

Morphology, Mechanical and Rheological Properties of Polylactic Acid Nanocomposite FilmGovind Sahu¹, M.S. Rajput¹, S.P. Mahapatra²¹ Department of Mechanical Engineering, National Institute of Technology, 492010 Raipur, Chhattisgarh, India² Department of Chemistry, National Institute of Technology, 492010 Raipur, Chhattisgarh, India

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Most of the presently used plastics for food packaging application are non-biodegradable and causes environmental problems. Many biopolymers can become a great alternative solution to prepare to biodegradable food packaging. Among the all available biopolymer polylactic acid (PLA) is most preferable due to its biodegradability and possesses great potential for food packaging application. However, poor mechanical and rheological properties limit their application, which is to be improved by adding some fillers, to replace the conventional plastic. Biodegradable PLA based nanocomposite film was prepared by incorporating calcium phosphate (CaP) nanoparticle by melt mixing method. The size of the CaP nanoparticle was analyzed by Zetasizer Nano ZS90. The morphology of nanocomposites has been studied with the scanning electron microscopy (SEM). The SEM result shows the smooth distribution of CaP nanoparticle inside the PLA matrix. Tensile strength and viscosity of nanocomposite film increase with incorporation of calcium phosphate nanoparticle.

Keywords: Polylactic acid, Calcium phosphate, Scanning electron microscopy, Tensile strength, Rheology.

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1. INTRODUCTION

In recent time most of the commercially available polymer causes pollution of the environment, because they are prepared from petroleum-based fuel sources. Production of these polymers releases several greenhouse gases especially CO₂. Hence, the researcher has made great attention toward the production of justifiable, eco-friendly polymers which can minimize the above-mentioned issues [1]. Among all the biopolymers PLA has great possibilities for the replacement of conventional plastics due to its inherent physical and mechanical properties, biocompatibility and biodegradability [2].

The increase of attention in the direction of thermoplastic materials is due to its many useful properties, mainly its melt processability, good elastic and optical properties. Also, the cost of getting the desired product is low as compare to thermosetting. Concerning all this reason the market of the PLA increased, particularly for the disposable and packaging applications. Various packaging material such as bottles, cups, films and other food containers can be prepared from the PLA [3]. However, due to its low mechanical and thermal stability during processing, poor barrier properties and brittleness limits their applications in various sectors. Due to above mentioned features, the use of PLA is deficient in the utilization of food packaging application [4].

The preparation of nanocomposites can become a possible alternative to overcome the above limitations by incorporating some nanofillers. The ratio of the surface area to volume of the fillers greatly affects the properties of the nanocomposites [3]. There are many nanoparticles which have been used as filler. Among them, carbon compounds [5] and inorganic materials [6] greatly influence the desired properties. CaP is gaining more attention toward the preparation of biodegradable and biocompatible composites. CaP has extensively been used in the biomedical field due to its exceptional physical, mechanical and chemical properties. Also,

copolymerization, blending with plasticizers has been adopted for the preparation of PLA based packaging materials by the researchers. But calcium phosphate as a filler material is not much elaborated. CaP can be great filler for enhancement of mechanical and physical properties. The improvement in the properties may consist of enhanced tensile strength, improved modulus and thermal stability and reduction in the gas permeability.

The objective of this study is to incorporate the calcium phosphate as a fully inorganic nanofillers to prepare high-performance biodegradable nanocomposites film. In this study, the PLA nanocomposite films were prepared by melt mixing of CaP nanoparticle into the PLA matrix. The morphology, tensile strength and rheological properties of the films were then examined to check the impact of CaP nanofillers filler on the PLA film.

2. EXPERIMENTAL

DL lactic acid, and stannous octoate catalyst, were procured from the standard supplier and Calcium phosphate 98 % extra pure nanopowder was also acquired from the standard supplier.

The synthesis of PLA was carried out in three necks round bottom flask from Lactic acid monomers according to the previous work [7, 8].

The PLA and CaP nanoparticle were dried at 60 °C under vacuum to avoid hydrolytic degradation during the melt mixing. CaP nanoparticle according to the formulation (given in Table 1) were then mixed with previously prepared PLA at 180 °C. followed by casting into the desired shape mould (prepared according to the ASTM standard for the tensile test and rheological analysis) and placed under vacuum for curing.

Table 1 – Formulation of PLA/CaP nanocomposites film

PLA	100	100	100	100	100
CaP wt. %	0	5	10	15	20

3. CHARACTERIZATIONS

The size and distribution of the CaP nanoparticles were determined by Zetasizer (Nano ZS, Malvern Instruments).

The scanning electron microscopy (SEM) with 15 kV accelerating voltage was used to study the surface morphology of the nanocomposite film. Prior to SEM analysis the sample was coated with a very thin layer of gold.

The tensile test of the nanocomposite film was performed at room temperature by universal testing machine (INSTRON dark series 7200). The crosshead speed was fixed to 5mm/min during the tensile test. Five test samples were examined for each composition and the average value of tensile strength were plotted.

