

## Investigation on the Potentials of Nanocomposites Derived from Polylactic Acid-Polycaprolactone Blends using different Nanofillers as Biomedical Implants

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In present work, an attempt is made to synthesize polymer bio-nanocomposites suitable for biomedical implants based on polylactic acid-polycaprolactone (PLA/PCL) blend reinforced with different nanofillers. The inorganic filler, montmorillonite nanoclay (MMT), whereas graphene oxide (GO) and reduced graphene oxide (rGO) served as carbon-based nanofillers within the composite. Blends of polylactic acid (PLA) and polyvinyl chloride (PCL) were reinforced with hydroxyapatite in order to generate superior materials. The tensile strength and Young's modulus of PLA-PCL blend nanocomposites show an increase of about 117% and 53%, respectively, when compared to pure PLA, whereas the elongation at break observes a decrease of 38%.

**Keywords:** Polylactic acid, Poly( $\epsilon$ -caprolactone), Graphene derivatives, Montmorillonite, Hydroxyapatite, Solvent casting.

### INTRODUCTION

Polymer nanocomposites (PNCs) are blends of polymers and nanoparticles that combine their respective strengths to develop materials with favourable mechanical, thermal and chemical characteristics. One unique class of sophisticated materials that is well-known is bionanocomposites. Nanoscale materials are viewed as materials with additional value, whereas the polymer matrix is recognized as having a biological origin. As excellent green technology materials, bio-nanocomposites can replicate biological materials and have outstanding biodegradable and biocompatible qualities [1,2].

The prospect of future sustainability is centered on the use of biodegradable polymers, which blend suitable matrices with fillers, enabling their widespread application across diverse fields. Among a broad spectrum of biopolymers utilized, polylactic acid (PLA) possess better biomechanical and functional characteristics. As a thermoplastic, biocompatible and biodegradable polymer, PLA finds application across various levels [3]. However, for optimal suitability in biomedical applications, it is imperative to enhance PLA's overall performance, focusing on aspects such as biodegradability, porosity and mechanical properties (e.g., tensile strength, elongation at

break and Young's modulus) [4]. Poly( $\epsilon$ -caprolactone) (PCL) demonstrates strong compatibility with other polymers, enabling the creation of blended materials with enhanced properties. Its biocompatibility and biodegradability further make it a strong contender for biomedical applications such as drug delivery systems and tissue engineering scaffolds [5-8]. A common strategy to achieve these improvements involves reinforcing the matrix material with nanofillers [9-11]. Both PLA and PCL are regarded as biomedical materials by Food and Drug Administration, USA due to their biocompatibility.

Montmorillonite, a naturally occurring clay mineral, exhibits a layered structure featuring a high aspect ratio, providing a substantial interfacial area for interaction with the polymer matrices [12]. Recently, there has proven to be a lot of interest in carbon based nanoparticles since they have the potential to develop polymer nanocomposites with enhanced characteristics. With their appealing properties, carbon-based fillers are popular in biological applications such as drug delivery, imaging, diagnostics, tissue engineering, biosensing and cancer treatment [13]. The most adaptable substance is graphene, which possesses unusual mechanical, chemical and thermal properties. Polymer composites with graphene show promise for usage in energy storage, biomedical applications and environmental

domains [14]. The derivatives of graphene like GO and rGO are used for composite preparation based on the special intrinsic properties of graphene [15]. The optimum composition for the graphene-based nanofiller is chosen to improve the properties, drawing from the findings related to the mechanical and biological traits of the polymeric nanocomposite films [16-22].

Hydroxyapatite, a naturally occurring mineral type of calcium apatite with the chemical formula  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , has biomimetic features for bone replacement and dental restorations. Nonetheless, its brittleness and limited fatigue resistance may require careful design considerations and the incorporation of hydroxyapatite in polymer to improve its mechanical performance in particular applications [19]. Thus, in this work, an attempt is made to investigate the effect of different nanofillers such as montmorillonite nanoclay, graphene oxide (GO) and reduced graphene oxide (rGO) and hydroxyapatite (HA) in the PLA-PCL blends for the suitability of the biomedical implants.

## EXPERIMENTAL

Poly(lactic acid) (PLA) (Mw 60000) and P1953 grade of polycaprolactone (PCL) were purchased from Otto Chemika-Biochemika-Reagents, Mumbai, India. Inorganic nanofiller montmorillonite nanoclay (MMT) was purchased from Sigma Aldrich, USA, while the organic nanofillers like graphene oxide (GO) and reduced graphene oxide (rGO) (0.8-2 nm diameter) were purchased from Shilpent Enterprises, India. The chemicals required for the synthesis of hydroxyapatite (HA) like calcium nitrate tetrahydrate (CNT) and phosphoric acid were purchased from Merck Life Science Pvt. Ltd. and ammonia from Spectrum Reagents & Chemicals Pvt. Ltd, Cochin, India.

**Characterization:** Universal testing machine (Shimadzu Corporation, Kyoto, Japan) with ASTM Standards D 882-88 was employed to assess the mechanical properties like tensile strength, elongation at break and Young's modulus. The hardness of composite material was analyzed by Barcol Hardness Testing Machine (ASTM D 2583). A Hitachi<sup>TM</sup> 3000 secondary electron scanning electron microscope instrument at 20 kV was used for the morphological investigation. A PANalytical X'Pert PRO diffractometer from Malvern Panalytical, Royston, UK, was used to measure XRD with a 1.54 Å Cu source in the secondary electron mode at 45 kV and scanning from 5 to 80°.

