Tensile and Physical Properties of Linear Low Density Polyethylene-natural Rubber Composite: Comparison between Size and Filler Types


1. INTRODUCTION

Electrical insulation plays an important role to protect high-voltage (HV) system from operation failure [1]. Several causes, such as electrical treeing and voids, can affect the functionality of insulators [2]. Thus, it is important for electrical insulating materials to have good tensile properties in addition to high dielectric strength and low dielectric constant [1].

Linear Low-Density Polyethylene (LLDPE) is widely used as electrical insulating materials in power cables [3]. The electrical insulating properties of LLDPE can be increased by the addition of nano-sized fillers or nanofillers [4, 5]. Nanofillers have larger surface area compared to micro-sized fillers with the same phr/volume. Most commonly used nanofillers are montmorillonite (MMT) [6] which can improve electrical insulating and tensile properties, carbon nanotube (CNT) and graphene [7]. The tensile strength of LLDPE nanocomposites increased with the content of nano-sized silica (or nanosilica) increased from 0 phr to 8 phr [8]. Increasing the content of MMT from 0 phr to 10 phr can also improve the tensile strength of LLDPE nanocomposites from 9.9±0.32 MPa to 13.8±0.52 MPa [9]. The addition of CNT from 0 phr to 1 phr increased the tensile strength of LLDPE from around 10 MPa to more than 35 MPa [10].

Natural rubber (NR) is native to Malaysia since the 1870s [11]. It is made from a renewable source to make heavy-duty tires, gloves, etc. [12]. NR-based electrical insulation was the only polymeric material used as a wire and cable up to the 1930s, when the first suitable synthetics became available [13]. The dielectric strength of NR ranges from 100 kV/mm to 215 kV/mm [14]. Rubber, with a low modulus of elasticity, can sustain a deformation of as much as 1000 percent and will return to its original dimensions after such deformation [15].

Silica is one of the reinforcing fillers used in natural rubber [16]. The mechanical properties of composites can be increased by adding nanosilica. The tensile strength of polyvinyl chloride (PVC) increases from...
4.18 MPa to 6.83 MPa as higher loading of nanosilica from 0wt% to 5.0wt% is added to the composite. At 5.0wt% filler loading of nanosilica, the tensile strength of PVC reaches its maximum value of 6.83 MPa, which is 63.37% higher than base PVC [17]. Natural fibers have been used as reinforcement for polymer composites due to their availability and desired properties [18] including good electrical resistance [19], and also due to their environmental-friendly properties [20, 21]. Ash, such as rice husk ash, coal waste ash, and palm oil ash, has been used to increase the mechanical properties of cement [22-24]. Palm oil fuel ash (POFA) can increase the tensile properties of a material. In a study done by Ooi et al. [25], the tensile strength and elongation at break of NR compound improved by 16% and 7.4% respectively, up to an optimum level of 1 phr.

In this study, LLDPE and NR had been combined to be the composite base (LLDPE-NR). Currently, there are almost no study done on LLDPE-NR composite which uses POFA and nanosilica as fillers. Previous research on LLDPE-NR that used nanosilica as filler only studied the electrical properties [5] and not its mechanical properties. Thus, the purpose of this paper is to study the effect of POFA and nanosilica fillers on the tensile and physical properties of LLDPE-NR composite.

2. MATERIALS AND METHODOLOGY

2.1. Materials  
Linear Low Density Polyethylene (LLDPE) and LLDPE-g-MAH were used in this study. The other material used was Natural Rubber SMR 20 (NR), obtained from Sabah Rubber Industry Board (LIGS). Fillers used were POFA, which were obtained from Faculty of Engineering, University Malaysia Sabah and sieved to achieve the finest size as below 300 µm, and 200 nm silicon dioxide (nanosilica) from Sigma-Aldrich.

2.2. Sample Preparation  
The samples were prepared using two-roll mill. The NR was masticated in the two-roll mill, and then other materials were combined according to the formulation in Table 1 using the two-roll mill. After that, the products obtained from the two-roll mill were moulded in a hot compression moulding machine into slabs of 1mm thickness.