The melt rheology of the PLA nanocomposite films was examined by the rotational rheometer MCR 102. The measurement was performed using 25 mm diameter parallel plate geometry in the dynamic frequency sweep mode. The experiment was conducted in the nitrogen atmosphere at 180 °C. The frequency test was conducted in the 1-500 rad/sec angular frequency range at constant (within 5 %) strain rate.

4. RESULTS AND DISCUSSIONS

The hydrodynamic diameters and size distributions of the nanocarriers determined by dynamic light scattering (DLS) is depicted in Fig. 1. From the figure, it is clear that the size of the CaP particle ranges 80-125 nm with a very narrow distribution.

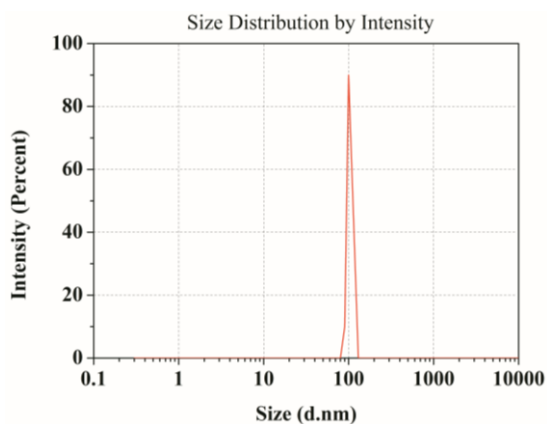


Fig. 1 – Particle size distribution of the CaP nanoparticle

Fig. 2 shows the scanning electron microphotograph of the PLA nanocomposites film sample. The result shows uniform dispersion of the CaP nanoparticle inside the PLA matrix. The surface texture of the nanocomposite film is also smooth and uniform. There is a smooth distribution of the nanoparticle throughout the matrix without aggregation up to 10 % of the filler loading. Aggregation of the particles takes place with a further increase in the filler loading as shown in the case of 15 % and 20 % of filler loading. The way of dispersion of the particle inside the matrix greatly affects the mechanical properties of the composites [9, 10]. Generally, the aggregation or higher size particle shows a higher viscosity than the uniformly distributed one.

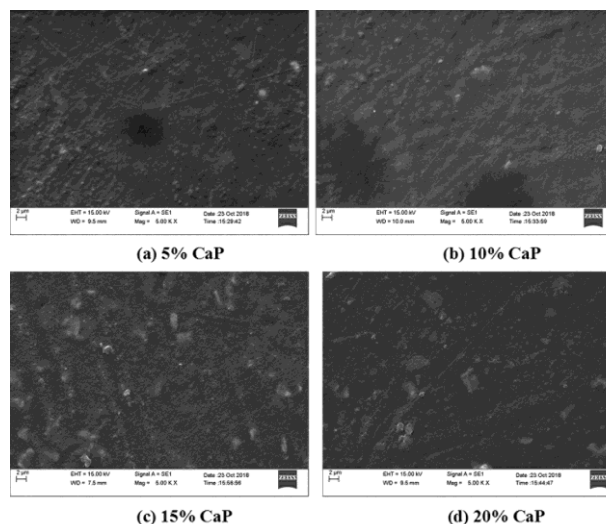


Fig. 2 – SEM microphotograph of the PLA/CaP nanocomposites film

The tensile strength of the PLA/CaP nanocomposite film is shown in the Fig. 3.

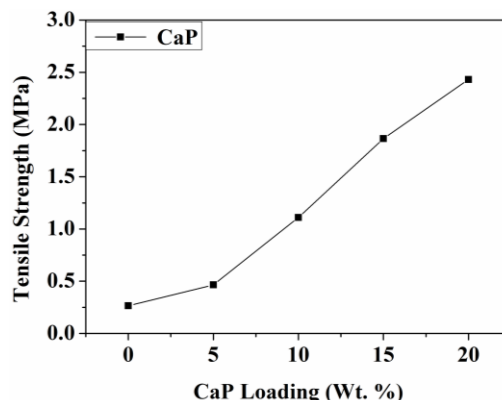


Fig. 3 – Tensile strength of the PLA/CaP nanocomposite film with filler loading

The tensile strength of the PLA nanocomposites film increases with the incorporation of CaP nanoparticle. The tensile strength of nanocomposite film increases due to the presence of load-carrying particle inside the matrix. The applied load is transferred from polymer to filler. The increase in tensile strength is achieved by the formation of the large interfacial area between the PLA matrix and the filler with reinforcement of CaP nanoparticle for effective load transfer [11].

Rheological property shows the response of composites material under the action of external load whether it deforms or flow. Rheology of composites is important for numerous operations such as; wet mixing and milling, casting, extrusion, spraying and printing etc. for preparation of desired products.

The complex viscosity of the nanocomposite film as a function of the filler content with different angular frequency was shown in the Fig. 4. This graph is plotted to study the individual impact of filler loading and frequency on the complex viscosity of the nanocomposites film.