**Preparation of PLA based nanocomposites with organic and inorganic nanofillers:** The polymeric nanocomposite solution was prepared by solvent casting method, by dissolving PLA in DCM followed by centrifugation. Fillers such as MMT, GO and rGO were dissolved in an appropriate solvent and incorporated into a PLA solution, with MMT ranging from 1 to 4 wt.% in 1 wt.% portions and GO and rGO from 0.02 to 0.1 wt.% in 0.02 wt.% portions, followed by stirring at room temperature for 6 h. Then, the PLA-MMT, PLA-GO, PLA-rGO solutions were casted on a petri dish by freeze drying at -4 °C for 48 h. The composite films were fabricated with uniform thickness.

**Synthesis of hydroxyapatite:** Hydroxyapatite was synthesized by sol-gel process. In this process,  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  were mixed in a ration of 1.67 (Ca/P) followed by the addition of ammonia while stirring till pH become 10. A gel

was formed after being aged at room temperature for 24 h. The calcined hydroxyapatite will be produced by employing drying in electric furnace (Toshniwal Electric furnace) at 800 °C.

**PLA-GO-HA nanocomposite film preparation:** The synthesized hydroxyapatite was used to prepare PLA-GO-HA composites by solvent casting with the compositions of GO as a parameter. The concentration of hydroxyapatite was adjusted between 10 and 45 wt.%, increasing in portions of 5 wt.%.

**Preparation of PLA-PCL blends:** The PLA-PCL blend solutions were prepared by mixing different weight ratio like 90:10, 80:20, 70:30, 60:40, 50:50 of PLA and PCL, respectively. It was dissolved in DCM solvent, to find the best combination for the further investigation.

**Preparation of PLA-PCL-GO nanocomposite film:** After the evaluation of mechanical properties of prepared PLA-PCL blends, the PLA to PCL ratio was fixed as 70:30. Then, the blend solution was prepared by dissolving in DCM solvent and the composition of GO was varied from 0.02 to 0.1 wt.% with an increment of 0.02 wt.%. After sonication and stirring, the composite solutions were dried to obtain the films.

**Preparation of PLA-PCL-GO-HA nanocomposite film:** According to the biomechanical characteristic results of the synthesized composites, the loading of GO in the PLA-PCL blend solution was fixed at 0.04 wt.%, while the hydroxyapatite content varied from 10 to 45 wt.% in 5 wt.% increments, and the PNC films were prepared *via* solvent casting.

## RESULTS AND DISCUSSION

### Mechanical properties

**PLA-MMT nanocomposites:** The sample images of pure PLA and PLA-MMT films are shown in Fig. 1a-c, respectively. The mechanical properties like tensile strength ( $\sigma_{\text{max}}$ ), elongation at break ( $\epsilon_b$ ) and Young's modulus (E) of prepared PLA-MMT nanocomposites were investigated and the results are shown in Fig. 2a-c. The tensile strength of pure PLA is 19.77 MPa, while that of the MMT nanocomposite show a decreasing trend from pristine PLA (Fig. 2a). Among the various compositions of MMT added, the composite containing 1 wt.% exhibits the greatest tensile strength (17.13 MPa). In Fig. 2b, it has been observed that elongation at break decreases in accordance with the composition of MMT nanocomposite and the lowest value is at 1 wt.% of GO (2.12%). The Young's modulus (Fig. 2c) of the nanocomposite films has lower value than pure PLA (924.86 MPa). The incorporation of MMT into PLA leads no improvements in mechanical properties. By controlling factors such as clay content, dispersion method and polymer/clay compatibility, the mechanical properties of PLA-MMT composites can be tailored to meet specific applications [12]. Since the PLA-MMT nanocomposite fails to meet the required properties, the investigation will transition to organic nanofillers for further analysis [23].

**PLA-GO/PLA-rGO nanocomposites:** The development of graphene-based bio-nanocomposites involved incorporating varying amounts of rGO and GO, ranging from 0.02 to 0.1 wt.%. To ensure accuracy in evaluating the mechanical characteristics, three samples from each composite film were examined, along

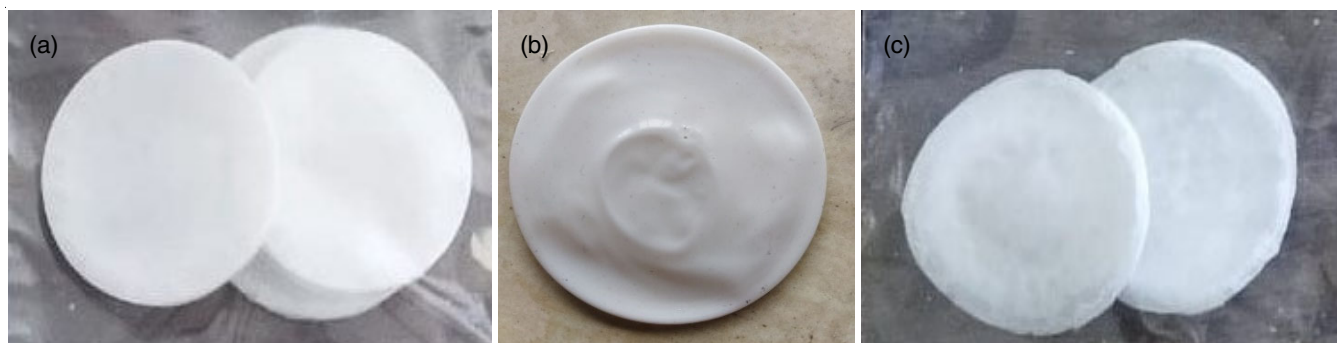


Fig. 1. PLA-MMT composite films with composition of (a) 0 wt.%, (b) 1 wt.% and (c) 4 wt.% MMT

