Thermal, mechanical and morphological properties of polyurethane–zirconia loading

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Abstract
The polyurethane (PU) has been showing a dramatic increase in applications related to material science and technology. However, the mechanical, physical and thermal properties could be further improved by loading PU with zirconia (Zr) to create renewable materials known as polyurethane–zirconia (PUZ) composites. In this study, PU matrix was treated with wt.% Zr at 0.5, 1.0, 1.5 and 2.0. In this study, the thermo-mechanical properties and the morphology were investigated of PU and PUZ nano-samples. The images of the scanning electron microscope (SEM) were the prime tool in investigating PU and PUZ surfaces and fractured surfaces showing vanishing the cracks and formation of agglomeration on the sample PUZ-1.5%. In addition, the tensile strength, Young’s modulus and maximum loading were improved by 36.7, 31.8 and 39.1%, respectively, at Zr loading of 1.5 wt.%. The flexural stress and the load were improved by 94.3% and 93.6%, respectively, when Zr loading was 1.5 wt.%. The the morphologies of the PU surface and Zr surfaces supported by SEM images. Regarding the storage modulus ability of PU and PUZ composites, Zr loading has negatively influenced E. The E functioning temperature was observed to move from 142 to 183°C. Another effect was determined by adding a small amount of Zr. This small amount was enough to shift the crystallization temperature (Tc) and the melting temperature (Tm) of PU from 125 to 129°C and from 150 to 144°C, respectively.

Keywords: polyurethane; zirconia; composites; mechanical properties; thermal stability

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1. INTRODUCTION
Polyurethane (PU) segmented and polyurethane-segmented zirconia (PUZ) are organic materials with urethane as the base host compound. PU and PUZ are classified as thermoset and thermoplastic polymer, respectively [1–3]. Chemically, PUs are formed from the chemical reaction of polyol and di-(isocyanate) as described in [4]. PU is considered by most researchers as one of the best host material [5]. In addition, PU was determined to be the best material equipped with important applications such as a result of having thermo-mechanical properties and capability of sensing to respond to external stimuli caused by heat, electrical or mechanical actions [6–8]. Moreover, PU is being polymeric material, it has wide applications in the medical field (biomedical), engineering (construction), industry (textile and automotive), manufacturing (insulating and adhesive materials, adhesives) and commercially (moulded components) [9–11]. In addition to various applications, PUs have been continuously proven status of strong and promising material in the medical field, computer technology, polymers and smart surfaces [12–14]. The PU ability is attributed to characteristics as promoting support to tissue formation in excisional wounds due to the biodegradability properties of PUs [15–17] and in bone repair and growth [18]. For PU applications in medicine, PU is equipped with very important properties such as simple fabrication, electrical insulator and biostability [19, 20]. Moreover, in the engineering field, the outstanding usage of PU is due to its degradable and its resistance to deep cracking and erosion, highly stiffening, flexural strength and tensile [21, 22]. Generally, PU nanocomposites are very optimistic in producing soft and tough biomedical implants [23, 24]. For the
above reasons, PU and PUZ are used in several fields in industry, medical and technology [25, 26].

The additive in this report is called zirconia (Zr). Zr is available naturally with characteristics of natural renewable polysaccharide polymer and can be obtained from various crops and is widely considered as a raw producing biodegradable products material [27–29]. Zr is very low cost and it is a strong competitor in many applications to thermoplastics produced from petroleum [30, 31]. The current usage of Zr is synthetic polymer filler in thermoplastic zirconia. The fundamental use of Zr as an additive to PU is to boost the mechanical properties and to enhance the crystallinity [32–34]. In a recent study, recently, the synthesis of non-isocyanate-based polyurethane (NIPU) has resulted in creating a new type of PUs; however, the domain of using NIPUs is still less than the original PU. The good matter with synthesis of NIPU is the synthesized without using the toxic material known as isocyanates [35].

In the last 40 years, PU has been investigated by an enormous number of researchers with very high-quality publications [36]. These studies shed the light on the following areas: preparation, structure, thermo-mechanical and morphological properties of PU systems [37–39]. Practically, PU was heavily investigated in the medical fields to design biomedical implant devices [40, 41]. In addition to PU, the nanocomposite PUZs were studied using a joint approach of solid-state reaction and intensive mixing conditions [42]. Hapiot and Lagrost [43] focused on the mechanism of production of new PU composites in term of applicability and time required for completing production [44]. The new production was regulated by adopting stabilizers as molecular weight regulators [45]. On the other side, the available thermoplastic Zr films were found in need of further investigation to meet the appropriate requirements in terms of hydrophobicity and water vapor barrier in addition to acquiring adequate mechanical properties [46]. This study on PU and PUZ composites was performed at varying percentages of Zr loading. The study includes the use of morphology, thermal activity and storage space in physical and mechanical properties. The study added significant mechanical properties results hoping to broaden the applicability of these new composites.

