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Development of Linear Low-Density Polyethylene/Graphene Nanoplatelet/Natural Rubber/Liquid Natural Rubber Nanocomposites for Enhanced Mechanical, Thermal, and Semiconductor Properties

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Linear low-density polyethylene (LLDPE) is a polyolefin with attractive properties such as low density, ease of processing, and recyclability. However, its low stiffness and high oxygen permeability restricts its use in durable packaging and necessitates modification of its mechanical and barrier properties. Adding fillers to the polymer matrix is one strategy to enhance product performance. In this study, natural rubber (NR, 5–25 wt%) was blended with LLDPE/graphene nanoplatelet (GNP) nanocomposites to produce thermoplastic elastomer films as potential packaging materials. Liquid natural rubber (LNR, 2–12 wt%) was added as a compatibilizing agent. The LLDPE:GNP:NR:LNR ratio of 66:4:20:10 provided optimal characteristics, such as improved mechanical strength and a 90.6 % increase in thermal conductivity (0.61 W/mK) compared to LLDPE alone (0.32 W/mK). This enhancement is attributed to better GNP dispersion and interfacial adhesion from NR and LNR, which improved stress transfer and heat conduction. In contrast, electrical conductivity decreased although the product remained a semiconductor ($\sim 10^{-8}$), likely due to the insulating effect of rubber disrupting the GNP network. Thermal conductivity declined sharply beyond 60 °C, likely due to phonon scattering and restricted filler mobility at higher temperatures, which hinder heat transfer. This novel LLDPE/GNP/NR/LNR nanocomposite shows potential as a durable packaging material with semiconductive electrical properties and high thermal resistance.

Keywords: Thermoplastics; graphene; elastomer; compatibilizer; conductivity

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Linear low-density polyethylene (LLDPE) is a type of polyethylene (PE) widely used in the market alongside low-density polyethylene (LDPE) and high-density polyethylene (HDPE), particularly in packaging applications. LLDPE is produced through the copolymerization of long-chain ethylene at low temperatures and pressures, and is characterized by its linear structure with short branching [1]. This polymer possesses several attractive properties, such as low density, ease of processing, and recyclability. However, its low stiffness and high oxygen permeability restrict its wider use in durable packaging applications, creating a need for strategies to overcome these flaws.

The addition of nanoscale fillers into the polymer matrix is one technique to address the limitations of individual polymer components [2]. Graphene-based and graphene-derived composites (graphite, graphene nanoplatelets, and carbon nanotubes) as nanoscale fillers have been increasingly studied and produced due to their usefulness in sensor, electrical, and electronics applications [3–6]. The graphene nanoplatelets (GNP) used in this study are exfoliated graphene materials characterized by properties such as a large surface area, electrical conductivity, mechanical strength, and electron mobility. Their combination with specific polymer groups results in composites with enhanced mechanical, thermal, and electrical properties, as well as improved elasticity [2, 3]. Graphene is particularly suitable as a nanoscale filler due to its physical characteristics, making it applicable in various fields such as medicine, biomedicine, drug delivery, and biosensing [5, 7].

LLDPE/GNP nanocomposites blended with natural rubber (NR) can expand the applications of these nanocomposite materials. The choice of NR over other elastomers, such as synthetic rubber or silicone rubber, is due to its lower cost, abundant availability in Malaysia, and superior mechanical properties [8]. Based on characterization analyses of the physical properties of LLDPE/GNP, NR can be combined with nanocomposites to enhance mechanical properties, thermal stability, crystallinity, and electrical conductivity. NR is an elastomer with excellent elasticity and flexibility. Due to its insulating properties, potential applications of NR include its use as a semiconductor, coating material, or rubber product.

This was previously investigated by Frasca et al. [9] who developed nanocomposites of chlorobutyl isoprene rubber/graphene/carbon black for rubber products with improved resistance to UV and weathering. Meanwhile, Chen et al. [10] successfully created montmorillonite/brominated butyl rubber nanocomposites with excellent gas barrier properties. Similarly, Natarajan et al. [11] suggested that nanocomposites containing elastomers such as rubber could be used in sensor applications for tyres, valves, gaskets, and engines.

To ensure compatibility in blending LLDPE/GNP/NR, liquid natural rubber (LNR) was utilized. LNR acts as a compatibilizer due to its low molecular weight and its composition of both rubber and non-rubber units [12]. It serves as a compatibilizing agent in the production of thermoplastic natural rubber (TPNR) by enhancing the bonding between LLDPE/GNP/NR through the presence of carbon groups and its reduced rubber viscosity [13]. The addition of LNR also increases the rubber component in the LLDPE/GNP nanocomposite, altering its final properties. Although LLDPE/GNP nanocomposites and various rubber-based nanocomposites have been studied separately, the combined use of LLDPE, GNP, NR, and LNR in a single system has not been systematically reported. This novel combination addresses the problem of LLDPE's low stiffness and oxygen permeability while simultaneously improving its functional properties. Therefore, the aim of this study was to develop and characterize LLDPE/GNP/NR/LNR nanocomposites with enhanced mechanical, thermal, and semiconductive properties for potential application as durable packaging materials.

EXPERIMENTAL

Chemicals and Materials

LLDPE (density: 0.918 g/cm³, melt flow index: 1.0 g/min, melting point: 120–160 °C) was obtained from Exxon Mobil Chemical Corporation and used as the thermoplastic resin for this study (Figure 1(a)). GNP grade KNG-150 (thickness: 5–15 nm, diameter: 5 µm, density: 2.25 g/cm³) was supplied by KNANO and utilized as a nanoscale filler (Figure 1(b)). NR classified as Standard Malaysian Rubber (SMR) CV, was provided by the Malaysian Rubber Board. The NR sample was stored in a dark room at room temperature (25 °C) (Figure 1(c)). Additionally, NR was used as the primary material for synthesizing liquid natural rubber (LNR) through chemical oxidation in the polymer processing laboratory at Universiti Kebangsaan Malaysia (UKM).

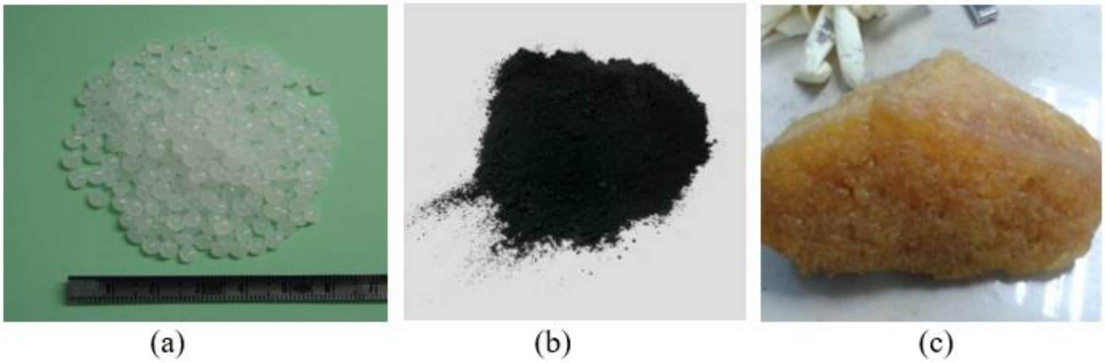


Figure 1. Main materials used in this study: (a) LLDPE, (b) GNP, and (c) NR.

