent effects can be seen clearly. Here, in order to reduce the influence of frequency on loss factors, the peak positions of 1 Hz tan δ curves were taken as the DMA glass transition temperature. The values of -4.5 °C and 64.5 °C were obtained for $T_{gs}$ and $T_{gh}$, respectively, which were higher than the results obtained from DSC. The reason caused this phenomenon is that the glass transition is a kinetic process, which takes place in a certain temperature and time range. As a result, $T_g$ values depends on both the measurement method and the data evaluation procedure (Amirkhizi et al. 2006; Sadeghinia et al. 2012).
Figure 6. $T_g$ obtained from loss factors vs. temperature curves:
(a) $T_{gs}$ at low temperature, (b) $T_{gh}$ at high temperature.

3.5 SEM

The morphology of the material is also important to determine the damping properties of the material. The fracture surface of the modified polyurea material was obtained by SEM and the distribution and presence of the holes are showed in Fig.7. As it can be seen, there are many holes in the fracture surface due to the reaction of isocyanates and water resulted in the reaction speed, which can lead air into the system. It belongs to porous material, and can explain the material damping from the perspective of the material morphology. The statistical results of the holes were plotted in Fig.8. The aperture of nearly 72% holes are less than 150μm and most of them are unconnected.

Figure 7. SEM images of fractured surface of the material, distribution and presence of the holes.
4. CONCLUSIONS

In this work, a modified polyurea was studied, including mechanical properties, thermal stabilities, microstructure and dynamic mechanical behavior. The tensile strength $\sigma_{\text{max}}$ of this material was 6.2 MPa, and elongation at break $\varepsilon_b$ was 340.4%. TG curves suggest that the initial decomposition temperature ($T_{\text{initial}}$) starting at 215.2 °C, and the residue at last is approximately 6.6%. The effect of the frequency on dynamic mechanical properties was investigated and the result shows that the modulus and loss factor increased with increasing of frequency, but for high temperature, the modulus are not rate dependent. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were conducted to investigated viscoelastic properties in the glass transition region, and two $T_g$ values were found, i.e., $T_{gs}$ and $T_{gh}$, because the micro-phase separation morphology of the material. The glass transition is a kinetic process, and strongly depends on both the measurement method and the data evaluation procedure. $T_{gs}$ is about -42.5 °C and $T_{gh}$ is around 33.7 °C determined by DSC, however, values of -4.5 °C and 64.5 °C were obtained for $T_{gs}$ and $T_{gh}$, respectively, when the test frequency was 1Hz of DMA. From the SEM photographs, the distribution of holes on the fracture surface is obtained, which can account for the damping partly.

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REFERENCES