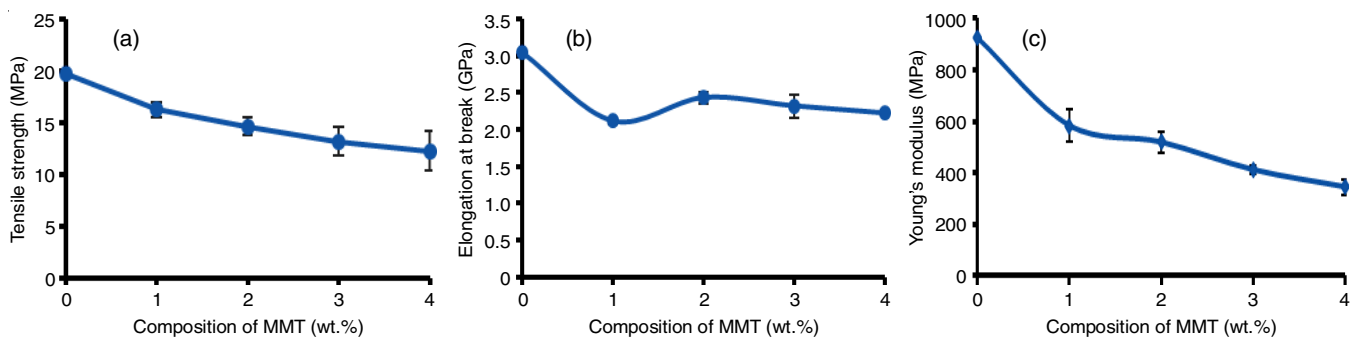


Fig. 2. Tensile strength (a), elongation at break (b), Young's modulus (c) vs. composition of PLA-MMT composite films

with calculations for the standard deviation. However, in case of rGO loading, the tensile strength decreased when compared to the value of pristine PLA. In Fig. 3a, the maximum tensile strength was recorded to be 18.12 MPa with the addition of 0.04 wt.% of rGO. A reduction in tensile strength is due to the clustering of rGO particles, demonstrating the significance for enhanced conditions for promoting their dispersion [20]. Fig. 3b depicts the percentage of elongation, with a minimum value of 2.24%, indicating a reduction compared to PLA. The Young's modulus also exhibited a reduction, with the optimal value (476.68 MPa) observed in the composition of 0.04 wt.%, as illustrated in Fig. 3c. The results indicate that the inclusion of GO enhances the PLA properties and the reason is attributed due to the presence of the higher degree of oxygen-containing functional groups present in GO. This increased compatibility facilitates better dispersion of GO within the polymer matrix, leading to improved mechanical properties and reinforcement. Additionally, provide the platforms for chemical interactions with polymer chains, leading to resilient interfacial bonding

between GO and the polymer matrix. It acts also as a barrier to prevent the agglomeration of graphene sheets, ensuring a more uniform dispersion within the polymer matrix. This uniform dispersion results in improved homogeneity and stability of the nanocomposite.

The mechanical properties were also assessed and as shown in Fig. 4a, the tensile strength of nanocomposite increased initially then decreased. The highest value observed with 0.02 wt.% of GO, *i.e.* 29.37 MPa, which is caused due to the surface area of GO facilitated a higher dispersion within the PLA (Fig. 4a-b). However, the elongation at break decreased steadily, reaching its lowest value at 0.02 wt.% (Fig. 4b), which is suitable for the biomaterial development. The highest value for the Young's modulus (990.864 MPa) was obtained at the same composition of GO, surpassing that of pure PLA (924.86 MPa) (Fig. 4c).

**PLA-GO-HA nanocomposites:** In a comparative analysis of nanofillers, graphene derivatives (GO and rGO) exhibit superior performance relative to nanoclay. Based on the preliminary studies, it is determined that GO is the optimal nanofiller for

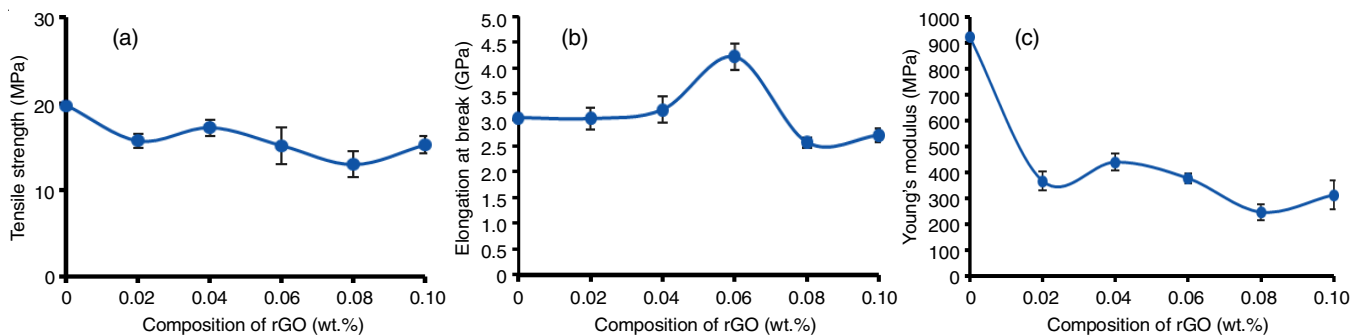


Fig. 3. Tensile strength (a), elongation at break (b), Young's modulus (c) vs. composition of PLA-rGO composite films