Table 1. Compositions of LLDPE/GNP/NR/LNR Nanocomposites prepared by in-situ and PREMIX (masterbatch) Methods.

Sample Code	LLDPE (wt%)	GNP (wt%)	NR (wt%)	LNR (wt%)	Preparation Method	Notes
LLDPE (control)	100	0	0	0	n/a	Baseline polymer
LLDPE/GNP4	96	4	0	0	In-situ	Effect of GNP filler
LLDPE/GNP5	95	5	0	0	In-situ	Higher GNP loading
LLDPE/GNP/NR20	76	4	20	0	In-situ	Influence of NR
LLDPE/GNP/NR20/LNR5	71	4	20	5	In-situ	Compatibilizer (low LNR)
LLDPE/GNP/NR20/LNR10	66	4	20	10	In-situ	**Optimized formulation**
LLDPE/GNP/NR20/LNR12	64	4	20	12	In-situ	Higher LNR loading
MB-LLDPE/GNP4	96	4	0	0	PREMIX	Masterbatch control
MB-LLDPE/GNP5	95	5	0	0	PREMIX	Higher GNP loading
MB-LLDPE/GNP/NR20	76	4	20	0	PREMIX	NR effect (MB)
MB-LLDPE/GNP/NR20/LNR10	66	4	20	10	PREMIX	Optimized MB

Sample Formulation

To investigate the influence of composition and processing route on nanocomposite properties, a series of LLDPE/GNP/NR/LNR samples were prepared with varying ratios of natural rubber (NR) and liquid natural rubber (LNR), while maintaining LLDPE as the matrix and graphene nanoplatelets (GNP) as the nanoscale filler. Formulations were designed to study the effects of single and combined additives as well as the role of the compatibilizer (LNR). In addition to the in-situ melt mixing method, selected samples were also prepared using the PREMIX (masterbatch) approach, whereby GNP was first dispersed in LLDPE prior to blending with NR and LNR. This allowed comparison of filler dispersion and interfacial adhesion between the two processing methods. The complete formulations are summarized in Table 1.

Characterization Methods

Preparation of LLDPE/GNP/NR/LNR Nanocomposites

The LLDPE/GNP/NR/LNR nanocomposites were prepared using the in-situ melt mixing method with an internal mixer (Brabender W50EHT, Germany), where NR and LNR were added at the 1st and 3rd minutes, respectively. The mixture was then blended for an additional 10 minutes. Besides the in-situ melt mixing method, the nanocomposites were also prepared using the premixing method, as previously reported [14]. For analysis, the prepared nanocomposites were formed into films with a thickness of 1 mm using a hot press machine.

Characterizations

A comparison of the mechanical and thermal properties was conducted on samples with varying material ratios and preparation methods (in-situ melt mixing versus premixing) to identify the best-performing sample for potential packaging applications.

Mechanical Properties

The tensile test, also known as the stress-strain test, was used to measure the tensile strength, Young's Modulus, elongation at breaking point, and stiffness of the studied composite. Dumbbell-shaped samples were used according to ISO 37-2 standard with a thickness of 1 mm, measured using a Mitutoyo Vernier calliper, with the average thickness and width of the sample taken into account. This characterization technique employed a Testometric M350-10CT machine with a crosshead speed of 10 mm/min based on ASTM 412, tested on 10 sample specimens at the Polymer Laboratory, FST, UKM. The samples were placed on a sample holder with a load of 5000 N applied. All measurements were carried out in triplicate for each formulation, and mean values with standard deviations are reported. Standard deviations are presented as error bars in the corresponding figures to reflect data variability and ensure the validity of the results. The results obtained using this computer software generated a stress-strain curve. Mechanical characterization is essential because packaging materials must withstand stretching, tearing, and handling during processing and use. Tensile strength reflects the material's ability to resist breaking under load, Young's modulus indicates stiffness important for dimensional stability, and elongation at break relates to flexibility and resistance to tearing. These parameters collectively determine the durability and functional performance of packaging films [15,16].

Electrical Conductivity Analysis (Impedance)

The electrical conductivity values of the samples were measured using a 1260 impedance analysis machine at room temperature (25 °C), with a frequency range from 1 Hz to 10^6 Hz. All tested samples were in the form of solid discs with a thickness of 2 mm and a diameter of 15 mm. The samples were coated with silver paint to make their surface conductive and prevent charging. The specimen to be tested was then placed between two solid iron discs, which acted as the sample holder. The sample holder used was the SE-70 Electrode type from Ando Electric Co. LTD, Tokyo, Japan. The impedance experiment was conducted using ZPlot software, while ZView software was used for data plotting and impedance data analysis. This characterization is relevant because packaging materials may be required to dissipate static charges or exhibit semiconductive behaviour to protect sensitive contents. Measuring electrical conductivity helps to determine whether the developed nanocomposites can function in specialized packaging applications, such as electronics or pharmaceutical products, where static charge control and safety are critical.

Thermal Conductivity Analysis

Thermal conductivity was measured using the flash method, which employs laser energy to heat the surface of the sample, using the NETZSCH LFA 447/2-41 instrument. The tested samples were in the form of discs with a diameter of 12.7 mm and a thickness of approximately 1 mm. The samples were coated with graphite and then placed in an electric furnace. Data was recorded using an infrared detector. Three key pieces of information obtained were thermal conductivity (λ, W/mK), thermal diffusivity (α, m^2/s), and heat capacity (C, J/gK). This characterization is important as packaging materials must withstand thermal stress during production processes such as heat sealing, and maintain stability under varying storage and transportation conditions. Improved thermal conductivity ensures better heat resistance and dimensional stability, thereby enhancing the safety and durability of packaging films for practical applications [17].

RESULTS AND DISCUSSION

To study the mechanical properties of the nanocomposite samples, data for tensile test parameters such as tensile strength, elongation at the breaking point, and Young's Modulus were recorded and compared for all samples. Overall, the presence of GNP improved the mechanical properties of the nanocomposites. On the other hand, the presence of NR significantly influenced these mechanical properties, indicating that NR imparted flexibility to the nanocomposites.

Tensile Strength

Comparison of Preparation Methods

Figure 2 shows a comparison of the tensile strength of samples containing different compositions of NR, LNR, and GNP, prepared using the PREMIX method and in-situ blending. Overall, the PREMIX method recorded better tensile strength compared to the in-situ blending method. This finding is consistent with observations in a previous study by Busu et al. [14] comparing the preparation methods of LLDPE/GNP nanocomposites. The improved performance can be attributed to better dispersion of GNP within the polymer matrix during premixing, which enhances the interfacial contact and filler–matrix adhesion [14,18]. Stronger adhesion promotes more efficient stress transfer from the LLDPE matrix to the graphene nanoplatelets, thereby increasing the tensile strength of the nanocomposite.