2.3. Tensile Test  
The tensile test was done on the samples cut into the shape of dumbbell with thickness, width, and length of 1mm, 19mm and 115mm, respectively, according to ASTM D638. The tensile tests were carried on a Universal Testing Machine, GOTECH AI-7000M, equipped with load capacity of 10kN at pulling jaw speed of 50mm/min. These tests rendered the values of tensile strength, elongation at break and tensile modulus of the samples.

| TABLE 1. Blending formulation of LLDPE-NR composites with respective fillers |
|-----------------------------|---|---|---|---|---|
| Sample | LLDPE | NR | LLDPE-g-MAH | POFA* | Nanosilica* |
| LN | 70 | 20 | 10 | -null- | -null- |
| LNP2 | 70 | 20 | 10 | 2 | -null- |
| LNP4 | 70 | 20 | 10 | 4 | -null- |
| LNP6 | 70 | 20 | 10 | 6 | -null- |
| LND2 | 70 | 20 | 10 | -null- | 2 |
| LND4 | 70 | 20 | 10 | -null- | 4 |
| LND6 | 70 | 20 | 10 | -null- | 6 |

*parts per hundred (phr) of LLDPE-NR weight

2.5. Water Absorption Test Method  
The standard used for water absorption test was ASTM D570. The initial weight of the samples was taken as W1. Then, the samples were immersed in distilled water in separate containers for 24 hours at room temperature. After that, the samples were taken out and any water on the surfaces was wiped off. The samples were weighted, and labelled as W2. The formula for calculating water absorption (%) of the samples was:

\[
\text{Water absorption (\%) } = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)
\]

3. RESULTS AND DISCUSSIONS

3.1. Mechanical Properties  
Table 2 shows the tensile strength of all samples. The tensile strength of LLDPE-NR composite (14.3 MPa) decreased with the addition of 2 phr of nanosilica to 11.7 MPa. This may be due to the poor interaction of nanosilica filler with the LLDPE-NR composite for small volume fractions [26]. However, the tensile strength increased as more nanosilica was added up to 6 phr. A similar trend can be seen in the study by Rong et al. [27], where the incorporation of nanosilica decreased the tensile strength of polypropylene (PP) in the lower loading region up to 2.0 vol% particle fraction, but then the tensile strength increased when the particle fraction reached 4.7 vol%. Lay et al. [28] also found that low filler loading of nanosilica at 1 phr decreased the tensile strength of NR composite, but higher filler loading up to 3 phr lead to higher tensile strength. In a study done by Kontou & Niaounakis [8], the tensile strength of LLDPE increased up to 4 wt% of nanosilica. They stated that the nanoparticles had a mobility to act as temporary crosslinks between the polymer chains, providing localised regions of enhanced strength that would resist the growth of cracks or cavities in the LLDPE.
The tensile strength of LLDPE-NR composite decreased as POFA loading was added up to 6 phr. In a study by Ooi et al. [25], POFA had a reinforcing effect on NR for a very low loading from 0.5 phr to 1 phr, then the tensile strength dropped at higher filler loadings. Ooi et al. [25] stated that the POFA particles could be fully wetted by the NR matrix, especially at a low POFA loading. The rubber chain would penetrate into the pores of POFA and become part of the filler (bound rubber). At higher filler loadings, however, POFA particles had the tendency to position themselves in agglomeration [25, 29], especially in humid conditions [29], which greatly affected the tensile strength and elongation at break. Due to agglomeration, Ooi et al. [25] stated that the filler could not be fully wetted by the NR. In this test, the ratio of NR to LLDPE was only 20:70. Thus, it was believed that the tensile strength of LLDPE-NR composites with POFA decreased with increased loading because of the agglomeration of POFA at higher filler loadings. In a study done by Ghanbari et al. [30], nanocomposites had larger yield stress compared to microcomposites, meaning that nano-sized fillers had greater influence on the interactions between particles. It was shown that LLDPE-NR composite with filler loading of nanosilica at 6 phr, LND6, had the highest tensile strength (14.4 MPa), followed by LLDPE-NR composite with no filler, LN (14.3 MPa). Sample LNP6 with POFA loading of 6 phr had the lowest tensile strength of 10.0 MPa.

The elongation at break (%) for all samples is shown in Table 2. The elongation at break of LLDPE-NR composite decreased from 274.8 % to 238.4 % at nanosilica loading of 2 phr. However, the addition of nanosilica up to 6 phr increased the elongation at break of LLDPE-NR composite to 295.9 %. In a study done by Rajkumar et al. [31], elongation at break (%) of Acrylonitrile Butadiene Rubber (NBR) increased with nanosilica loading. Rajkumar et al. reasoned that the elongation at break increased with loading because of the layer of silicate structure restricted the tearing of polymer molecules under stretching during tensile test [31]. In other words; the elasticity of the LLDPE-NR composite increased with loading.

