Effect of Metal Oxide Nanoparticles on Mechanical and Optical Properties of Bioblend (PLA/PCL)

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An important development in the plastics industry involves the production of bio-nanocomposites through the combination of metal oxide nanoparticles with polylacticacid (PLA) and polycaprolactone (PCL). Various quantities of nanoparticles, such as zirconium dioxide (ZrO_2) and magnesium oxide (MgO), were employed to fabricate and analyze different combinations of the PLA/PCL blend. The blend contains 60% PLA and 40% PCL, with different concentrations of nanoparticles ranging between 0%, 0.75%, 1.5%, and 2.5%. The FTIR and mechanical properties study showed a direct correlation between the increase in nano-oxide fraction and the enhancement of tensile strength, tear resistance, elongation at break, and modulus of elasticity. UV-VIS transmission test confirmed that the impact of ZrO2 and MgO NPs have reduced the permeability in contrast to the pure PLA/PCL blend. The increased opacity caused by reinforcement which is responsible for the decrease in permeability. Also, we conducted contact angle measurements for both the reinforced and the pure (PLA/PCL) films. As oxides are hydrophobic, our findings show an obvious connection between the percentage of reinforcements and the rise in contact angle.

Keywords: Polylacticacid; Polycaprolactone; Food Packing; Nanoparticles
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1. Introduction

A lack of petroleum resources and rising environmental concerns have led to a large increase in the need for biodegradable materials. Examples of natural polymers include starch, protein, and cellulose, and polymers created from natural monomers include (PLA). Also, (PCL) is produced from petroleum [1,2]. The increased use of non-biodegradable plastics that aren't petroleum-based has caused an important rise in pollution of the environment [3]. The packaging industry is significantly liable for the substantial quantities of plastic waste that end up in certain landfills [4]. Using bio-based polymers is an option for solving these issues. The manufacturing of environmentally friendly plastics includes several processes, such as the polymerization of bio-based monomers, the extraction of natural polymers from biomass, and the extraction of micropolymers [5].

PLA is now the most effective biodegradable polymer in use. However, the fragility and low resistance to heat of the material limit its use. By mixing PLA with other biodegradable polymers, it can modify the way it behaves, ensuring its natural degradation [6-9]. PCL exhibits the features of being flexible and available, and it may be mixed evenly with a wide range of polymers [10-13].

The aim of this work is to create mixtures of PLA and PCL that can increase the tensile strength of PCL and improve the ductility and toughness of PLA. PLA/PCL blends are widely used in biomedical applications due to their biocompatibility and biodegradability. These include scaffolds, managed delivery systems, and implants. An advantage of using PLA/PCL mixes is being able to control the usefulness of products due to the relatively slow degradation rate of PCL compared to PLA. A full study has been done over the past twenty years on the preparation and evaluation of PLA/PCL blends [14].

Adding the nanofiller to the matrix changes the biopolymer's physical and chemical properties, as well as its mechanical, thermal, and barrier properties [15-17].

Zirconium oxide (ZrO_2) has advantages that include great thermal stability, resistance to friction and chemicals, as well as unique mechanical strength, hardness, and fracture toughness [18,19]. Magnesium-based nanoparticles (Mg-based NPs) have become popular in biomedical applications due to their antimicrobial abilities, unique mechanical qualities, and ability to enhance bone cell proliferation [20-22].

Previous studies have demonstrated that the production of Zinc oxide nanoparticles was successfully shown by the analysis of FTIR patterns. The production of ZnO-NPs was carried out using hydrothermal methods. Subsequently, a blend of polylactic acid and polycaprolactone (PLA/PCL, 80/20 wt/wt) was prepared by melt mixing. The blend was then loaded with 2, 4, and 6 wt.% of ZnO-NPs. The mechanical examination of the Bio Nano composites reveals that the tensile modulus experiences an increase of around 5.4%, 11.1%, and 24% with the addition of 2, 4, and 6 wt.% of ZnO-NPs to the blend sample, respectively [23].