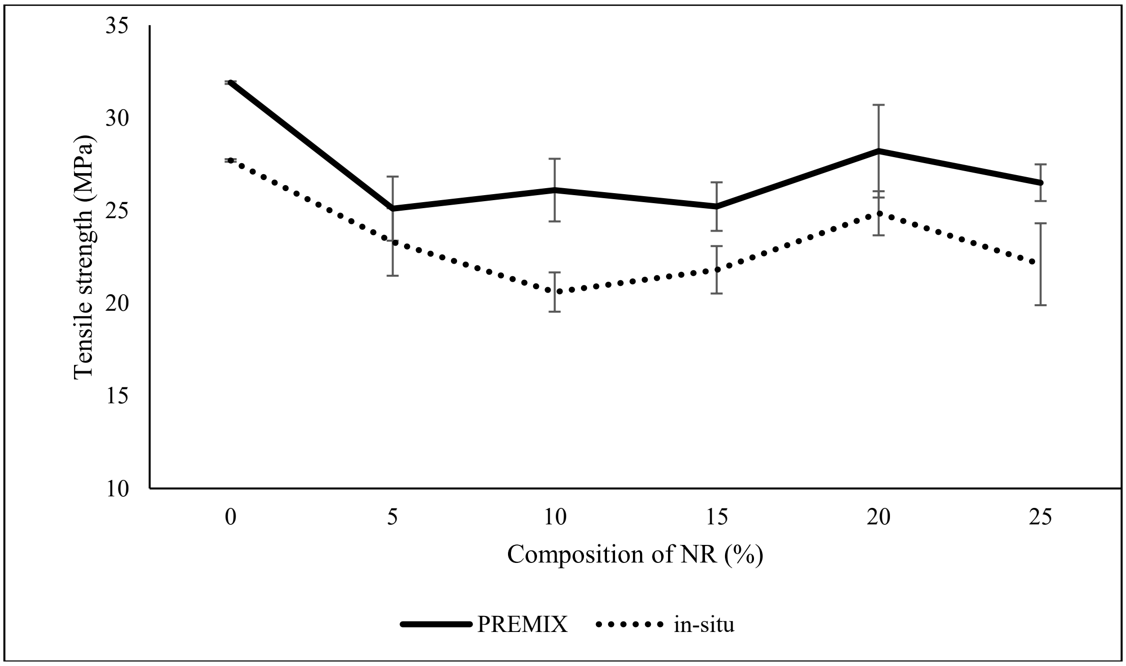
Effect of NR, LNR, and GNP Addition

The addition of 20 % NR resulted in an increase in the tensile strength of the LLDPE thermoplastic, which recorded the highest value compared to the control LLDPE sample, at 264.8 % (Figure 2(a)). This observation aligns with the findings of Rezaei-Abadchi et al. [19], who produced LLDPE/NR thermoplastic with field tyre rubber as an alternative elastomer material. The incorporation of fillers is believed to contribute to enhancing the material's mechanical properties and its resistance to stress in the final product. For packaging applications, higher tensile strength is particularly important because it ensures that films and containers can withstand stresses during handling, sealing, and transportation without tearing or failing [20]. Thus, the observed improvement in tensile strength directly supports the suitability of the developed nanocomposites as durable packaging materials. However, the presence of NR decreased the tensile strength of LLDPE/GNP. According to Attaran et al. [21], the tensile strength of their LDPE nanocomposites decreased as the amount of rubber (epoxidized natural rubber) increased in the nanocomposites, which reduced the LDPE content, thus affecting its ability to maintain good tensile strength. Similar findings were reported by Razmjooei et al. [22] and Nakason et al. [23], who both observed a decrease in tensile strength after adding rubber components to LLDPE and HDPE thermoplastics, respectively.

Meanwhile, a similar trend was observed when LNR was incorporated into LLDPE/GNP/NR (Figure

2(b)). Firstly, the addition of the optimum amount of LNR (10 %) improved the tensile strength of the resulting nanocomposite samples compared to the LLDPE control by 139.6 %. This 10 % LNR addition also resulted in the LLDPE/GNP/NR/LNR sample with the best tensile strength. The change in tensile strength can be attributed to the sensitivity of LNR's compatibilizing effect, which arises from its ability to promote interfacial crosslinking between the LLDPE matrix and the NR phase. This ability is often referred to as the "crosslinking power" of LNR. This crosslinking power is most effective at an optimum content, defined here as the concentration at which LNR achieves the best interfacial bonding and homogeneity within the blend. In this study, the optimum content where tensile strength was maximized was observed at 10 wt% LNR. Beyond this level, the excess LNR led to poorer dispersion and increased non-homogeneity, thereby reducing the effectiveness of crosslinking and diminishing tensile strength. Dahlan et al. [24] reported that the crosslinking of LNR becomes ineffective beyond the optimum content due to the polymer blend becoming increasingly non-homogeneous. Overall, the tensile strength of the nanocomposites was found to decrease with the addition of LNR compared to LLDPE/GNP and LLDPE/GNP/NR. This occurred because the flexibility of the samples increased with the amount of LNR in the polymer matrix. Additionally, the efficiency of stress transfer from the matrix phase to the filler decreased due to the formation of a rubber phase network, which further reduced the tensile strength [25].

As shown in Figure 2(c), the addition of GNP (1–4 %) in the NR/LNR thermoplastic demonstrated an increase in tensile strength, highlighting the effect of GNP on the mechanical strength within the polymer matrix. The effect of nanoparticle agglomeration at higher GNP levels (5 %) resulted in a decrease in the tensile strength of the material. However, the tensile strength of LLDPE/GNP/NR/LNR was lower overall, compared to LLDPE/GNP. This could be due to the presence of NR, which reduced the tensile strength of the polymer matrix. Based on the overall tensile strength results, we concluded that the ideal composition for GNP:NR:LNR in the production of LLDPE/GNP/NR/LNR nanocomposites was 4:20:0. This composition provided a desirable compromise between strength, contributed by GNP, and flexibility, contributed by NR, which is essential for packaging applications that require materials to resist tearing while still being pliable enough for processing and handling.



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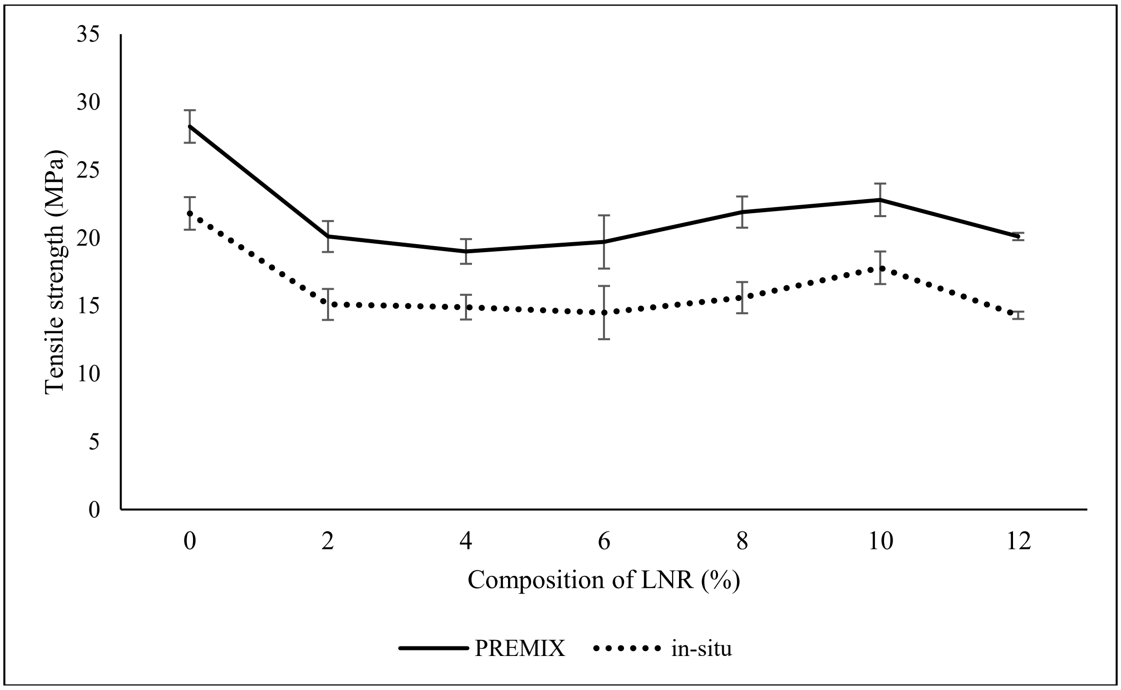