2. MATERIALS USED AND METHODOLOGY

In this experiment, two core materials were used: PU and Zr whose properties are shown in Table 1. An imported PU (Global Innovations-Polycarbonates Bayer Material Science AG, D-51368 Leverkusen, Germany) and unmodified Zr Gelose 80 powder was obtained from Sigma-Aldrich, St. Louis, MO, USA.

| Material     | Chemical formula | Molar mass (g/mole) | Colour   |
|--------------|------------------|---------------------|----------|
| PU           | C_{27}H_{36}N_{2}O_{10} | 548.589             | Yellow   |
| Zirconia     | Zr               | 91.22               | White    |

2.1. Preparation of the samples and experimental setting

The samples’ preparation was performed according to the flowchart shown in Figure 1. The first step includes mixing PU at weight percentage (wt.%) of 0.5, 1.0, 1.5 and 2.0 with the host Zr to form four samples of PU-Zr (named onward as PUZ) in addition to neat PU, which is normally used as a standard sample for comparison. The PUZ was then treated with the acid to form a homogeneous solution. The five samples were named as PU, PUZ-0.5, PUZ-1.0, PUZ-1.5 and PUZ-2.0. The dimensions of each sample were set at height of 20.0 mm, length at 11.0 mm and width at 2.9 mm.

2.2. Instrumentation

The scanning electron microscope (SEM) used in this research work was imported from Hitachi USA, model TM 3000, Somerset, NJ, USA. SEM images for all samples were obtained with 3D features. The other test of the samples was the tensile properties according to the standard associated with Type V-638-ASTM method standard [6] and by applying a 200-Newton load Instron universal testing machine (INSTRON 5567, a product of Konigsallee, Düsseldorf, Germany). The first mechanical test was the tensile test, which was carried out at room temperature using a 50-mm per min crosshead. The 3-point flexural test was carried out according to the UK-Instron 8801 and ASTM D790 standards relating to the sample shape. The test was carried out using the Universal Testing Machine (100 kV) and at speed of 10 mm/min. In addition, Charpy impact strength test was performed based on the ASTM D5942 standard for both unnotched and single-notched samples at normal room temperature and with the assisting of a pendulum impact machine (MT3016, UK), which was characterized by Terco15 J. The dynamic mechanical analysis (DMA) was the last that was investigated using Pyris Diamond DMA (Waltham, MA, USA) and thermally controlled to determine the storage (\(E'_s\)) and the corresponding loss modulus (\(E''_s\)). The investigation was performed by utilizing the frequency
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Figure 2. (a) PU and (b) Zr SEM microphotographs.

of the spectra set at DMA 1-Hertz and operated between 50°C to 150°C and heated at a rate of 2°C/min. The force which applied using the cantilever method is 6.35 Newtons and the displacement is 20 μm.

3. RESULTS AND DISCUSSION

The results of the experimental sections were conducted according to the priority of the results obtained. The tests such as SEM, mechanical, flexural, impact and DMA in addition to their corresponding analysis and discussion are illustrated in the following sections.

3.1. SEM of Zr and neat PU

Before preparing the samples for SEM investigation, two sheets of glass should be cleaned and smooth with no irregularities. Then PU sample was dropping a tiny PU on a clean surface, while for Zr, spreading the powder on a different sheet of glass based on the procedure presented by [47]. Figure 2a and b show the morphologies of the PU surface and Zr surface, respectively. PU surface appears smooth, while the Zr particles of different sizes appeared separated from each other with no agglomeration, which reflects the nature of spreading Zr powder.