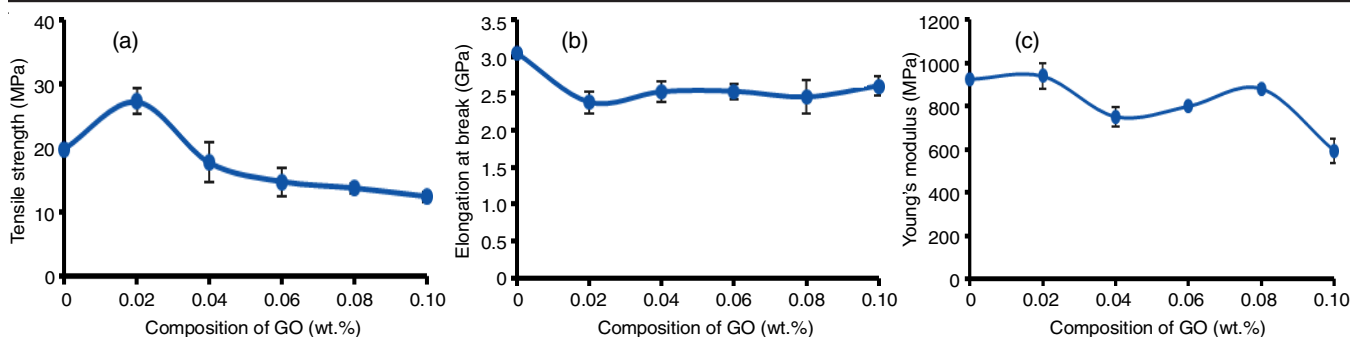


Fig. 4. Tensile strength (a), elongation at break (b), Young's modulus (c) vs. composition of PLA-GO composite films

enhancing the properties of PLA. The PLA-GO (0.02 wt.%) display stronger mechanical properties than PLA-rGO nanocomposite. To enhance the properties of PLA-GO nanocomposite, bioactive material nano hydroxyapatite was introduced, combined with polymers ranging from 10 to 45 wt.% of HA. Upon the addition of 20% by weight of hydroxyapatite, the composite attains its maximum tensile strength of 35.69 MPa, Young's modulus of 1190.36 MPa, and elongation at break of 1.97% (Fig. 5a-c). The mechanical properties of hydroxyapatite-based polymer composites can be significantly influenced by the particle size and distribution of the hydroxyapatite filler within the polymer matrix [24]. According to investigation, even low loading of GO and hydroxyapatite has a great effect on the bulk mechanical properties.

**Preparation of PLA-PCL blend:** Blends of PLA and PCL with 90/10, 80/20, 70/30, 60/40 and 50/50 compositions were prepared by solvent casting method at room temperature. Out of various weight ratios tested, the combination of PLA and PCL at a ratio of 70:30 demonstrated superior mechanical properties. By blending them, an equilibrium can be attained

in mechanical properties, providing superior strength, modulus and elongation at break relative to pure PLA [17]. Figs. 6a and 6c demonstrate a pattern in which both tensile strength and Young's modulus show an initial increase with the increasing ratio of polylactic acid to polycaprolactone. However, beyond a certain ratio, both properties begin to decline. Significantly, at 70/30 ratio of PLA/PCL, the properties exhibit an improvement surpassing that of pure PLA. This observation suggests an optimal composition where the combination of PLA and PCL yields superior mechanical properties compared to PLA alone. At the ratio of 70:30, there is a decrease in the percentage of elongation (Fig. 6b). The obtained results are attributed to the effective mixing technique, which involved optimal stirring duration and sonication to minimize agglomeration.

**Synthesis of PLA-PCL-GO composites:** The effect of GO on the PLA-PCL blend solution was examined by incorporating varying amounts of GO into 70:30 blend. The incorporation of GO, particularly at optimal concentrations, can increase the tensile strength of PLA-PCL blends. Here, GO was loaded from 0.02 to 0.1 wt.% with an increment of 0.02 wt.%. The prop-

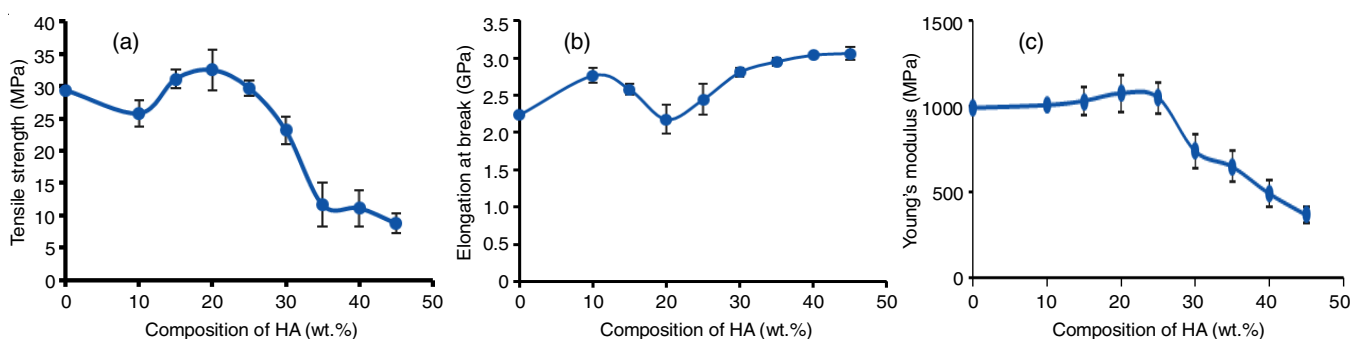


Fig. 5. Tensile strength (a), elongation at break (b), Young's modulus (c) vs. composition of PLA-GO-HA composite films