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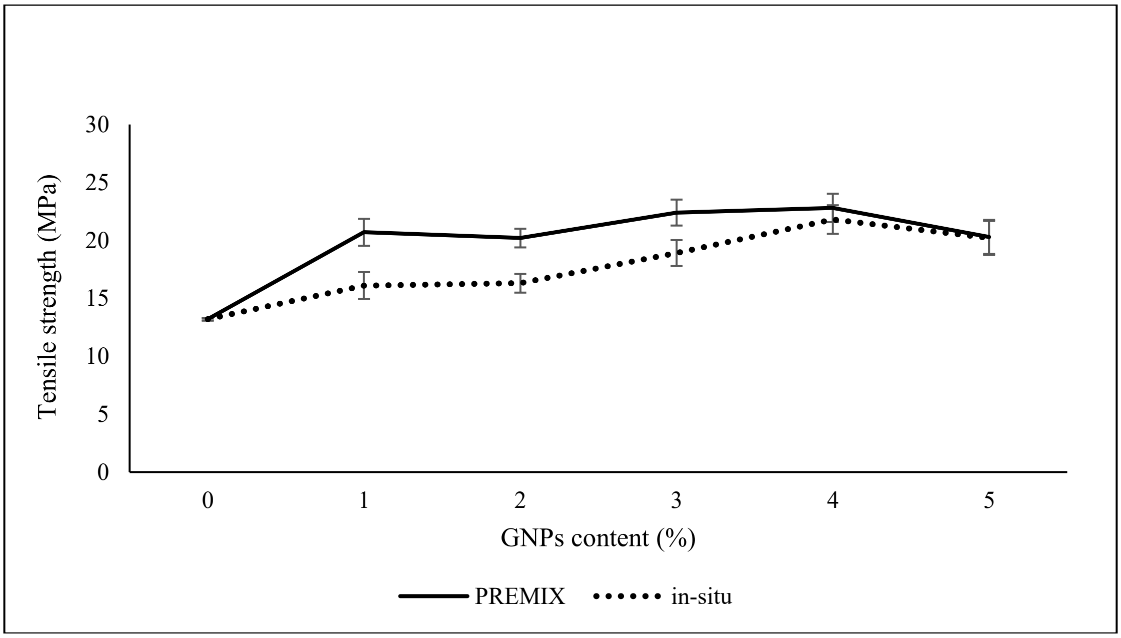

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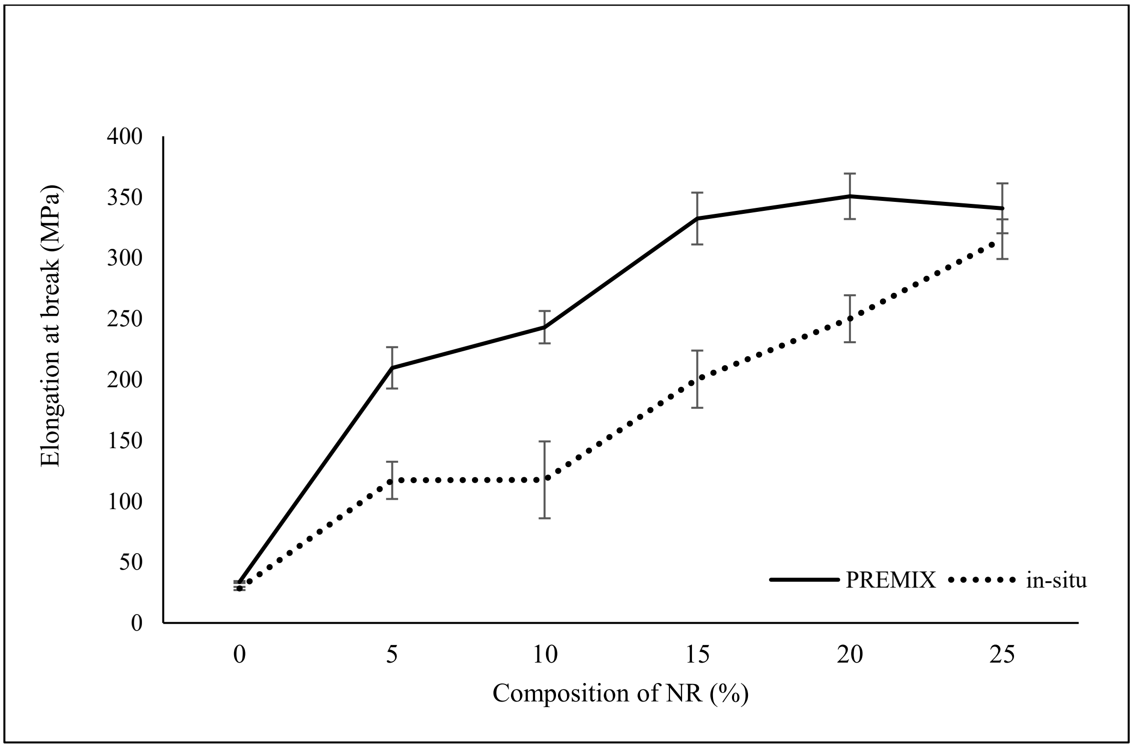
Figure 2. Comparison of tensile strength of samples with different compositions: (a) NR (fixed at 4% GNP, 0% LNR), (b) LNR (fixed at 20% NR, 4% GNP), and (c) GNP (fixed at 20% NR, 10% LNR).

Elongation at Break

Comparison of Preparation Methods

Figure 3 shows a comparison of elongation at break values for samples with different compositions of NR, LNR, and GNP, prepared using the PREMIX Method and in-situ blending. Overall, the PREMIX method demonstrated better elongation at break values compared to the in-situ blending method when NR and LNR components were included (Figure 3(a-b)). This is consistent with observations from previous studies comparing preparation methods, which showed better material dispersion within the polymer matrix through the PREMIX approach.

In contrast, the addition of GNP reduced elongation at break values, as the mechanical strength of GNP lowered the material's elastic properties (Figure 3(c)). This can be attributed to the role of GNP in providing strong tensile properties with increasing composition, thereby reducing the elongation at break. Nanocomposites prepared using the PREMIX method exhibited higher elongation at break values compared to those prepared by the in-situ method. The PREMIX preparation facilitated good dispersion of GNP but led to a reduction in elongation values. On the other hand, the in-situ method, which was less effective in dispersing GNP, resulted in a more dominant rubber component. Higher elongation at break values are desirable for flexible packaging applications because they indicate greater stretchability and resistance to tearing during handling, sealing, and transportation [26]. This property ensures that the material can maintain its integrity under mechanical stress while still offering flexibility for practical uses.