As the POFA filler loading increased from 2 phr to 6 phr in the LLDPE-NR composites, the elongation at break (%) decreased to 227.6. Ibrahim et al. [29] reported similar findings, where the elongation at break (%) of unsaturated polyester (UP) decreased with higher loading of POFA. Ibrahim et al. related their results with the reduction of volume of matrix as more POFA was added to the UP, where the elastic properties were only obtained from the UP matrix [29]. In other words, the elasticity of LLDPE-NR composite with POFA was only obtained from the LLDPE-NR matrix. The higher loading of POFA reduced the volume of matrix of LLDPE-NR composite, which led to the decreasing trend of elongation at break (%).

Table 2 shows the tensile modulus (MPa) of all samples. The addition of POFA at 2 phr decreased the tensile modulus of LLDPE-NR composite. The tensile modulus increased from 264.2 MPa to 388.6 MPa with increased loading. In a study done by Ismail et al. [32], the tensile modulus of PP/recycled NR composites increased as the POFA loading increased up to 10 phr. They reasoned that the addition of POFA caused a reduction in chain mobility, while increasing the rigidity of composites at the same time [32]. Behzad et al. [33] reported that the tensile modulus of high density polyethylene (HDPE) increased with wood flour content. Sahari et al. [34] also reported that the higher the content of bio-filler, the higher the tensile modulus of plasticised sugar palm starch. Thus, the addition of POFA in LLDPE-NR composite increased the rigidity, or tensile modulus, of the composites with increased filler loading.

The addition of nanosilica at 2 phr decreased the tensile modulus of LLDPE-NR composite. However, the tensile modulus increased from 278.6 MPa to 432.4 MPa as more nanosilica filler was added into the composite. In another study by Makmud et al. [35], a similar trend was observed where the tensile modulus of LLDPE-NR composite decreased with nano-scale MMT at 2 phr, then increased with MMT at 4 phr. According to Fu et al. [36], the addition of rigid particles to a polymer matrix would improve its modulus since the rigidity of inorganic fillers are much higher than that of organic polymers. This was also supported by Lay et al. [28] which stated that the modulus would increase due to the embedding of nanosilica particles in polymer matrix. Thus, the addition of inorganic fillers (nanosilica) in the LLDPE-NR composited increased the rigidity, or tensile modulus, of composite with increased loading.

### Table 2. Results of tensile tests for all samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>Tensile Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LN</td>
<td>14.3</td>
<td>274.8</td>
<td>302.9</td>
</tr>
<tr>
<td>LNP2</td>
<td>11.9</td>
<td>249.1</td>
<td>264.2</td>
</tr>
<tr>
<td>LNP4</td>
<td>11.2</td>
<td>227.6</td>
<td>281.0</td>
</tr>
<tr>
<td>LNP6</td>
<td>10.0</td>
<td>221.0</td>
<td>388.6</td>
</tr>
<tr>
<td>LND2</td>
<td>11.7</td>
<td>238.4</td>
<td>278.7</td>
</tr>
<tr>
<td>LND4</td>
<td>12.4</td>
<td>251.2</td>
<td>351.4</td>
</tr>
<tr>
<td>LND6</td>
<td>14.4</td>
<td>295.9</td>
<td>432.4</td>
</tr>
</tbody>
</table>

### 3.2. Surface Analysis

The SEM images of LN (Figure 1) and LNP6 (Figure 2) are shown below. In Figure 1, it is apparent that the NR has blended well in the LLDPE matrix, thus explaining the high tensile strength, high tensile modulus and high elongation at break compared to LLDPE-NR composites with fillers.
Meanwhile, in Figure 2, the areas marked in white circles show the agglomeration of POFA within the composites. There are also voids within the samples. The agglomerated POFA caused the voids to happen when the POFA was pulled out during the tensile test. Similar findings have been by Ooi et al. [25], where at higher filler loadings, agglomeration of POFA had caused the detachment of filler. This strengthened the claim that agglomeration of POFA due to higher filler loading caused lower tensile strength of LLDPE-NR composite.