Enhancing the strength of wood powder (WP) by using polycaprolactone (PCL) and polylactic acid (PLA) composites. The strength impact of PLA/PCL bioblend and PLA/PCL/WP composites exhibited superior performance compared to pure PLA, as its mechanical properties such as tensile strength, Shore D hardness, and impact resistance. Moreover, the elongation at break and Shore D hardness exhibited similarity to PLA, indicating that these traits were not substantially influenced by high WP concentrations. The water interaction of the PLA/PCL/WP composites was boosted, as shown by the contact angle, whereas the elastic modulus and tensile strength were seen to decrease [24].

2. Experimental Part

The PLA with density of 1.25 g/cm^3 was supplied from BASF India. The PCL was supplied from Sigma-Aldrich. The THF solution was purchased from HiMedia Laboratories (India). The ZrO_2 and MgO nanoparticles were supplied from SkySpring Nanomaterials (USA).

The PLA was weighed (2.1g) using an electron scale and then dissolved in THF to obtain a viscous solution. The dissolution process was carried out by slowly warming the solution to 55°C for 2 hours using a magnetic stirrer. The PCL is prepared using the same method. Then, mix the solutions of PLA and PCL. After that, pour the mixture into a petri dish and allow it to evaporate at room temperature for a day to ensure the complete removal of the solvent. The preparation involved creating film samples of PLA/PCL with varying filler quantities (0.75, 1.5, and 2.25%) of MgO and ZrO_2 with similar experiments and the same technique. The thickness of PLA/PCL/MgO and PLA/PCL/ZrO_2 nanocomposites was found to be 110 micrometers using a digital micrometer.

The spectroscopic studies were carried out using a Shimadzu UV-1900 UV-visible spectrophotometer in the wavelength range of 200-800 nm. The material's infrared spectra were obtained using a Shimadzu 8400S Fourier-transform infrared (FTIR) spectrometer in the wavenumber range of 400-4000 cm^{-1}.

As per the ASTM D-882 standard, the modulus of elasticity, tensile strength, and elongation are measured using a 10 N load cell in tensile mode. The tested films were divided into strips of 1 cm in width and 10 cm in length. The starting gauge length and speed were both set at 10 mm/min. The equation used to calculate the tensile strength (σ_s) and Young's modulus (E) is as follows:

$$\sigma_s = \frac{F}{A} \quad (1)$$

$$E = \frac{FL_0}{A\Delta L} \quad (2)$$

where F is the force exerted on an object under tension, L_0 is the original length, A is the cross-section area, ΔL is the length of the object changes [25]

The tear strengths of the films were assessed using the trouser tear method, following the guidelines of ASTM D-1922, with the same Universal Electronic Dinamometer. A 50 mm cut was made in the center of one end of the 7 cm long and 3 cm wide sample. An impact pendulum tester is used to determine the amount of force required to displace a slit a certain distance from the edge of the sample.

Contact angle analysis of distilled water generated by each sample was recorded using a Firsttenangstroms FTA32 goniometer. Each sample has a distinct droplet image.

3. Results and Discussion

The chemical formula of PCL is $C_6H_{10}O_2$, while that of PLA is $C_3H_4O_2$. The unique peaks observed in PCL and PLA can be attributed to the existence of CH bonds and CO double bonds. The presence of a peak at 1768 cm^{-1} in PLA and a peak at 1730 cm^{-1} in PCL indicates the presence of bond vibration [6]. The peaks at 2939.5 and 2866.2 cm^{-1} in Fig. (1) indicate the stretching of C-H bonds in PCL.