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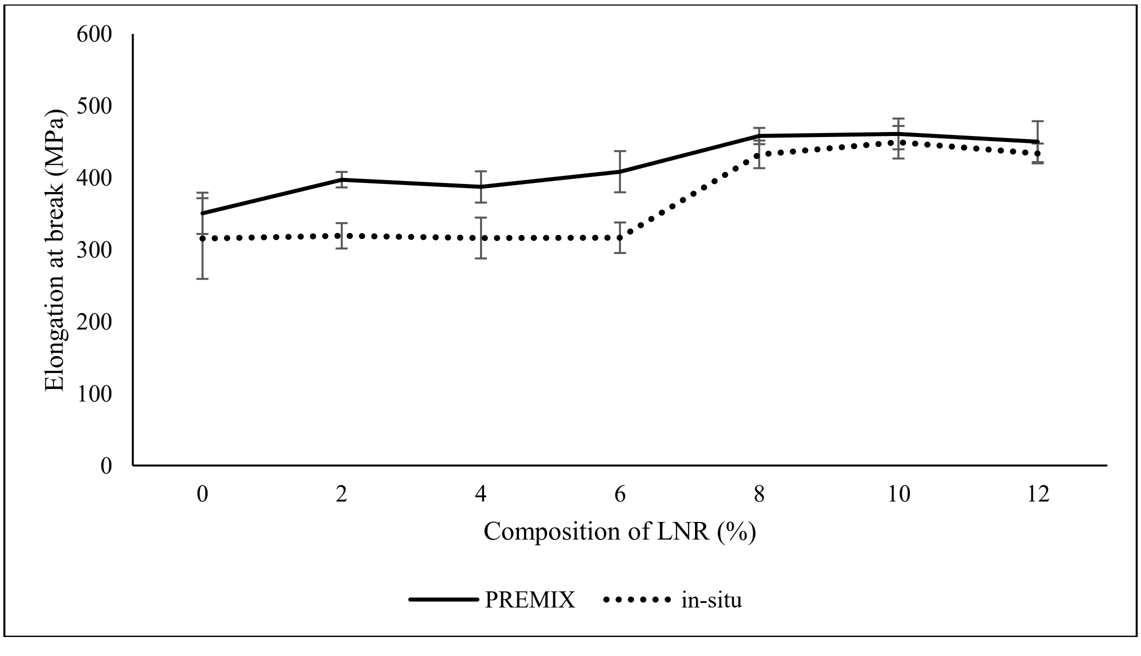

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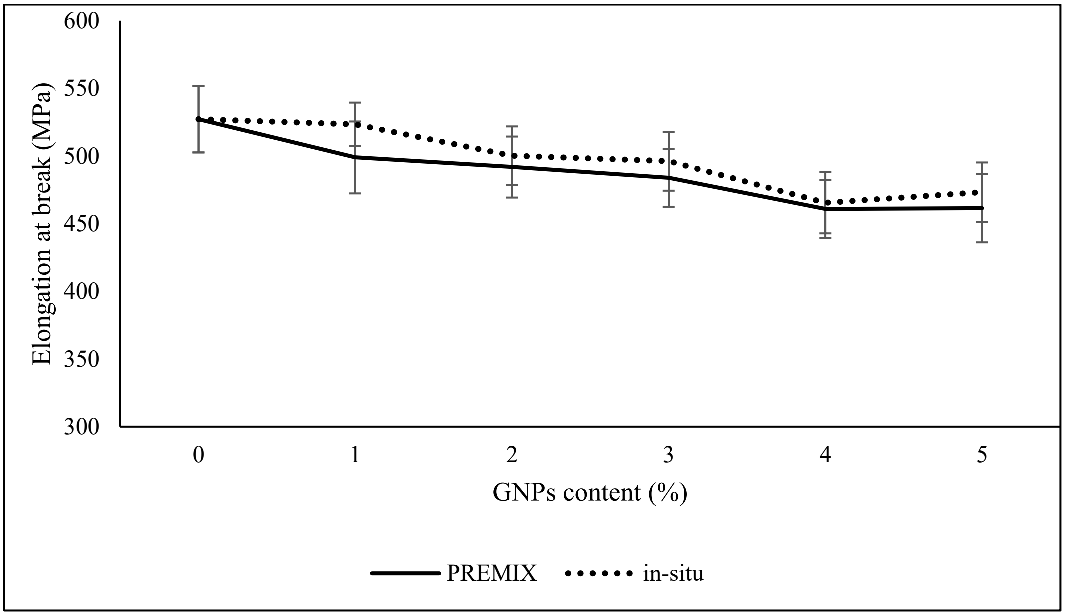


(c)

Figure 3. Comparison of elongation at break values for samples with different compositions: (a) NR (fixed at 4% GNP, 0% LNR), (b) LNR (fixed at 20% NR, 4% GNP), and (c) GNP (fixed at 20% NR, 10% LNR)).

Effect of NR, LNR, and GNP Addition

The trend of adding rubber components such as NR and LNR was found to increase the elongation at break values of the samples due to the elastic properties of rubber. The addition of NR and LNR also enhanced the elongation at break values of the nanocomposite samples prepared in this study. This may be attributed to the rubber phase coverage in the nanocomposites, which is believed to reduce fracture resistance, thereby leading to higher elongation at break values. Plasticization within the blend may also occur with the presence of rubber, further increasing these values [27]. In contrast, a higher GNP content tends to reduce elongation because the rigid nanoplatelets restrict polymer chain mobility within the matrix [28]. This limited chain movement decreases the material's ability to stretch under stress, leading to lower elongation at break values despite improvements in tensile strength.

Young's Modulus

Comparison of Preparation Methods

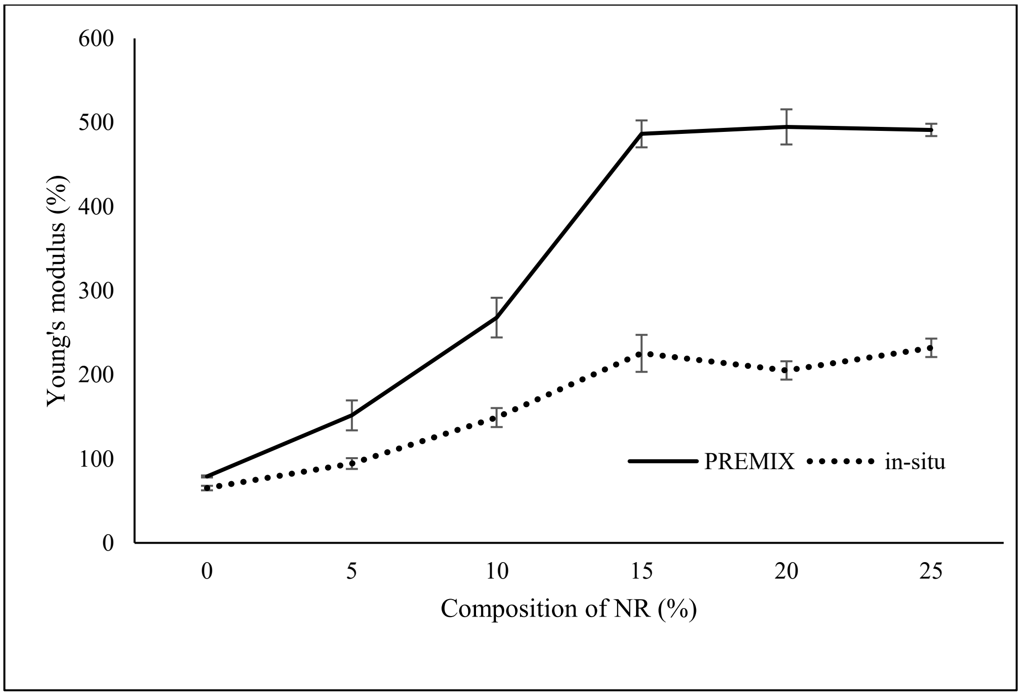
Figure 4 illustrates the comparison of Young's modulus results for samples containing different compositions of NR, LNR, and GNP, prepared using the PREMIX method and in-situ blending. As with the previous experiment, the PREMIX method yielded higher Young's modulus readings compared to the in-situ blending method when NR and LNR rubber components were incorporated into the polymer matrix (Figure 4(a-b)). Taken together with the earlier tensile strength and elongation results, these findings indicate a consistent mechanical performance trend: the PREMIX method improved filler dispersion, leading to stronger filler–matrix adhesion and higher tensile strength, while the addition of NR and LNR enhanced elongation and flexibility. However, higher GNP loading increased stiffness and restricts chain mobility, which raised Young's modulus but reduced elongation [29]. This demonstrates the need to optimize the GNP and rubber content to achieve a balanced combination of strength, stiffness, and flexibility suitable for packaging applications.

