Thermomechanical and Magnetic Properties of TPU/NR Blends with Low Loading of NiZn

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Abstract Thermoplastic polyurethane blending with natural rubber has changed the properties of both origin of these polymer materials. Then, this blend was added with NiZn ferrite as the magnetic filler, at low loading between 1 to 5% only. Other than that, liquid natural rubber (LNR) was also added as compatibilizer. This process was carried out using melt mixing technique to produce polymer magnetic composites. The study found, NiZn ferrite at 3% is the optimum filler loading. The thermal stability of the composites increased with the increasing of NiZn ferrite. LNR was not successful in its role as compatibilizer. The addition of NiZn ferrite improved the magnetic properties on saturation magnetization and remanence magnetization but decreases the value of coercivity force.

Keywords Thermoplastic polyurethane, Natural rubber, Thermomechanical, Magnetic, NiZn ferrite.

Introduction Nowadays, the trend of research has focused on new polymer materials resulting from a blend of two or more types of polymer and this process is a priority because the properties of the blended polymers are better than that present in a single polymer component. Furthermore, according to Abu-Abdeen & Elamer [1], some modifications in terms of characterization of processing, durability and cost can be achieved through a mixture of polymers. Modifications in the behavior and the improvement of the polymer properties have made it an ideal material for use in aerospace, transportation, packaging and food industries [2]. The other hand, the composite material can be produced from a combination of metal, ceramic, and polymer. Most composite materials consist of two phases: a matrix; the continuous phase and the other around are the fillers. The original purpose of filler added to polymeric materials is to lower the cost by reducing the use of polymer matrix in the composite. However, with an advances in science and technology, the goal now is to improve processing, increase the desired properties such as mechanical, physical, thermal, magnetic, electrical, reducing the density of the material, etc. It is known, the nature of the polymer are electrically insulating and non-magnetic. Both of these properties can be altered by adding materials that are conductive filler and magnetic powder into the polymer [3]. The magnetic polymer composite has many advantages such as easy machining process in a variety of sizes to select the form of complex, high production rates, low cost and resistance to corrosion [4–6]. With a series of simple polymer, a combination of good properties of magnetic polymer composites can be produced [3].

In this study, the filler material used is the magnetic nickel zinc (NiZn) ferrite in thermoplastic polyurethane (TPU) / natural rubber (NR) blend as matrix. TPU which have two phases structure; soft and hard segment [7] and blended with NR that comes with elastic, thermal and resilient properties. TPU are easily processing [8] and make it possible to be blended with NR which provides low compounding temperature [9]. There have been many previous studies that use NiZn ferrite as filler in the polymer matrix, and study the effect of filler loading of magnetic properties. In addition, a study on the electrical properties, microwave absorption, dielectric, thermal stability and others also has been studied. Boon et al. [10] studied the effect of magnetic, dielectric and thermal stability of epoxy composites in the form of a thin film for the purpose of electronic. They found the saturation magnetization increased with increasing filler loading NiZn. Cheng-Hsiung et al. [11] in a study of synthesized NiZn ferrite by combustion method and to study the effect of microwave absorption in PU-plastic and also studied the effect of particle size of ferrite. In addition, Majid et al. [12] synthesized and characterized
NiZn ferrite and MWCNT in PVDF and C_{3}H_{6}O_{3} in applications of sea-bed logging. Rastislav et al. [13] was used NiZn ferrite as filler in the PVC for their study of electromagnetic wave absorption properties. Moayad et al. [14-15] also study the magnetic, thermal conductivity and DMA analysis of the composite TPNR composite filled NiZn ferrite. Similarly, Yu et al. [16] that used the same matrix but with hybrid of NiZn ferrite and MWCNT as filler and their research was focused on magnetic properties and microstructure. Beside studied the effect of low loading of NiZn on tensile properties and swelling behavior on previous paper [17-18] now we also investigated the thermomechanical properties which about to measure loss weight and degradation progress in composite via thermogravimetry analysis (TGA) and also the effect of temperature on the viscoelastic properties of composites using dynamic mechanical analysis (DMA).