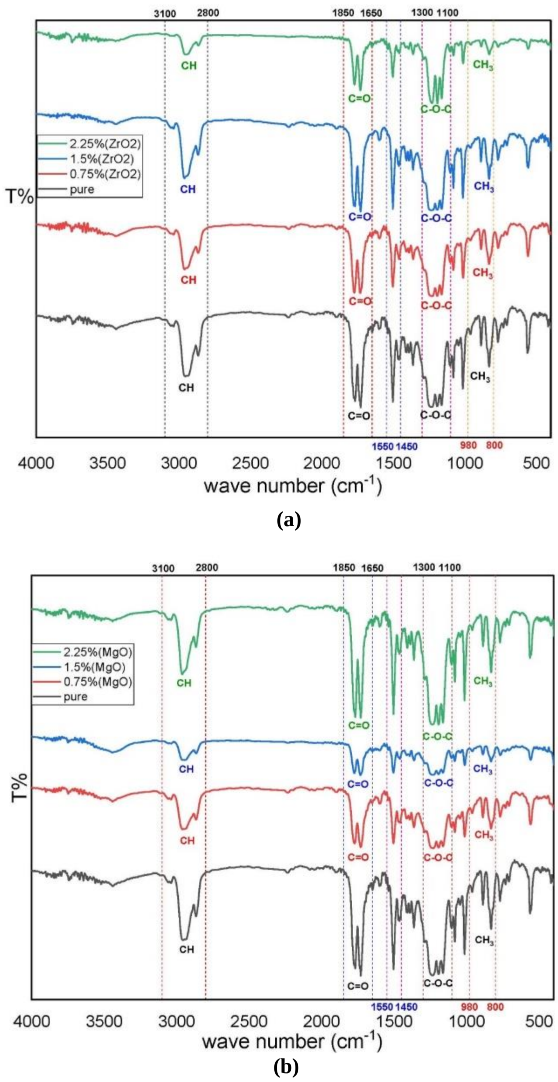
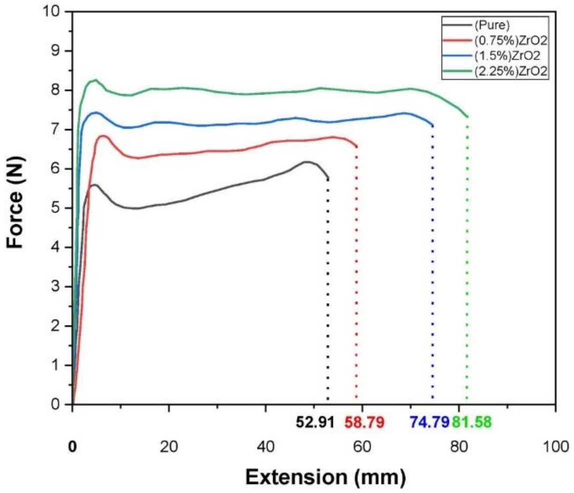


Fig. (1) FTIR of bioblend PLA/PCL with nanoparticles (a) ZrO_2 (b) MgO

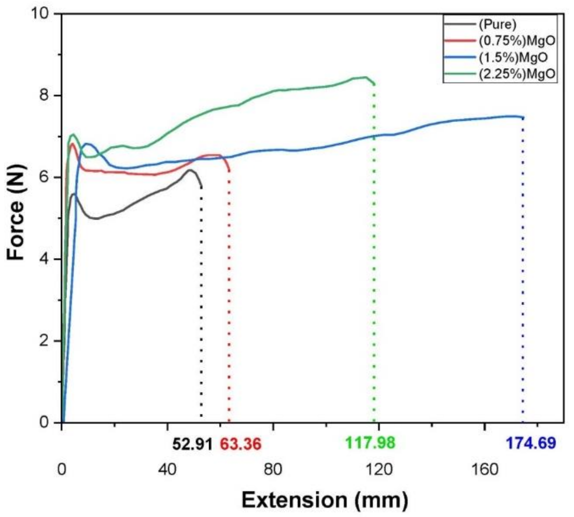
The presence of the aliphatic C-O-C ether group was observed within the frequency range of 1163-1236 cm^{-1} in PCL, while it was observed in PLA. The range of 962-831 cm^{-1} showed the stretching of the carbonate chain in PCL and PLA, which was caused by the oscillation band of the CH_3 methyl group [8]. There is no evidence of any new interaction between PLA/PCL and MgONPs, while PLA/PCL/MgO films have infrared bands that are similar to those of PLA/PCL film. The proof of creation of the

PLA/PCL/MgO nanocomposites has been verified [26]. Similarly, this concept can be applied to films that are made of a nanocomposite material containing PLA, PCL, and ZrO_2 [27].

Figure (2) shows stress-strain curves obtained from the tensile testing of the produced films. The statistical data for film elongation at break (EAB), tensile strength (TS), and elastic modulus (EM) can be found in Table (1).