Effect of NR, LNR, and GNP Addition

The reduction in material stiffness can be observed through Young's modulus readings, which showed increased values when NR and LNR were incorporated into the nanocomposites at their optimal compositions of 20 % and 10 %, respectively. This observation aligns with the elastic properties of rubber, which do not exhibit rigid material characteristics and can enhance a material's modulus. This finding corresponds to the study by Pazhooh et al. [30], who noted that the presence of rubber reduced the mechanical properties of materials due to size disparities limiting NR bonds per unit area and restricting full interaction with the polymer matrix. Changes in GNP content (Figure 4(c)) exhibited a similar trend to elongation at break, where increased amounts of GNP resulted in a significant increase in material stiffness, subsequently reducing Young's modulus readings.

However, the addition of a rubber component, particularly LNR, led to decreased and inconsistent Young's modulus values. This phenomenon was also reported by Aguilar-Bolados et al. [31], who observed a decline in Young's modulus in their nanocomposites as more rubber was added. Attaran et al. [21] attributed this behaviour to the dilution effect of secondary rubber components. The presence of rubber within the polymer matrix allows for segmental movement of polymer chains under tensile stress applied to the nanocomposite samples, thereby reducing the Young's modulus [32]. For packaging applications, this reduction reflects a shift in the stiffness–flexibility balance: while a lower modulus means reduced rigidity, it simultaneously provides greater flexibility, which is advantageous for films and wraps that must bend and stretch without cracking. Thus, although less stiffness may weaken structural integrity, a moderate reduction in modulus can improve handling and durability in flexible packaging.

The degree of chain restriction and crosslink density within the composite containing rubber contributes to molecular chain deformation. As the number of rubber chains on the polymer matrix surface increases, elongation at break decreases, leading to lower modulus values. Alwaan et al. [33] explained that this condition is due to the dilution effect within the polymer matrix caused by high rubber content. Their study revealed the lowest Young's modulus value (a 71.4 % reduction) occurred when 30 % natural rubber was incorporated into LLDPE/natural rubber blends.



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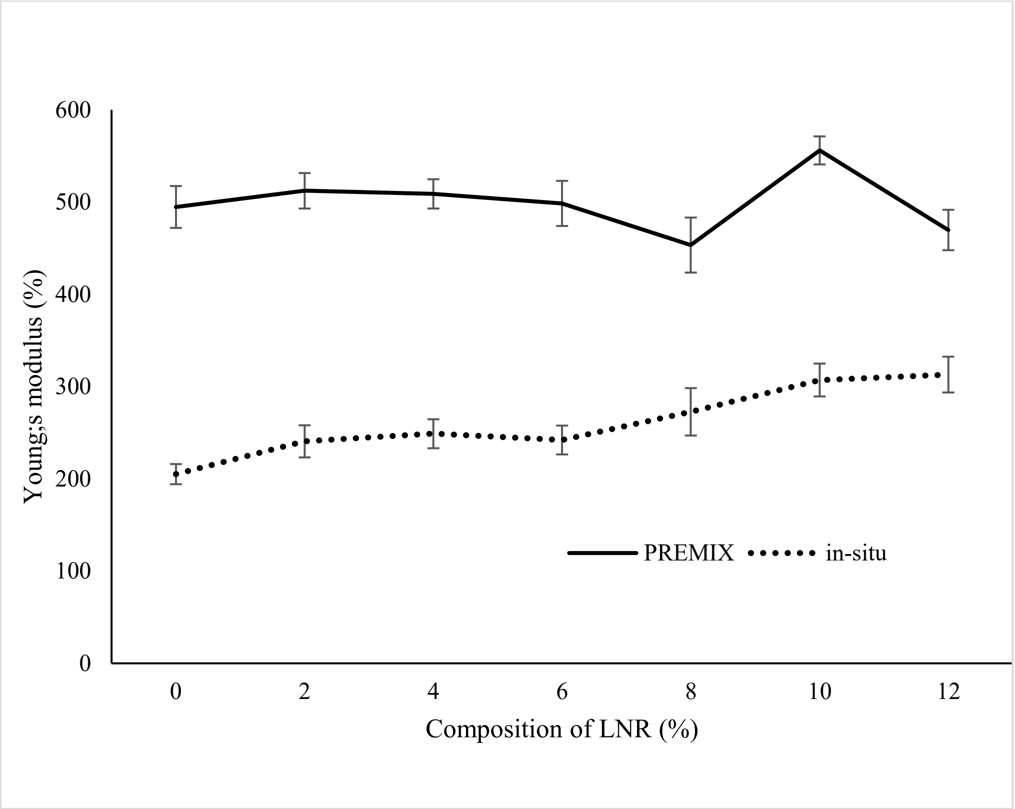

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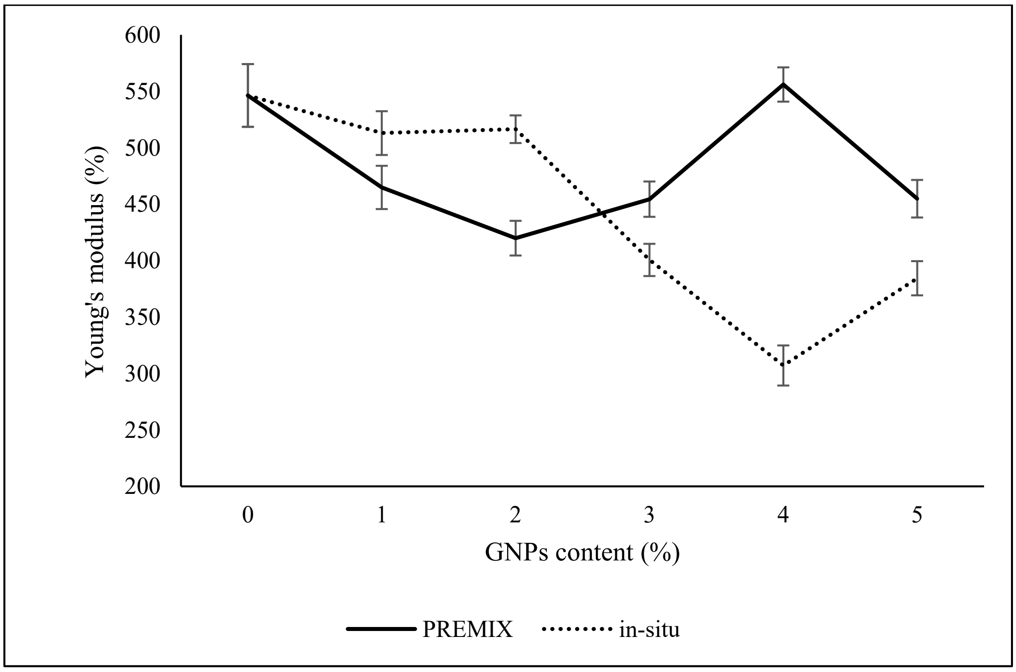