Experimental
Materials
The materials used in this research include thermoplastic polyurethane, natural rubber, natural rubber and liquid ferrite nickel zinc (NiZn). Thermoplastic polyurethane (TPU) is a type of polyester-based 11T80 PEARLTHANE with A82 Shore hardness obtained from MERQUINSA Company. Natural rubber (NR) grade SMR-L with a density of 0.92g cm^{-3} supplied by the Rubber Institute of Malaysia (RRIM). Liquid natural rubber (LNR) is available in research laboratories with natural rubber photo oxidation degradation method [19, 20]. NiZn ferrite was used as filler supplied by Nanostructures & Amorphous Materials, Inc. USA, where its purity is 98.5\% and particle size of 3 -10 nm, with Ni_{3}, Zn_{0.5}, Fe_{2}O_{4} as its chemical formula.

Preparation of TPU/NR composites
As this study was carried out from the previous, the samples were prepared by the optimal composition for TPU / NR and LNR i.e. 85TPU/15NR and 85TPU/5NR/10LNR [21], as well as a filler content of 1 to 5% by weight. The TPU/NR blends were prepared by melt blending technique using laboratory internal mixer (model RheoHaake 600p) Blending was carried out at temperature 180\degree C, with a mixing speed of 60rpm for 10 min and then pressed at 185\degree C under 45MPa of pressure for about 2 min using hot press (Carver Laboratory Press) into thin sheets.

Characterizations of TPU/NR composites
The thermogravimetric analysis carried out using Mettler Toledo (STGA/ SDTA851e). Each of the test sample compositions performed three times and the average values were taken. Samples provided for analysis needs to have weight <20 mg. Each piece of the sample is introduced into an aluminum tray and heated with heating rate of 10 \degree C per minute in the temperature range 30 \degree C to 600 \degree C. The result has been plotted by the instrument as a function of weight percent to temperature changes. Dynamic mechanical analysis performed upon the sample using the machine dynamic mechanical analysis (DMA) from TA Instruments. The temperature range begins at temperature -60 \degree C to 120 \degree C with temperature rise of 5\degree C/ min. The test frequency used was 1 Hz and 20 \mu m amplitude. Samples were cut in square size of 13 mm x 10 mm with a thickness of 3 mm. Clamp type used is single cantilever clamp with bending mode. DMA analysis begins with cooling the samples to a temperature of -60\degree C using liquid nitrogen. Modulus value of storage, loss modulus and tan \delta were plotted against temperature. The magnetic properties were measured using vibrating sample magnetometer (VSM model LDJ 9600) at room temperature. The measurements were carried out in a maximum field of 12kOe. Magnetic parameters such as saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) were determined.

Results and Discussion
Thermomechanical properties
Thermogravimetric analysis (TGA)
One of the main objectives of this analysis is to measure the weight loss with increasing temperature. Indeed, the analysis of TGA is to see the effectiveness of nanoparticles as filler to the degradation of composite TPU/NR and TPU/NR/LNR that apply when the temperature is increased. Thermogravimetric analysis is used to determine the real weight of filler in the matrix, filler uniformity and degradation temperature of the composites. Residue weight at the end of the experiment was referring to the content of NiZn. Thus, it is expected in this analysis, the residue weight is increasing equally with the increased NiZn ferrite loading.