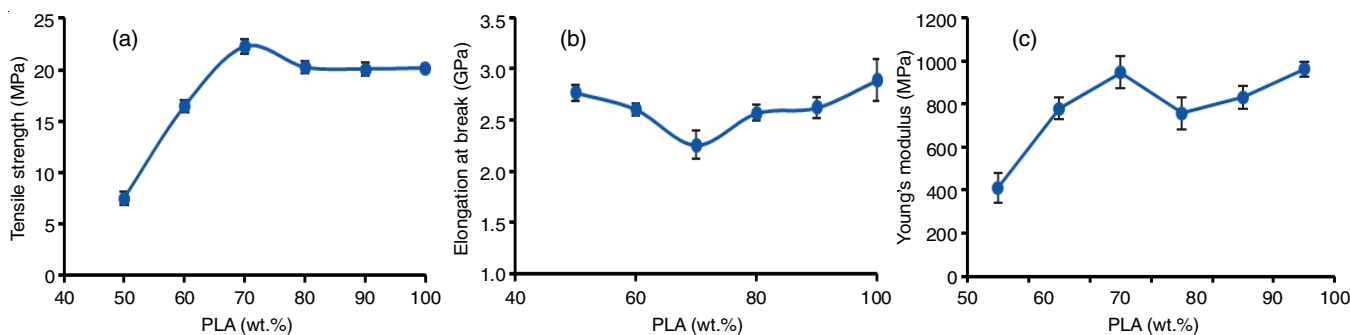


Fig. 6. Tensile strength (a), elongation at break (b), Young's modulus (c) vs. composition of PLA-PCL blend



erties of PLA-PCL blend films improved when 0.04 wt.% of GO was added, outperforming PLA-based nanocomposite films with GO (Fig. 7a-c). The uniform distribution ensures that the reinforcing properties of GO are consistently distributed across the nanocomposite film, minimizing weak areas and improving overall mechanical performance. The tensile strength of blend-GO is 32.6497 MPa at 0.04 wt.% addition of GO (Fig. 7a). The GO reinforcement could elevate the Young's modulus of PLA-PCL blends, the highest value is 1264.957 MPa shown in Fig. 7c. The improvement is due to the reinforcing effect of GO, which limits the polymer chain mobility through the effective dispersion of GO particles [25,26].

**PLA-PCL-GO-HA nanocomposites:** The influence of hydroxyapatite (HA) on the PLA-PCL-GO nanocomposite was investigated, keeping GO loading at 0.04 wt.% while varying the hydroxyapatite content from 10 to 45 wt.%. The study of the mechanical properties on PLA-PCL-GO-HA composite films reveals that the material exhibits improved tensile strength (Fig. 8a) of 42.97 MPa, a lower elongation at break (Fig. 8b) is 2.2% and a higher Young's modulus (Fig. 8c) is 1416 MPa at 15 wt.% of hydroxyapatite addition. The enhancement in the result of the improved dispersion of hydroxyapatite within the base polymer, achieved through thorough mixing and sonication.

**Comparison of mechanical properties of PLA based nanocomposites:** The mechanical characteristics of PLA-based nanocomposites and 70:30 blend-based nanocomposites were analyzed and their values compared, as depicted in Fig. 9. The results show that loading of small amount of GO to pure PLA and 70:30 blend, the mechanical properties were improved remarkably. With the incorporation of hydroxyapatite, the enhancement in the mechanical properties increased. The nanocompo-

site, specifically PLA-PCL-GO-HA, which exhibited superior mechanical properties ( $\sigma_{\max} = 42.9719$  MPa,  $\epsilon_b = 2.2063\%$ ,  $E = 1416.98$  MPa), is deemed suitable for the biomedical implant applications. The nanocomposites based on PLA-PCL blend synthesized with the incorporation of hydroxyapatite and GO show the promising implant properties.

**Hardness of PLA-GO-HA nanocomposite films:** The relationship between tensile strength and hardness can also be influenced by factors such as material composition, heat treatment and microstructure [24,27,28]. Increasing the volume fraction of hydroxyapatite typically leads to improvements in the strength and hardness due to the higher concentration of reinforcing particles. The results of this research imply that there is a direct relationship between the tensile strength and hardness when PLA and hydroxyapatite are mixed together, as shown in Fig. 10.

**Morphological studies:** The SEM images of the PLA and its nanocomposite films such as PLA-GO, PLA-GO-HA, PLA-PCL-GO, PLA-PCL-GO-HA are shown in Fig. 11a-e. The surface of PLA films was irregular and exist some pores distributed over the surface. The SEM images exhibit the relationships between the water vapour transmission, mechanical properties and the structural characteristics of the films. In case of PLA-GO composite films, the size of pores was smaller compared to pure PLA. The material strength was enhanced by the incorporation of hydroxyapatite, which is encapsulated within the pores. In PLA-PCL blend, the pores were diminished, so the material properties were enhanced by the addition of GO and hydroxyapatite in appropriate proportion.

**XRD studies:** In semi-crystalline polymer blends, the intensities of the peaks observed in XRD patterns vary with the concentration of each polymer during the crystallization of both

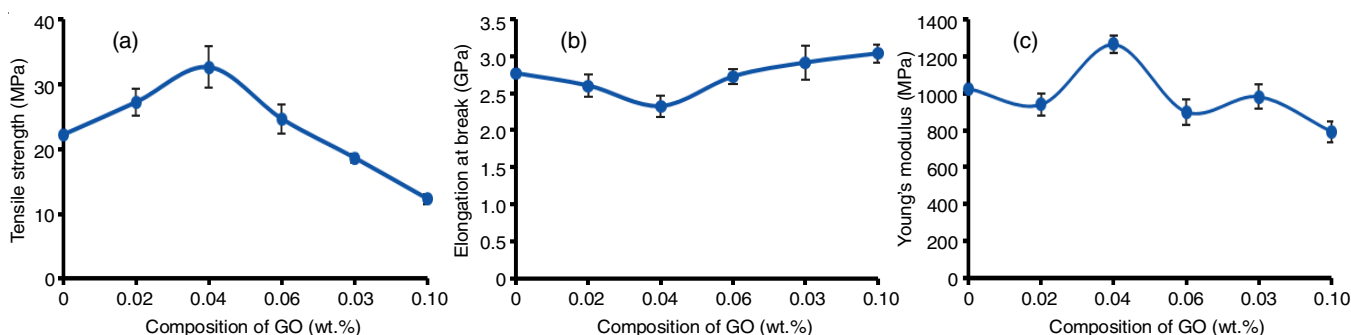


Fig. 7. Tensile strength (a), elongation at break (b), Young's modulus (c) vs. composition of 70:30 PLA-PCL-GO composite films