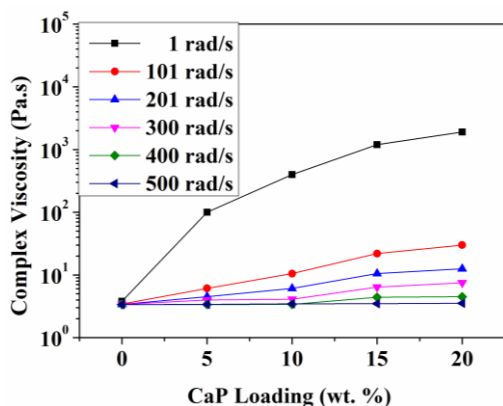


Fig. 4 – Variation of Complex Viscosity of PLA/CaP nanocomposites with filler loading at a various angular frequency

From the figure, it is clear that the complex viscosity of the nanocomposite films increases with filler concentration and decreases with increasing angular frequency. The enhancement in the viscosity with the filler concentration was more pronounced when the frequency is sufficiently low for the particle to restrain mobility of the polymer melt. The effect of filler concentration was dominated at higher frequency domain.

The melt flow of particulate composites is affected by the size and concentration of the addition of inorganic fillers [12]. Commonly, the complex viscosity of the composites increases with increasing filler concentration which depends on the hydrodynamic force exerted by the surface of the particle or agglomerates [13].

Along with the complex viscosity, the storage modulus (G') and loss modulus (G'') of the nanocomposites were also measured. The storage and loss modulus of the PLA/CaP nanocomposites with angular frequency are shown in the Fig. 5 and Fig. 6 respectively.

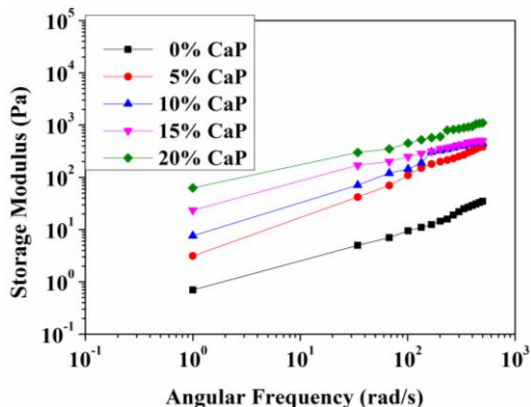


Fig. 5 – Storage modulus of PLA/CaP nanocomposite film with angular frequency

The storage and loss modulus of the PLA/CaP nanocomposite films are higher than that of the pure PLA because the addition of CaP resists the movement of PLA chains and increases the friction of PLA chains.

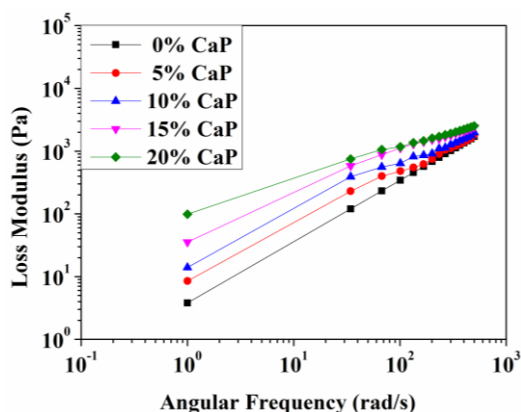


Fig. 6 – Loss modulus of PLA/CaP nanocomposite film with angular frequency

This indicates that PLA/CaP nanocomposites show the solid-like behavior as both the moduli monotonically increases with the incorporation CaP nanoparticle content.

Incorporation of CaP nanoparticle greatly affects the G' and G'' of the nanocomposite film at a lower frequency only and separates from each other. At higher frequency, the values of both moduli are converging and separation reduces. This behavior is results of having sufficient time for the PLA to respond against stress developed in the PLA melt. Incorporation of the CaP nanoparticle to the PLA changes the relaxation time spectrum which turns into the change in the viscoelastic properties of the composite film. Formation of PLA and filler network is the main reason for increasing loss and storage modulus of the composites film.

5. CONCLUSIONS

Biodegradable PLA/CaP nanocomposite films were prepared by melt mixing method. Result of SEM analysis describes the uniform distribution of the CaP nanoparticle throughout the PLA matrix. At lower filler concentration agglomeration of nanoparticle was absent. Further increase in filler concentration the particle to particle contact increases, which forms aggregation. The tensile strength of the nanocomposite film was increased with CaP concentration. The increase in tensile strength is caused by the formation of stress transferring interface between PLA matrix and the CaP nanoparticle. The increase in tensile strength also confirms the compatibility of the matrix and reinforcement.

The rheological studies conclude that pure PLA shows the Newtonian behaviour in the observed frequency range. The PLA/CaP nanocomposite shows strong shear thinning behaviour. This also concludes that melt behaviour of the PLA increases with the reinforcement of the CaP nanoparticle. It is also concluded that the storage and loss modulus of the composites greatly depends on filler content at a lower frequency only. The increase in tensile strength and complex viscosity conclude the good interfacial adhesion between the PLA matrix and CaP nanoparticle.

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