Based on the results of TGA curves in Figure 1, the thermal stability of both nanocomposites increased with increasing filler loading. However, the decomposition behavior can be observed on both of these nanocomposites, seem not show the same pattern starts at 60\% decomposition and at a temperature of 350 \degree C. This may be because, before 350 \degree C, the mass at beginning heating process is still consistent and no free volume (porosity) for the movement of polymer chains. However, with increasing temperature, vibration of molecular chains become active and the chain termination occurs [16]. This process also occurs at levels that vary among all the samples and it can be seen from the shape of the curve.
In Tables 1 and 2, $T_{10}$ and $T_{50}$ is the temperature at 10% and 50% weight loss of the samples. NiZn ferrite can slow down the diffusion of decomposition in the gas phase, in which NiZn ferrite serves as a heat absorber. More heat energy is needed due to the presence of NiZn ferrite [16]. Conduction of heat for polymer phase as matrix has been blocked and can delay the decomposition process of the nanocomposite. When the filler content increases, the more nanoparticles will be scattered around the polymer chain and delay the heat conduction and this may caused to improve the stability of nanocomposites.

![Thermogravimetric curves](image)

**Figure 1:** Thermogravimetric curves of (a) TPU/NR (b) TPU/NR/LNR

$T_{10}$ values for both nanocomposite showed no significant increase with the increasing of NiZn ferrite loading, but for the $T_{50}$ pattern increased up to 3% of the filler. This indicated that the presence of NiZn ferrite until optimum loading has improved the stability of the composite; even involve only slight differences in degrees Celsius [22]. Gordana et al. [23] in their study stated that the thermal stability of the polymer blends can be improved with the addition of filler. On the filler loading of 4% and 5%, it was found that the $T_{50}$ slightly decreased. This shows, the addition of NiZn ferrite when exceeds the optimum loading was disturbing the thermal stability of the composite. If comparison is made between the two types of nanocomposites, we found that no changes either in the presence of LNR or not.
The final temperature for the degradation of the TPU/NR nanocomposite is higher than the TPU/NR/LNR composites. This may be due to the decomposition of TPU/NR/LNR being able to be achieved at lower temperatures which showed the stability of these composites is lower. The addition of LNR in TPU and NR are not helpful in terms of stability of this composite. The previous tables also shown the residue for both TPU/NR and TPU/NR/LNR nanocomposites filled NiZn ferrite. The percent of residue after the end of the experiment is almost the same as the actual value, and do not show significant changes.

### Dynamic Mechanical Analysis (DMA)

In the dynamic mechanical analysis, the behavior and loss modulus with temperature changes have been tested. Figure 2 shows a plot of storage modulus vs. temperature for TPU/NR and TPU/NR/LNR nanocomposites. Storage modulus for both composites decreased between the temperature ranges of -50°C to 0 °C. A sudden change in the temperature range is related to the glass transition temperature ($T_g$) of the composite. Then, the increase of storage modulus is caused by an increasing in the addition of filler loading [16]. Also, both composites with 3% NiZn loading showed the highest storage modulus value. According to Zanetti et al. [24], the higher the filler content, the higher potential to increase the modulus. In addition, the filler nanoparticles dispersed uniformly create the good filler-matrix interface and the interaction enhanced [25]. Increase filler loading that cause an increase in the storage modulus is also evidence in the study of Xiaodong et al. [26] and Aruna & Deba [27]. According to Yu [28], up to optimum loading, nanoparticles are well dispersed in the matrix and then the storage modulus increased with increasing filler. However, when the filler loading increased over the optimum loading, the nanoparticles are likely to form agglomerates. This will reduce the filler aspect ratio and limiting the stress transfer to the matrix. This explained the decreasing in storage modulus value at 4% and 5% of NiZn ferrite.

When compared the storage modulus for both composites at 3% of filler, we found the value for TPU/NR/LNR showed the highest. This is due to the good filler dispersion assisted by LNR and a good filler-matrix interface interaction, which in turn increasing the effect of bonding between them. At -40 °C, the storage modulus increased from 425 MPa to 475 MPa for TPU/NR and from 900 MPa to 1100 MPa for TPU/NR/LNR, with NiZn ferrite filler addition of 1% to 3% by weight. The increase in modulus below the $T_g$ is evidence that the loading of NiZn ferrite in matrix assisted as reinforcement in TPU/NR and TPU/NR/LNR. Filler-matrix interaction and compatibility between the two are also the major factor in this analysis.