3.2. Tensile/impact fractured surface of PUZ by SEM

Figure 3a–d shows the SEM fractured surfaces of the four PUZ samples loaded with wt.% Zr of 0.5, 1.0, 1.5 and 2.0, respectively. The white dots that appear on the surface of the PU-Zr composites represent the presence of Zr. It is noticeable that as the loading of the Zr percentage increases, the number of white dots along with corresponding sizes is showing increasing density and size. The increase in density is a consequence of the increase in density, while the enlargement is attributed to the agglomeration formation, which affects the physio-mechanical properties of the composites [48]. The other important effect of increasing Zr loading is the gradual disappearance of the cracks. Figure 3a (Zr wt.% of 0.5) shows the cracks clearly on the surface and as the Zr loading increases, these cracks are getting filled. For higher Zr wt.% shown in Figure 3a–d, the cracks disappeared while the agglomeration of Zr powder becomes obvious. SEM images suggest that the tensile strength increases as Zr wt.% loading increases. The increase in Zr wt.% shows different fractured tensile surfaces. At Zr of 0.5 wt.% Zr shown in Figure 3a, no obvious cracks were observed in the fractured surface [49]. However, as the Zr wt.% increases to a higher percentage, clear signs for cracks on the fracture surface can be observed. The crack on the surface becomes of PUZ 1.0, PUZ-1.5 and PUZ-2.0 as depicted in Figure 3b–d. The appearance of cracks influences the tensile strength. Images in Figure 3 suggest that the fracture tensile increases first until PUZ-1.0 and then decreases for the remaining two samples reflecting the effect of the agglomeration of Zr in PU matrix.

The other test was about the impact fracture of PUZ at different Zr loading as shown in Figure 4a and d. The images of SEM belonging to the impact PUZ fractured surface show the increasing density of the dots related to Zr loading similarly to what has been observed for SEM tensile strength. However, the difference of the SEM tensile fracture images has no cracks possibly due to the abrupt cutting the surface compared to the slow cutting surface in tensile fracture. Images of SEM tensile fracture support the findings in Figure 3, which have shown improvement in the mechanical properties until the agglomeration started to form in PUZ nano-samples.

3.3. Mechanical test

The mechanical tests include the following tests: tensile strength, modulus of Young, maximum load and elongation. All these tests were carried out on the neat PU and the other four samples of PUZ at Zr loading of wt.% 0.5, 1.0, 1.5 and 2.0 as shown in Figure 5a–d, respectively. The tensile strength that is shown in Figure 5a indicates that the tensile strength of the neat PU is 8.19 MPa, which is similar to the test reported by [50]. As a result of Zr loading to form PUZ matrix, the tensile strength increases gradually to the maximum value of 11.22 MPa at PUZ-1.5 showing a significant increase of about 36.7%. The tensile strength decreases then to 10.5 MPa for PUZ-2.0 showing a decrease of 27.6% compared to the neat PU. This behaviour is attributed to the versatile behaviour of PU concerning susceptible change due to adding Zr at low percentages besides temperature. The highest tensile strength for PUZ-1.5 was followed by a slight decrease, which was explained...
by [43] in terms of the change of rubber to plastic. This result is in agreement with SEM investigations presented in Figure 4, which was explained earlier due to the adverse effect of the formation of Zr agglomerated. The other mechanical tests are presented in the remaining parts of Figure 5 according to having the same trend of interpretation that relates to the increase in Zr additive and the disappearing of the cracks. Young’s modulus test for the same five samples is shown in Figure 5b. Young’s modulus of PUZ attains the highest rigidity becoming very stiff at 1408.32 MPa for PUZ-1.5. An interpretation of this behaviour was reported by [46] based on the molecular level assuming that Zr fillers bonded to the PU molecular chain causing molecular mobility restriction, which reduces flexibility and increases stiffness. Figure 5c shows the maximum load that can be carried by PU or PUZ composites before breaking down is correlated with the elasticity and brittleness. PUZ-1.5 appears to hold the maximum load of 341.65 N recording a percentage increase by 39.1% referenced to neat PU. As Zr loading increases to wt.% of 2.0, the maximum

Figure 3. PUZ fracture tensile at Zr wt.% at 0.5 (a), 1.0 (b), 1.5 (c) and 2.0 (d).

Figure 4. PUZ impact fracture SEM images of Zr wt.% at 0.5 (a), 1.0 (b), 1.5 (c) and 2.0 (d).
load held by PUZ composites was slightly higher than PUZ-1.5. The last mechanical test was the elongation at break as shown in Figure 5d. The neat PU sample shows elongation at break at 1.05% (equivalent to an increase of 5%), suggesting that PU has elastic properties in addition to rigidity. As Zr loading increases, the rigidity decreases and the elasticity increases taking the elongation at break to 1.81% compared to PU sample for PUZ-1.5. Beyond 1.5 wt.% Zr, the elongation at break of PUZ-2.0 reduced slightly; however, it still shows that PUZ is more elastic than PU. The significance of these findings is an industrial indicator regarding the durability of the sample in applications such as packaging. Apparently, Zr loading eases the rigidity of PUZ composites and increases the elongation at break.