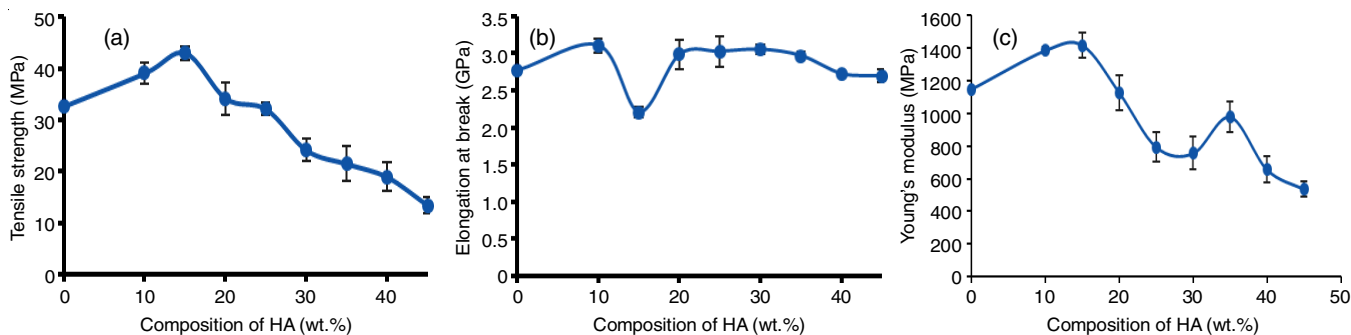


Fig. 8. Tensile strength (a), elongation at break (b), Young's modulus (c) vs. composition of PLA-PCL-GO-HA composite films