### Table 1: The observed data, $T_{10}$, $T_{50}$ and residue weight of filler for TPU/NR

<table>
<thead>
<tr>
<th>NiZn ferrite filler</th>
<th>$T_{10}$ (°C)</th>
<th>$T_{50}$ (°C)</th>
<th>Residue weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>340</td>
<td>370</td>
<td>1.03</td>
</tr>
<tr>
<td>2%</td>
<td>315</td>
<td>390</td>
<td>2.5</td>
</tr>
<tr>
<td>3%</td>
<td>335</td>
<td>395</td>
<td>3.6</td>
</tr>
<tr>
<td>4%</td>
<td>330</td>
<td>390</td>
<td>4.9</td>
</tr>
<tr>
<td>5%</td>
<td>330</td>
<td>370</td>
<td>5.3</td>
</tr>
</tbody>
</table>

### Table 2: The observed data, $T_{10}$, $T_{50}$ and residue weight of filler for TPU/NR

<table>
<thead>
<tr>
<th>NiZn ferrite filler</th>
<th>$T_{10}$ (°C)</th>
<th>$T_{50}$ (°C)</th>
<th>Residue weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>320</td>
<td>380</td>
<td>1.1</td>
</tr>
<tr>
<td>2%</td>
<td>335</td>
<td>390</td>
<td>2.2</td>
</tr>
<tr>
<td>3%</td>
<td>330</td>
<td>395</td>
<td>3.8</td>
</tr>
<tr>
<td>4%</td>
<td>310</td>
<td>360</td>
<td>4.2</td>
</tr>
<tr>
<td>5%</td>
<td>320</td>
<td>400</td>
<td>5.6</td>
</tr>
</tbody>
</table>

The final temperature for the degradation of the TPU/NR nanocomposite is higher than the TPU/NR/LNR composites. This may be due to the decomposition of TPU/NR/LNR being able to be achieved at lower temperatures which showed the stability of these composites is lower. The addition of LNR in TPU and NR are not helpful in terms of stability of this composite. The previous tables also shown the residue for both TPU/NR and TPU/NR/LNR nanocomposites filled NiZn ferrite. The percent of residue after the end of the experiment is almost the same as the actual value, and do not show significant changes.
Figure 2: Storage modulus of (a) TPU/NR and (b) TPU/NR/LNR with different loading of NiZn ferrite.

The bond between the filler-matrix directly proportional to the storage modulus but it is inversely proportional to tan δ [28], as plotted in Figure 3. Strong interaction between filler and matrix was reducing the molecular chain movement at the interface, then it will reduce the value of tan δ. The figure also shows the plot of tan δ and temperature of TPU/NR and TPU/NR/ NR composites, in various range of NiZn ferrite loading. Tan δ exhibits a maximum value at temperature about -10 °C to -20 °C, which can be changed by changing the NiZn ferrite loading [26]. For both type of composites, there was an increasing in value of tan δ with the addition 3% of filler. This is the effect of energy dissipation through the friction of filler nanoparticles and interaction between filler - matrix interface of TPU/NR and TPU/NR/ LNR.