(a)



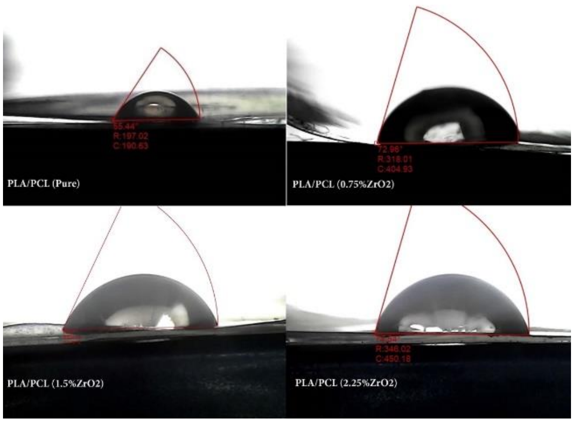
(b)

Fig. (2) Mechanical properties stress-strain curve of bioblend PLA/PCL with nanoparticles (a) ZrO_2 (b) MgO

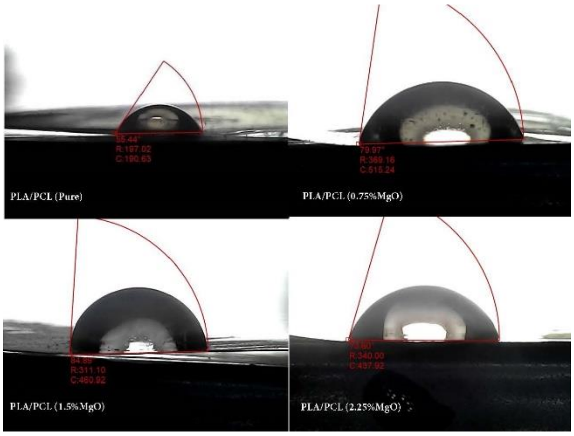
Studies suggest that films made only from PLA/PCL exhibit a notable increased tensile strength (TS) of about 31.09 MPa. The addition of nano-MgO at a maximum concentration of 2.25% improves the TS and EM of the films compared to PLA/PCL films. The increased stiffness (elastic modulus) of the reinforced MgO NPs occurs by reducing the mobility of the chains. Also, the efficient transfer of stress from the nanoparticles to the PLA/PCL chains results in an enhancement of the tensile strength. The inclusion of MgO NPs significantly enhances the elastic modulus of PLA/PCL films compared to basic PLA/PCL sheets. Nano-fillers tend to accumulate in particular regions due to their high surface energy, while the mix content remains in the background. The mechanical properties get worse as the number of nanoparticles increases, which means that MgO NPs are less effective at strengthening. The presence of agglomerated nano-fillers in the matrix reduces the efficacy of filler material. The aggregated nanofillers behave as flaws, leading to increased stress on the film and finally fracture. The behavior of ZrO_2 particles showed an identical characteristic to that of MgO particles [28-30].

The tear resistance of the pure PLA/PCL film was found to be 11.41 mN/mm. The addition of ZrO_2 and MgO nanoparticles improves a material's tear resistance by modifying the path of tear propagation, effectively reducing or preventing the risk of fractures. By using ZrO_2 with a range of 12.30 to 15.93 mN/mm and MgO with a range of 11.82 to 15.45 mN/mm, the tear resistance is greatly enhanced. The nanoparticles exhibited a strong interaction with the PLA/PCL matrix at the interface, resulting in improved tear strength for the samples containing 2.25% ZrO_2 and MgO nanoparticles.

The water wettability of PLA/PCL, PLA/PCL/MgO, and PLA/PCL/ZrO_2 films was determined by measuring the interfacial contact angles as shown in Fig. (3). Table (2) presents the measured contact angles. The contact angle likely increased with the addition of ZrO_2 and MgO nanoparticles due to the combined effect of the higher surface area and hydrophobic nature of the nanoparticles [31].