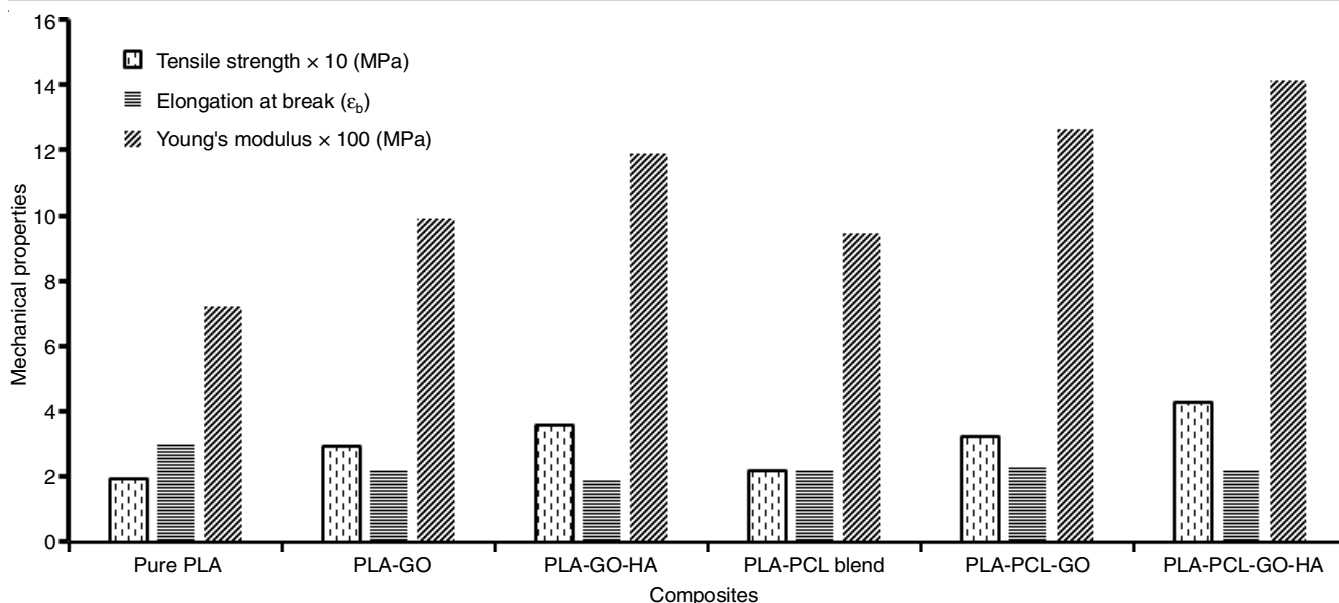


Fig. 9. Bar chart of the mechanical properties of composite films

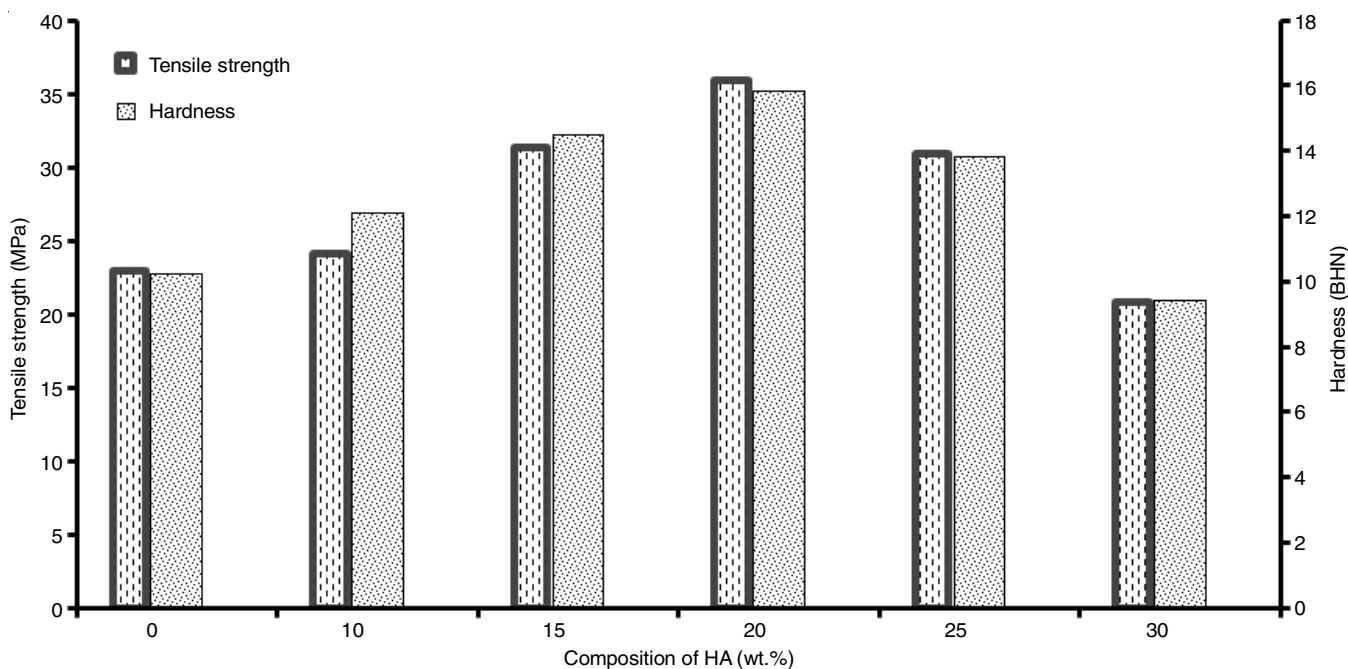


Fig. 10. Tensile strength and hardness vs. composition of PLA-GO-HA composite films

components independently. According to the present study, the X-ray diffraction pattern of pristine PLA features two key peaks at  $2\theta = 19.1^\circ$ . The XRD patterns of PLA-rGO polymeric composite was similar to PLA because of the relevant diffraction peaks of neat PLA were observed in all the cases. An examination of the XRD patterns for both PLA-rGO and PLA-GO, while PLA-GO-HA exhibited multiple characteristic peaks at  $2\theta 18.70^\circ$ ,  $20.76^\circ$ ,  $21.92^\circ$ ,  $24.25^\circ$  and  $26.93^\circ$  (Fig. 12a).

The XRD pattern for PLA-PCL blend at 70/30 displays several peaks with lower intensity, indicating the crystalline contribution from PCL (Fig. 12b). Compared to pure PLA, the other PLA/PCL blends show the reduced peak intensities, suggesting that the filler materials influence the crystalline

structure of the PLA and PCL matrix. It was observed that GO exhibits a characteristic diffraction peak at approximately  $2\theta 16.8^\circ$ , in connection with a d-spacing of 0.53 nm, which implied a typical peak associated with GO in PLA-PCL blend.

### Conclusion

According to the investigation, even low addition of GO and hydroxyapatite has a great effect on the bulk mechanical properties. This enhancement in the mechanical properties may have an impact in the biomedical applications. After the preliminary studies, it is concluded that polylactic acid (PLA) with 0.02 wt.% GO surpasses in performance than pure PLA. The nanocomposite containing 0.02 wt.% GO displayed the maxi-