(c)

Figure 4. Comparison of Young’s modulus values for samples with varying compositions: (a) NR (4% GNP, 0% LNR), (b) LNR (20% NR, 4% GNP), (c) GNP (20% NR, 10% LNR).

Table 2. Electrical Conductivity of Selected Samples.

Sample Code	LLDPE (wt%)	GNP (wt%)	NR (wt%)	LNR (wt%)	Electrical Conductivity (S/cm)
LLDPE	100	0	0	0	4.09×10^{-10}
LLDPE/GNP4	96	4	0	0	5.21×10^{-9}
MB-LLDPE/GNP4	96	4	0	0	1.02×10^{-8}
LLDPE/GNP/NR20	76	4	20	0	3.03×10^{-9}
MB-LLDPE/GNP/NR20	76	4	20	0	6.73×10^{-8}
LLDPE/GNP/NR20/LNR10	66	4	20	10	4.77×10^{-9}
MB-LLDPE/GNP/NR20/LNR10	66	4	20	10	4.59×10^{-8}

Electrical Conductivity

LLDPE/GNP nanocomposites have demonstrated good electrical conductivity as GNP is an electrical conductor [3]. However, the inclusion of rubber components led to a slight reduction in electrical impedance values (Table 2). For example, the conductivity decreased by ~42 % when NR was added to LLDPE/GNP (from 5.21×10^{-9} S/cm to 3.03×10^{-9} S/cm). Similarly, the addition of both NR and LNR reduced conductivity by ~8 % compared to LLDPE/GNP (from 5.21×10^{-9} S/cm to 4.77×10^{-9} S/cm). Electrical conductivity persisted in materials containing NR/LNR, possibly because rubber components can act as dopants through protonation or by inducing conformational changes within the GNP network [13,34]. The minimal decline in electrical conductivity upon the addition of rubber components may also be attributed to reduced phase separation between LLDPE/GNP and NR/LNR. This indicates that while some conductivity is sacrificed, the nanocomposites still maintain semi-conductive behaviour suitable for packaging applications requiring controlled static dissipation.

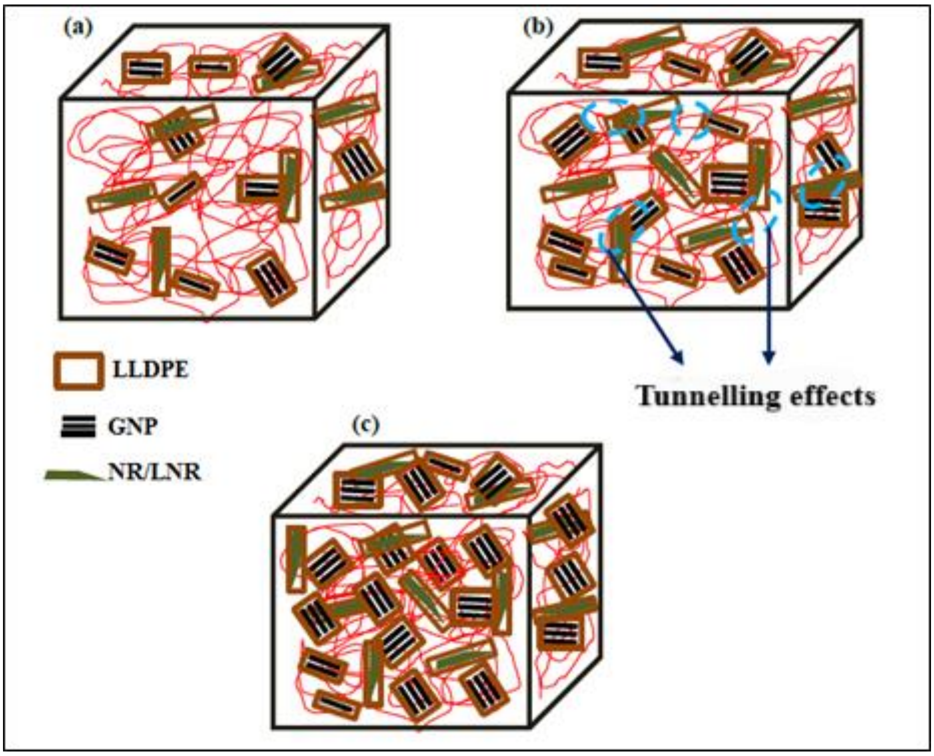

Figure 5. Percolation process in nanocomposites
Adopted from Khanam et al. (2016)

According to Khanam et al. [35], the differences in electrical conductivity of composite materials are attributed to three main stages (Figure 5). This has been observed in previous studies on LLDPE/GNPs nanocomposites. Initially, low electrical conductivity occurs when the filler dispersion is minimal (Figure 5(a)). As the filler dispersion increases, large clusters gradually form, leading to an increase in the material's conductivity. At this stage, tunnelling effects are observed between adjacent graphene sheets (Figure 5(b)). Subsequently, as the content of graphene sheets increases, a complete conductive pathway is formed from the contact of graphene sheets at the percolation threshold (Figure 5(c)). Furthermore, as the dispersion of conductive filler increases, the conductive network also expands until it reaches the maximum conductivity limit. In the study of electrical conductivity in samples with added NR and LNR, the GNP composition was fixed at 4 %. Thus, based on the electrical conductivity data of LLDPE/GNP nanocomposites blended with NR and LNR, the conductive network was found to be relatively unaffected, as its values remained within the approximate range for semiconductors. Maintaining this semiconductive property is advantageous for potential applications because it allows the material to dissipate static charges while avoiding full electrical conductivity, which is particularly useful in packaging for sensitive electronic or pharmaceutical products. This balance helps ensure product protection, safety, and durability in real-world applications.

Thermal Conductivity Analysis

The amounts of GNP, NR, and LNR in the tested samples were 4 %, 20 %, and 10 %, respectively, selected based on their superior physico-mechanical properties demonstrated in prior analyses. As shown in Table 3, the thermal conductivity of the LLDPE polymer samples generally increased with the addition of GNP, NR, and LNR to the polymer matrix.