3.4. Flexural test
Flexural test, load at yield and deflection were performed on the neat PU as well as PUZ-four samples as shown in Figure 6a–c, respectively. The test was carried out by imposing a load at the middle of a 2-end supported sample. The test requires flexural test before the sample is failing under compressive strength. The flexural tests of PU and PUZ composites at different Zr loading are shown in Figure 6a. The neat PU sample can hold compressive stress up to 65.82 MPa in agreement with the findings of [47]. As Zr loading increases, the sample holds maximum compressive stress up to 122.78 MPa at Zr wt.% of 0.5 and up to 127.89 MPa at Zr wt.% of 1.5 showing a percentage increase by 94.35 compared to PU result. As Zr wt.% reached 2.0, PUZ-2.0 shows a decrease bringing the flexural back to almost to same value of PUZ-0.5. The tests of the maximum load at the yield of PU and PUZ composites are shown in Figure 6b. The maximum yield shows stress at the beginning of the deformation into plastic from being partially in the rigid phase. Testing the maximum load at yield is used to possibility of reshaping the material and to become susceptible either to cutting or shearing. The determined load of the neat PU was 39.49 N. As Zr loading increases, the load increases reaching 79.48 N at Zr wt.% of 1.5 recording an increase by 93.6% compared to PU amole. This result coincides with the assessment reached by the flexural test. The yield of PU sample suggests that PU is vulnerable to external parameters such as pressure or loading. The previous results have shown that PUZ composites at Zr 2.0% still express elastic properties, which, in general, is better than the elastic level of the neat PU. The last mechanical test is the deflection that is caused by applying load at the centre of the supported sample. Figure 6c shows the deflection results. Neat PU shows that the deflection is 14.32 mm, which increases as Zr loading increasing achieving 29.41 mm for PUZ-1.5, suggesting that the sample attains the best elasticity.
Based on the result of PU, the elasticity of PUZ-2.0 reaches 105% and improvement of the maximum loading was reported at 86%.

3.5. Impact test

The impact test is expressed by the intensity (energy/surface area) and it can be done by using enough well distributed over the surface of the sample. The impact tests may or may not be performed using normal sample or by creating a notch on the surface by a sharp razor based on the machine standards.

The first measurement of impact factor was carried out on both un-notched PU and un-notched PUZ composites. Figure 7a shows that the impact factor of un-notched PU was $6.33 \times 10^{-3} \text{ J/mm}^2$. For the same sample, as Zr loading increases, the impact test increases doubling its value at $13.34 \times 10^{-3} \text{ J/mm}^2$ for PUZ-1.5, showing 110.7% increase compared to neat PU. Beyond the percentage of Zr 1.5%, the impact factor declined. The increase in impact level is attributed to filling the cracks shown by SEM images (Section 3.2). Moreover, the impact factor of PUZ-2.0 declines to $9.97 \times 10^{-3} \text{ J/mm}^2$, showing an increase of 54.6% compared to notched neat PU sample. The results briefly show that the impact factor of PUZ-1.5 improved by slightly more than 110% based on the neat PU result.

The last mechanical test was performed on notched PU and PUZ composites samples as shown in Figure 7b. For the notched neat PU sample, the impact strength was $4.31 \times 10^{-3} \text{ J/mm}^2$. This result represents a reduction by 47% compared to the un-notched sample as shown in Figure 7a. Moreover, the impact strength of PUZ composites increases as Zr percentage loading increases showing a maximum of $7.01 \times 10^{-3} \text{ J/mm}^2$ at Zr percentage of 1.5, which represents an increase by 62.6% compared to the neat notched PU sample. Similar to un-notched PUZ samples, the impact strength of the notched PUZ-2.0 decreases to $5.54 \times 10^{-3} \text{ J/mm}^2$ representing an increase of 28.3% compared to the notched PU sample. The notching seemingly influences the smoothness resulting in lowering the impact strength [30].

Table 2 contains the findings of the mechanical tests of (tensile strength, Young’s modulus, maximum load and elongation at break); flexural (flexural stress, load at the yield and deflection); and impact strength of notched and un-notched samples for PU and PUZ with Zr loading of 0.5, 1.0, 1.5 and 2.0 wt.%. 