3.3 Physical Properties

Table 3 shows the water absorption value (%) of all samples after being soaked in distilled water for 24 hours. The water absorption value of LLDPE-NR composites increased with POFA loading as it is evident in Table 3. Sample LNP6 with POFA loading of 6 phr had the highest water absorption value.

Meanwhile, water absorption value (%) decreased significantly with nanosilica fillers. According to Zhao et al. [37], the percentage of water absorption in epoxy resin decreased with increasing nano-alumina particle content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LN</td>
<td>0.68</td>
</tr>
<tr>
<td>LNP2</td>
<td>1.10</td>
</tr>
<tr>
<td>LNP4</td>
<td>1.15</td>
</tr>
<tr>
<td>LNP6</td>
<td>1.20</td>
</tr>
<tr>
<td>LND2</td>
<td>0.35</td>
</tr>
<tr>
<td>LND4</td>
<td>0.44</td>
</tr>
<tr>
<td>LND6</td>
<td>0.38</td>
</tr>
</tbody>
</table>

They attributed this to the presence of nanoparticles which could increase the path length for moisture absorption. In this study, when increasing the loading of nanosilica in the LLDPE-NR composite, the nanosilica increased the path length for moisture absorption of the composite, which resulted in decreasing water absorption value (%) of LLDPE-NR composite. Although water absorption increased with nanosilica loading, but it was still lower than unfilled LLDPE-NR composite. Due to their small size, the surface interaction between nanosilica particles became magnified, hence agglomeration came into effect [38]. Lau reported similar findings, where increasing the content of nanosilica would increase the water absorption value of polyethylene attributed to the agglomeration which would inevitably penetrate into the nanosilica structure [39].

According to Nikolajevic [40], the increase of the amount of water absorbed by the insulation would increase the degradations of electrical characteristics of insulation. In other words, the lesser the amount of water absorbed by the insulation, the lesser the degradations of electrical characteristics of insulation, making it a better electrical insulation material. From this test, LND2 has the lowest water absorption value.

4. CONCLUSION

Nanosilica filler improved the tensile properties of LLDPE-NR composite up to 6 phr. The best loading of nanosilica was 6 phr, where it increased the tensile strength, elongation and tensile modulus of LLDPE-NR composite by 0.5%, 7.7% and 42.7%, respectively. Meanwhile, the tensile properties of LLDPE-NR decreased with increasing POFA content. SEM image showed the agglomerated POFA on LLDPE-NR surface, which affected the tensile strength of LLDPE-NR. However, tensile modulus of LLDPE-NR was improved by 1.3 % with POFA content of 6 phr. Physical properties of LLDPE-NR improved as the water absorption value decreased significantly when added with nanosilica compared to neat LLDPE-NR. Meanwhile, the water absorption value increased with POFA loading.
5. ACKNOWLEDGEMENT

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6. REFERENCES

32. Ismail, H., Khoon, T.B., Hayeemasa, N. and Husseinsyah, S., "Effect of oil palm ash on the properties of


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Faculty of Science and Natural Resources, University Malaysia Sabah, Jalan UMS, Sabah, Malaysia
Institute of High Voltage & High Current (UTM IVAT), Faculty of Electrical Engineering, University Technology Malaysia, Johor, Malaysia
Center for Composites, Institute of Vehicle System and Engineering (IVeSE), University Technology Malaysia (UTM), Johor, Malaysia

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چکیده
محاسبات میکروپلاستیک برای اندازه‌گیری پیوستگی فلیکسیتی (POFA) در مقیاس میکرو ساخته شده امر است. پیوستگی فلیکسیتی کم کننده اثرات ضروری بر افزایش نیروی برش و افزایش نیروی برش به دست می‌آید. این افزایش می‌تواند با وارد کردن خاکستر در بخش ساختمانی و افزایش برش و افزایش نیروی برش نیروی برش و افزایش نیروی برش با توجه به تغییراتی که در آنها وجود دارد، کاهش یابد. این افزایش نیروی برش با وارد کردن خاکستر در بخش ساختمانی و افزایش برش و افزایش نیروی برش نیروی برش و افزایش نیروی برش با توجه به تغییراتی که در آنها وجود دارد، کاهش یابد. این افزایش نیروی برش با وارد کردن خاکستر در بخش ساختمانی و افزایش برش و افزایش نیروی برش نیروی برش و افزایش نیروی برش با توجه به تغییراتی که در آنها وجود دارد، کاهش یابد.