Morphology, Thermal Degradation and Dynamic Mechanical Properties of Polyurea used as Explosive-Proof Elastomer

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Abstract. It is well known that the blast affected the explosion and terrorism, not only human life, but also the building structure. In order to prevent these, protective materials are developed. One of them is polyurea. In this work, the elemental composition and microstructure of the selected polyurea sheet samples are characterized. Thermal, dynamic mechanical, tensile, and hardness properties are also studied. It is found that carbon and oxygen are the main compositions, while silicon, fluorine, and titanium are presented as minor ones. The modulus and loss factor increase as the frequency and temperature increase. The elongation property is over 100% and the hardness is around 90 Shore A.

1. Introduction

Because of the destroying property of the explosion, it is manifested that the blast and fragmentation can affect the injury and death [1-3]. It is revealed that some elastomeric polymers can improve the coated structure from the blast of the explosion. Polyurea is one of them, which consists of both soft and hard regions [4-8]. It is applied for civilian and military purposes.

It is well known that the dynamic mechanical properties of materials consisted of storage modulus (\(E'\)), loss modulus (\(E''\)) and loss factor (\(\tan \delta\)). These values considered the amount energy stored as the elastic energy and the energy dissipated during the straining process. The \(E'\) is defined as evaluated the elastic property of the materials and represented the modulus in the bending of specimens. It decreases rapidly and then reaches a plateau, according to the temperature increased. Until at higher temperatures, the elongation rubber modulus maintains a constant value and independent with the frequencies. The \(E''\) which is exhibited the amount of the energy absorbed by the materials under the alternating stress action indicated the viscous performance of the viscoelastic materials. It increases with the temperature increased to the maximum value around the glass transition temperature (\(T_g\)) and then decreased rapidly affected by the change in the intramolecular friction. The \(\tan \delta\) is defined as the ratio between the \(E''\) and \(E'\) and where the \(\delta\) equaled the phase angle between the stress and the strain. The peaks of the \(\tan \delta\) increased as the frequency increased. It is also revealed by other authors that the changes of these dynamic mechanical properties, such as \(E'\), \(E''\), and \(\tan \delta\) are varied with the temperature and frequency increase [9-17].

This work, the microstructure and elemental composition of polyurea samples are studied using a scanning electron microscope coupled with an energy dispersive X-ray spectrometer (SEM-EDS). Thermogravimetric (TG), dynamic mechanical analysis (DMA), universal testing machine (UTM),
and Shore A durometer are carried out to test the thermal, dynamic mechanical, tensile, and hardness properties, respectively.

2. Experimental

2.1 Sample

Five samples of polyurea sheets were selected from various products of the Seashore Resources Pte.Ltd. (Singapore), which made by the spray coating technology. They were the difference in colorations, such as dark-gray, gray, light gray, red-brown and smoke gray, labeled as PU-1, PU-2, PU-3, PU-4, and PU-5, with the thickness of 0.43, 2.08, 1.60, 1.82 and 1.07 mm, respectively, as shown in figure 1.

![Figure 1. The polyurea sheet samples](image)

2.2 Methods

2.2.1 SEM-EDS. The microstructure and elemental composition of the samples were analyzed using a scanning electron microscope (SEM) QUANTA 450 (FEI Company, USA) coupled with an energy dispersive X-ray spectrometer (EDS) X-Max (Oxford Instruments, UK) at the Science Equipment Center of Faculty of Science (Kasetsart University, Thailand). The SEM system was operated at 15 kV, and magnification of 10,000X and 30,000X. Quantitative analysis of the XRF spectra was performed using the INCA program (Oxford Instruments, UK). Prior to characterize, their surface was coated with gold using Sputter coater SC7620 (Quorum, UK). For each sample, X-ray spectra were reported at three different positions.

2.2.2 Thermal degradation. The thermal degradation of the samples was analyzed by a TGA2 (Mettler Toledo, Switzerland) at the Mettler-Toledo (Thailand) Limited (Bangkok, Thailand), with approximately 9.50± to 1.00 mg. sample weight, under the nitrogen atmosphere at a heating rate of 10°C/min. from 25 to 700°C. For each sample were conducted three records to assure acceptable results.

2.2.3 Dynamic property. The dynamic properties of the samples were carried out with a dynamic mechanical analyzer (DMA), DMA1 (Mettler Toledo, Switzerland) at the Mettler-Toledo (Thailand) Limited (Bangkok, Thailand). Measurements were designed by applying a temperature range from -100 to 140°C at the constant rate of 10°C/min., while the frequencies were changed from 1, 3, and 5 Hz. Three records for each sample were analyzed.

2.2.4 Hardness. The ASTM standard 2240, ISO/R868 was carried out to test the hardness of the samples at the Faculty of Science of Chiang Mai University (Chiang Mai, Thailand), with a Cone 35 of 1.3 mm in diameter, 0 – 2.5 mm depth of indentation and 250 g gross weight.

2.2.5 Tensile property. A universal testing machine (UTM) was used to test the tensile properties of the samples, prepared with the standard shape specimens at the Faculty of Engineering of Chulalongkorn University (Bangkok, Thailand).

3. Results and discussions

The result using EDS, as shown in Table 1, showed the elemental composition of the polyurea sheet samples composed of C and O that were as the main composition, while Si, F, and Ti seemed to be the minor ones. It was shown the presence of C and O were approximately 62.7-74.9 and 17.1-28.7 wt%, respectively. Si was found between 0.2 to 1.7 wt%, while Ti which detected in sample PU-1, PU-2,
PU-3, and PU-5 was the only element that was added to modify the polyurea structure [18]. Fe which only found in sample PU-4 and PU-5 was added as the pigment to show reddish-brown coloration. S and Cl were found in sample PU-1 which were introduced as the chain extenders; dimethylthio-toluenediamine (DMTDA) and 4, 4’-methylenebis-(3-chloro, 2, 6-diethyl)-aniline (MCDEA), respectively. Other elements such as F, Na, Mg, Al, Ca, and K which showed in some samples were added as additives, fillers, and pigments.