3.6. Dynamic mechanical analysis

The dynamic mechanical analysis can be resulted by applying an external sinusoidal oscillating force followed by the response of testing material. There are a few types of sinusoidal force such as creating a force that causes strain or stress, which appeared in the form of tension, compression or torsion. The strain/stress
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Table 2. The mechanical tests results and impact strength of Zirconia.

| Test          | Mechanical test | Zirconia loading (wt.%) | Increase % at Zr |
|---------------|-----------------|-------------------------|-----------------|
|               |                 | 0       | 0.5 | 1.0 | 1.5 | 2.0 | 1.5% | 2.0% |
| Tensile       | Tensile strength (MPa) | 8.19 | 8.77 | 9.9 | 11.22 | 10.45 | 36.7 | 27.6 |
|               | Young's modulus (MPa) | 1068.86 | 1215.55 | 1296.44 | 1408.32 | 1372.11 | 31.8 | 28.4 |
|               | Maximum load (N) | 245.69 | 278.29 | 308.33 | 341.65 | 325.98 | 39.1 | 32.7 |
|               | Elongation at break (%) | 1.05 | 1.23 | 1.29 | 1.48 | 1.81 | 40.1 | 72.4 |
|               | Flexural stress at yield (MPa) | 65.82 | 122.78 | 125.57 | 127.89 | 120.65 | 94.3 | 83.3 |
| Flexural      | Load at yield (N) | 39.49 | 72.88 | 74.11 | 76.48 | 75.21 | 93.3 | 90.4 |
|               | Deflection (mm) | 14.32 | 24.23 | 27.55 | 29.41 | 26.46 | 105.3 | 86.1 |
| Impact strength | Un-notched (10⁻³ (J/mm²) | 6.33 | 10.12 | 11.54 | 13.34 | 9.79 | 110.7 | 54.6 |
|               | Single-notched (10⁻³ (J/mm²) | 4.31 | 5.89 | 6.11 | 7.01 | 5.54 | 62.6 | 28.3 |

DMA and the corresponding viscoelastic measurements were used to investigate the storage modulus (E) and the loss modulus (E′). During DMA measurements, a linear viscoelastic region may appear if there is no dependency between modulus and the applied stress or strain. Moreover, DMA measurements express the behaviour of the glass transition temperature (T_g), storage and loss moduli, and shifting of temperature.

The results of E PU and PUZ composites are shown in Figure 8. The highest value of E of PU and PUZ composites appears at about 14°C and E starts fading rapidly with increasing temperature. The effect of Zr loading shows that E decreases with increasing Zr loading 0.5 to 2.0 wt.%. The presence of E tends to the minimum as the temperature reaches about 183°C for PU sample and the temperature is receding to lower temperature as Zr loading increase shifting to 142°C for PUZ-2.0 sample.

The results of the loss modulus (E′) as a function of temperature and Zr loading are shown in Figure 9. The result of E′ shows that PU crystallizes at 125°C compared to crystallization of PUZ-0.5, which occurs at 129°C. The results suggest that loading small amounts of Zr results in shifting crystallization temperature (T_c) of PU. A possible interpretation of the effect of adding Zr was the possible crystallization due of nucleation in addition to the increase of the OZU surface area that might enhance the crystallization process.
The last parameter investigated in this study is the loss tangent, which is known as $\tan \delta$ as shown in Figure 10. The loss tangent is defined by ratio of $E'/E''$. The benefit of measuring the loss tangent of neat PU or PUZ composites is to estimate the melting temperature ($T_m$). $T_m$ of neat PU is about 150°C, which shifts to 144°C for PU-2.0.

4. CONCLUSIONS

The recent industrial and technological demands for improving the thermo-mechanical properties of PU have been involving nanotechnology to produce better and much effective materials. Recent research in the field of nanotechnology has revealed significant improvement of the thermo-mechanical properties by loading PU with Zr to produce PUZ composites with wt.% 0.5, 1.0, 1.5 and 2.0. PU and PUZ composites were tested by SEM for morphology and cracks appearance. In addition, the same samples were tested for mechanical properties (tensile strength, elongation, Young's modulus, maximum load at yield and flexural test). The last test was about analysing DMA characteristics. SEM images of the fracture surface of PU and PUZ composites have shown the gradual disappearance of cracks on the surface as Zr loading increases and the formation of agglomerated Zr over the surface. The tensile strength, Young's modulus and maximum load were improved by 36.7, 31.8 and 39.1%, respectively, as Zr loading reaches wt. 1.5 wt.%. The flexural stress and the maximum load were improved by 94.3% and 93.6%, respectively, when Zr loading was 1.5 wt.%. The impact strength of un-notched and notched samples was improved by 110.7% and 62.6%, respectively, at Zr loading of 1.5 wt.%. Regarding the storage modulus ability of PU and PUZ composite, Zr loading has negatively influenced $E$ while the functioning temperature was shifted from 142°C to 183°C. It was observed that loading PU with small amount of Zr shifts the crystallization temperature ($T_c$) and the melting temperature ($T_m$) of PU from 125°C to 129°C and from 150°C to 144°C, respectively. The characteristic of PUZ composite may lead to a better understanding of these new composites as a precursor to future medicinal uses.

CONFLICT OF INTEREST

The authors declare that no conflict of interest.

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