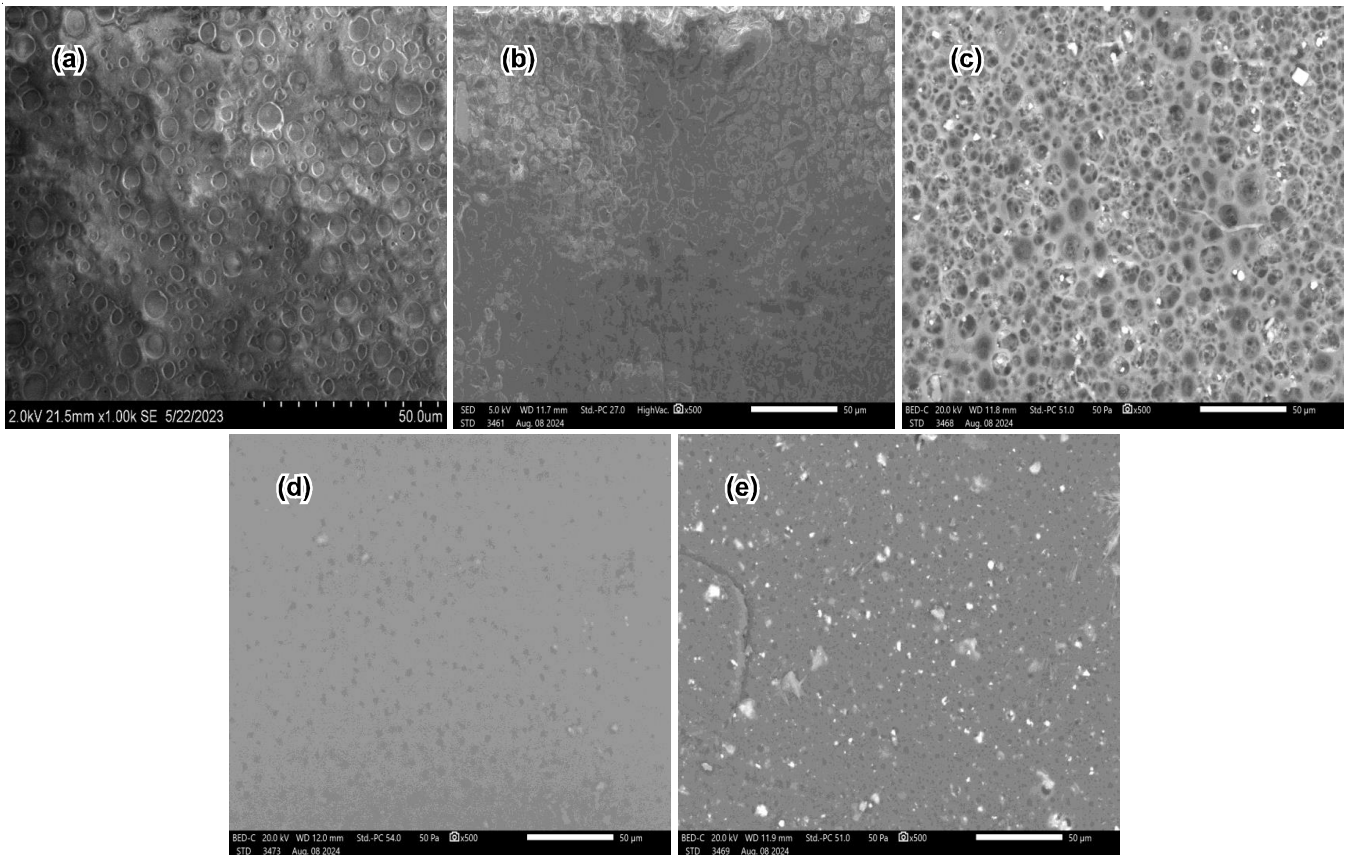


Fig. 11. SEM images of (a) PLA, (b) PLA-GO, (c) PLA-GO-HA, (d) PLA-PCL-GO, (e) PLA-PCL-GO-HA composite films

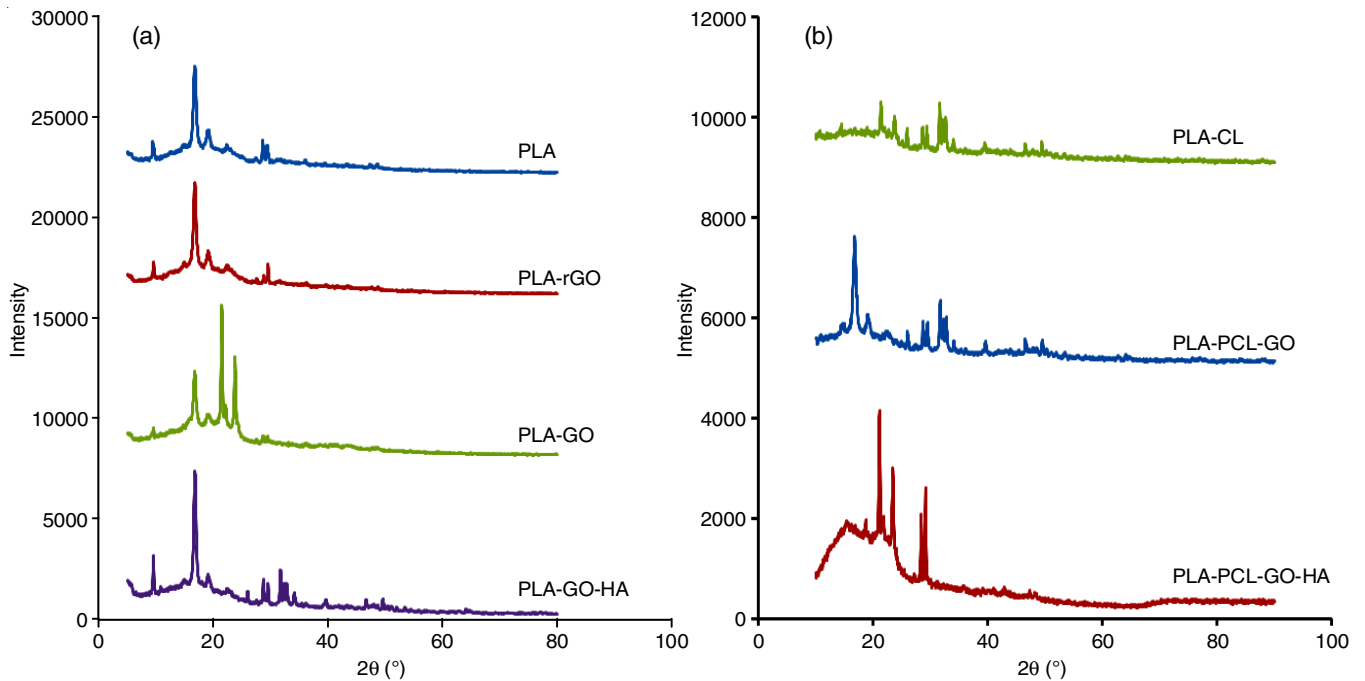


Fig. 12. XRD patterns of (a) PLA, PLA-rGO, PLA-GO, PLA-GO-HA and (b) PLA-CL, PLA-PCL-GO, PLA-PCL-GO-HA composite films

imum tensile strength and Young's modulus around 49% and 7% higher than that of pure PLA and elongation at break was reduced by 26% than pure PLA. The nanocomposites containing both 0.02 wt.% GO and 20 wt.% hydroxyapatite displayed tensile strength and Young's modulus enhancement of around 82%

and 29% higher than pure PLA and elongation at break was reduced by 35%. Whereas the nanocomposite containing 0.04 wt.% GO in PLA-PCL blend displayed enhanced tensile strength and Young's modulus of around 65% and 37% respectively higher than that of pure PLA and elongation at break

was reduced by 31%. Similarly, the nanocomposites containing both 0.04 wt.% GO and 15 wt.% hydroxyapatite displayed tensile strength and Young's modulus around 117% and 53% higher than pure PLA and elongation at break was reduced by 38%. While investigating its suitability of application as biomedical implants, they exhibit promising properties.

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#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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