(a)



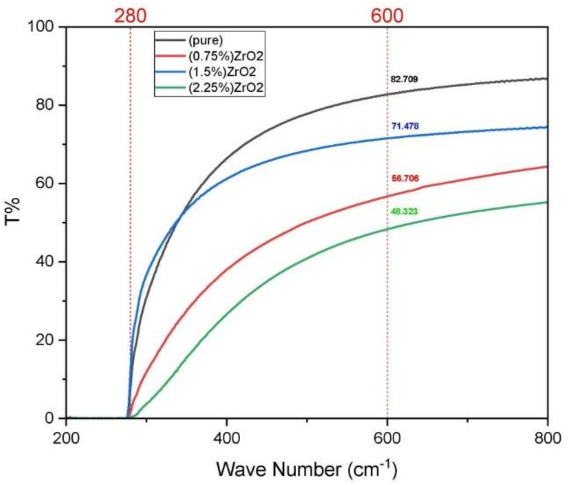
(b)

Fig. (3) Contact angle of bioblend PLA/PCL with nanoparticles (a) ZrO_2 (b) MgO

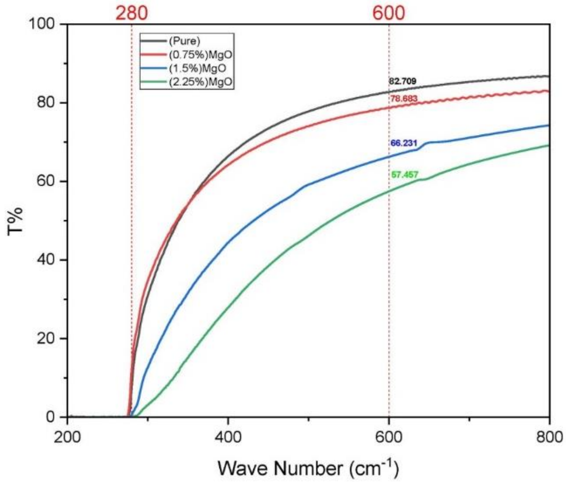
Table (2) Contact angle for bioblend PLA/PCL with nanoparticles

Sample	Contact Angle (θ)
Pure	55.29
ZrO_2 (0.75%)	72.96
ZrO_2 (1.5%)	63.57
ZrO_2 (2.25%)	74.54
MgO (0.75%)	79.97
MgO (1.5%)	84.89
MgO (2.25%)	73.80

Figure (4) shows the UV-visible transmission spectra of the pure PLA/PCL films and the (PLA/PCL) films with (ZrO_2 and MgO) NPs. The results indicated that the transparent PLA/PCL films showed the best degree of visibility compared to the other films.



(a)



(b)

Fig. (4) UV-visible transmission of bioblend PLA/PCL with nanoparticles (a) ZrO_2 (b) MgO

The dispersion of nanoparticles mostly limits the expected improvement in UV protection when using increasing amounts of MgO. Also, the ZrO_2 particles had similar features to the MgO particles. Protecting oneself from UV radiation is important, and this study provides evidence to support this claim. There is a high need for films with excellent UV-preventing abilities and excellent transparency, as they are used in food packaging [28,32].

4. Conclusion

The effective formation of nanocomposite films containing (PLA/PCL/MgO) and (PLA/PCL/ZrO_2) was confirmed. The enhanced ductility upon the addition of ZrO_2 and MgO nanoparticles was shown. The incorporation of ZrO_2 and MgO led to better tensile strength and elongation at break and an obvious rise in elastic modulus and tear resistance as compared to pure PLA/PCL bio-blend films. Also, it led to a large rise in the contact angle, enhancing the hydrophobicity of the surface. The pure films exhibited the highest level of transparency when compared to films supported by nanoparticles such as ZrO_2 and MgO.

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Table (1) Mechanical properties of bioblend PLA/PCL with nanoparticles

Sample	Tensile strength (MPa)	Elongation (%)	E-Modulus (MPa)	Tear/Thickness (mN/mm)
Pure	31.09	74.9	701	11.4113
ZrO_2 (0.75)	34	87	796	12.3084
ZrO_2 (1.5)	37	122.3	1041	13.5941
ZrO_2 (2.25)	41.75	129	1358	15.9305
MgO (0.75)	33.5	86.12	887	11.8244
MgO (1.5)	36	248.6	1098	13.4434
MgO (2.25)	42.25	168.6	1689	15.4543