Selected nanocomposite samples of LLDPE/GNP with 0 %, 4 %, and 5 % GNP content revealed that a higher percentage of GNP contributed to enhanced thermal conductivity. However, samples blended with 4 % NR and LNR demonstrated superior physico-mechanical properties compared to those with 5 % GNP. Thermal conductivity was observed to further increase with higher NR and LNR content. This trend aligns with the findings of Teng et al. [36], who recorded an increase in thermal conductivity in samples with higher filler and blending agent content. Similarly, Xie and Yang [37] reported an improvement in the thermal conductivity of their composite as the NR content increased, which was attributed to the T_g of NR typically occurring within the range of 100–300 K, facilitating effective thermal conductivity. For packaging applications, improved thermal conductivity is beneficial because it enhances heat management during processes such as sealing, and contributes to stability when the material is exposed to varying storage or transport temperatures, ensuring the integrity of packaged products.

Theoretically, good dispersion of materials leads to enhanced thermal conductivity, making such composites suitable for applications requiring resistance to temperature fluctuations and extreme conditions [38]. Ngo and Truong [39] reported that isolated and widely-spaced fillers resulted in minimal or no contact between fillers, leading to low thermal conductivity.

In this study, the thermal conductivity behaviour of LLDPE/GNPs/NR/LNR films differed slightly from their electrical conductivity. The electrical conductivity of similar nanocomposites decreases with the inclusion of rubber components due to disrupted percolation networks and the presence of amorphous regions, which reduce the degree of crystallinity. However, the preparation of thermal conductivity samples likely increased the degree of crystallinity, as rubber components are known to crystallize at lower temperatures when subjected to additional forces during sample preparation. This promotes phonon scattering for efficient heat transfer [35]. Furthermore, the good compatibility effect of LNR enhances thermal conductivity by improving filler-to-filler contact within the polymer matrix.

Table 3. Thermal Conductivity of Selected Samples.

Sample Code	LLDPE (wt%)	GNP (wt%)	NR (wt%)	LNR (wt%)	Thermal Conductivity (W/mK)
LLDPE	100	0	0	0	0.32
MB-LLDPE/GNP4	96	4	0	0	0.55
MB-LLDPE/GNP5	95	5	0	0	0.59
MB-LLDPE/GNP/NR20	76	4	20	0	0.57
MB-LLDPE/GNP/NR20/LNR10	66	4	20	10	0.61

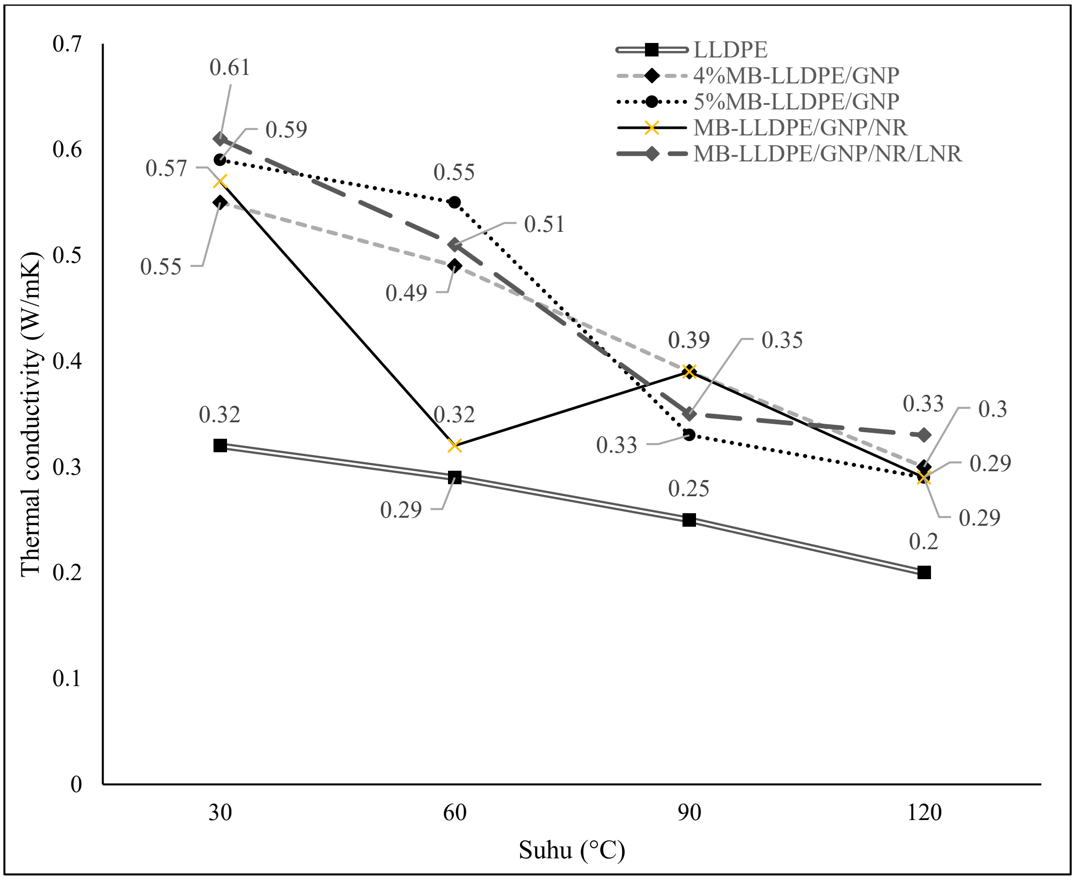

Figure 6. The effect of temperature on the thermal conductivity of the samples.

Figure 6 illustrates the effect of increasing temperature on thermal conductivity, starting from 30 °C to 120 °C. Overall, the thermal conductivity of the samples decreased with rising temperatures. This is attributed to disrupted phonon movement, which hinders heat transfer. Thermal resistance also increases as phonon mobility between filler nanoparticles becomes more obstructed at higher temperatures. Additionally, differences in material composition within the LLDPE-GNP-NR-LNR matrix limit thermal transfer at elevated temperatures. A sharp decline in thermal conductivity was observed beyond 60 °C, suggesting that the prepared nanocomposite films were most effective for applications at room temperature and up to 60 °C.

CONCLUSION

To explore their potential use in packaging applications, LLDPE/GNP nanocomposite films were produced by incorporating rubber components such as NR and LNR. The presence of rubber components also improved the flexibility of the LLDPE/GNP nanocomposites. The measured electrical conductivity values indicated that the LLDPE/GNP/NR/LNR nanocomposites exhibited semiconductor properties (~10^{-8}). The optimal NR and LNR ratio for the product was 20:10, with an LLDPE:GNP ratio of 66:4. Characterization for product application purposes showed promising potential for this nanocomposite. The thermal conductivity of the nanocomposite film (0.61 W/mK) increased by 90.6 % compared to LLDPE (0.32 W/mK). Thermal conductivity analysis showed that the material maintained stable heat transfer up to ~60 °C, beyond which a sharp decline was observed. The thermal conductivity trend of the samples differed slightly from the electrical conductivity results when rubber components were added. Thermal conductivity also increased with higher rubber content, while electrical conductivity decreased.

This study employed multiple characterization techniques, including tensile testing, impedance analysis, and laser flash thermal conductivity measurement, which collectively provided insights into mechanical, electrical, and thermal properties. However, some limitations must be noted. The study was restricted to laboratory-scale sample sizes, and long-term stability under real packaging conditions (e.g., humidity, repeated thermal cycling, or mechanical fatigue) was not assessed. Furthermore, while mean values with error bars were reported, more detailed statistical analysis would enhance data robustness. Future work should therefore focus on large-scale validation, extended durability testing, and broader compositional optimization to confirm industrial applicability.

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