The SEM analysis showed the microstructure which consisted of both partially and fully softened regions, that were likewise the other author [19]. They showed the nanometer size hard domains, as shown in figure 2. It was known that polyurea which was mixed with micro- and nano-particles resulted to modify its properties [8]. The hard domains in polyurea were reported that they acted as both inter-chain links and nanometer-size reinforcements making a nano-scale composite material with a unique set of mechanical properties [19].

| Sample | C   | O   | F   | Na  | Mg  | Al  | Si  | S   | Cl  | Ca  | K   | Ti  | Fe   |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| PU-1   | 62.7| 28.7| nd  | 0.6 | 0.3 | 0.4 | 1.7 | 0.1 | 0.4 | 0.2 | 0.3 | 4.5 | nd   |
| PU-2   | 73.1| 20.4| 4.4 | 0.2 | nd  | 0.2 | 0.7 | nd  | nd  | nd  | 0.2 | 0.5 | nd   |
| PU-3   | 74.9| 24.4| nd  | nd  | nd  | 0.2 | nd  | nd  | nd  | nd  | 0.6 | nd  | nd   |
| PU-4   | 73.0| 17.1| 9.2 | nd  | nd  | 0.1 | 0.4 | nd  | nd  | 0.1 | nd  | 0.2 |
| PU-5   | 74.8| 24.0| nd  | nd  | 0.2 | nd  | 0.6 | nd  | nd  | nd  | 0.5 | 0.1 |

Note: nd equals to non-detectable; less than 0.1 wt

The thermal behavior of the samples was evaluated by the TGA and the thermal gravimetrical trace was shown in figure 3. The thermogram of PU-1 exhibited a single-step decomposition profile, while others showed more than ones.
Figure 2. The SEM micrographs of the polyurea sheet samples with magnification at 30,000X
The obtained values of the $E'$, $E''$, and $T_g$ resulted in the various frequencies, such as 1, 3, and 5 Hz, as presented in table 2 and figure 4. It was shown that the $E'$, $E''$, and $T_g$ values were mostly in agreement with the previous works, except PU-5 which these values differed from them. It was found that the higher the $T_g$ was, the higher the frequency was.

Figure 3. The thermal degradation tests for polyurea sheet samples.
Table 2. The DMA data of polyurea sheet samples.

| Sample | Storage modulus, $E'$ (Mpa) | Loss modulus, $E''$ (Mpa) | Glass transition temperature, $T_g$ (ºC) |
|--------|-----------------------------|---------------------------|---------------------------------------|
|        | 1 Hz | 3 Hz | 5 Hz | 1 Hz | 3 Hz | 5 Hz | 1 Hz | 3 Hz | 5 Hz |
| PU-1   | 3910 | 4265 | 4220 | 142.4 | 143.4 | 143.6 | 68.02 | 73.88 | 79.39 |
| PU-2   | 2530 | 2600 | 2650 | 6.8   | 8.1   | 8.5   | -10.02 | -11.89 | -8.63 |
| PU-3   | 3820 | 3790 | 3800 | 237.2 | 237.1 | 237.0 | -16.00 | -9.97  | -6.73 |
| PU-4   | 2350 | 2370 | 2390 | 125.0 | 120.4 | 119.5 | -19.77 | -16.33 | -15.67 |
| PU-5   | 2040 | 2010 | 2050 | 135.5 | 132.9 | 133.7 | -15.80 | -17.62 | -17.05 |

![DMA Graph](image1.png)

![DMA Graph](image2.png)
Figure 4. The storage modulus (E') and loss modulus (E'"")(with various frequency curves of polyurea sheet samples.

It was also found that the tensile strength, modulus, and elongation at break were varied approximately between 7 - 20 MPa, 500 - 770 and 100 - 440%, respectively, as shown in table 3.

The values of the hardness at different points were also found between 87.0-99.0 Shore A, as illustrated in table 4.

| Sample | Tensile strength (MPa) | Elongation at Break (%) | Modulus (MPa) |
|--------|------------------------|-------------------------|---------------|
| PU-1   | 18                     | 260                     | 735           |
| PU-2   | 20                     | 440                     | 770           |
| PU-3   | 15                     | 375                     | 710           |
| PU-4   | 7                      | 100                     | 500           |
| PU-5   | 19                     | 500                     | 550           |

Table 4. The hardness property of the polyurea sheet samples.

| Sample | Hardness, Shore A |
|--------|-------------------|
| PU-1   | 99.0              |
| PU-2   | 87.0              |
| PU-3   | 94.0              |
| PU-4   | 87.0              |
| PU-5   | 90.0              |

4. Conclusion
Polyurea sheet samples were successfully characterized, including microstructure, dynamic mechanical behavior, thermal stabilities, tensile and hardness properties.

They were analyzed by SEM-EDS, in order to characterize the materials used and obtain the information on their production technology, especially the elemental addition, such as Ti and Fe for the structural modification and pigment, respectively. The surface morphology using SEM showed amorphous nature which contained both the micro- and nano-particles. The EDS results showed the
presence of C, O, and Si in all samples. Other elements were added as the chain extenders, additives, fillers, and pigments.

Using TGA, DMA, UTM, and Durometer methods were possible to demonstrate the thermal, tensile, and hardness properties of the polyurea sheet samples, respectively.

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