From the results obtained on the previous figure for the two types of composites, it was found that the Tₜ shifts to the right side, which means that the Tₜ growing up on 3% NiZn ferrite, which is the optimum loading of filler. This means, the mobilization of the rubber molecules were suppressed due to the existence of NiZn ferrite. The value of tan δ of the composites derived from the contributions of both the matrix and filler. NiZn ferrite filler addition has reduced the weight percent of TPU/NR, TPU/NR/LNR in composites, where reducing the hysteresis loss of the composite under dynamic conditions. However, at the loading of 4% and 5% NiZn, the Tₜ decreasing.
Valuation of magnetic properties of a material was important to understand the usability of the product [29]. Magnetic properties of the composites TPU/NR filled NiZn ferrite is explained using a hysteresis loop vs. magnetic field and Figure 4 shows that kind of plot in the range of magnetic fields at room temperature. Practically, all the samples had the same form of hysteresis loop. From that, we can concluded, the composite is a soft magnetic at room temperature due to the resulting hysteresis loop which is narrow with a small coercivity. Saturation magnetization ($M_s$), remanence ($M_r$), saturation magnetic field and coercivity force ($H_c$) are the parameters of the magnetic properties that can be obtained from the magnetic hysteresis loop. The degree of alignment magnet moment increased with the magnetic field. Magnetic moments in the sample align parallel to the direction of the applied magnetic field. Magnetization increased rapidly in the region of low magnetic field before reaching a constant value called the saturation magnetization ($M_s$). When the magnetic field is kept constant, $M_s$ is found to increase with increasing of filler in the matrix. Composite tend to follow the nature of the ferrite when the filler loading increased. Remanence magnetization ($M_r$) refers to the magnetization that remains in a magnetic material when the magnetic field is removed. It is the degree of magnetic resistance for a material, which is the magnetic induction remaining in a magnetic material when an external magnetic field is removed. The remanence enhancement was deemed to change the interaction between the particles. The value $M_s$ and $M_r$ for magnetic polymer composites increased with an increasing in fractional volume magnetic fillers in the polymer [10, 30]. $M_s$ for composite TPU/NR increased linearly with the increasing in $M_s$ as shown in Figure 5(a). The $M_s$ and $M_r$ increased, while the $H_c$ decreased with increasing filler [30, 31]. $H_c$ was forced to return the magnetization force to zero and it can exhibit magnetic moment of filler having alignment of the magnetic field in the matrix. When the $M_s$ of the sample demagnetization, the magnetic moment will be forced to align all fields demagnetized to zero [25]. Align the spin or magnetic moment filler was easily occur if the interaction between filler particle is a strong ferrite filler.

Figure 4: The room-temperature magnetization curves of TPU/NR blends with various filler loading of NiZn ferrite.
This means that, at low filler composition, orientation of the magnetic moment predicted difficult is because the existence of obstacles or barriers to higher polymer matrix of the rotation filler particles. According to Youyi et al. [30] and El-Nashar et al. [29], the value of $H_c$ decreases with increasing filler loading, as can be seen in Figure 5(b). They stated, $H_c$ impairment when NiZn ferrite filler loading at 2% to 5%, the deep rising of magnetic interaction happened between NiZn ferrite nano particles. Makled et al. [31] also stated in their research, the value of $H_c$ will decreased at high filler loading due to increased interaction between magnetic particles in the matrix.

Figure 5: (a) Saturation magnetization and remanence magnetization of TPU/NR blends with various filler loading of NiZn ferrite (b) Coercive force ($H_c$) of TPU/NR blends with various filler loading of NiZn ferrite.

Conclusion

The addition of NiZn ferrite up to 3% has clearly indicated as optimum loading of this type of filler for composite TPU/NR and TPU/NR/LNR. The stability for both composite also increased with the increasing NiZn ferrite loading. The amount of residue also almost the same to the fillers used which are from 1 to 5 weight percent. The addition of LNR does not help in terms of stability of TPU/NR/LNR composite because no significant changes that can be seen when compared to composites without LNR. The storage modulus, the peak tan $\delta$ and the $T_g$ increased up to 3% of NiZn ferrite. In the study of the magnetic properties, the addition of NiZn ferrite has increased the $M_s$ and $M_r$ but reduced $H_c$. The addition of fillers should be well dispersed in the matrix, thus will improve the properties of composite. However, if the filler content is more than the optimum percent that can be represented by a matrix, the filler is not well dispersed and tend to form agglomerates.

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References


