POLYLACTIC ACID/ MAGNESIUM OXIDE NANOCOMPOSITE FILMS FOR FOOD PACKAGING APPLICATIONS

Chetan Swaroop[1], Mukul Shukla[1,2,3]

[1]Mechanical Engineering Department, Motilal Nehru National Institute of Technology, Allahabad, India

Email: chetanswaroop019@gmail.com

[2] School of Mechanical and Aerospace Engineering, Faculty of Engineering and Physical Sciences, Queen's University, Belfast, UK

[3] Department of Mechanical Engineering Technology, University of Johannesburg, South Africa

Email: m.shukla@qub.ac.uk, mukulshukla@mnnit.ac.in, mshukla@uj.ac.za,

Keywords: biopolymer, nanocomposite, mechanical and optical properties, antibacterial packaging, flow cytometry

ABSTRACT

This study was aimed at developing flexible nanocomposite (NC) films for active food packaging applications by incorporation of Magnesium oxide (MgO) nanoparticles (NPs) into Polylactic acid (PLA) biopolymer using the solvent casting technique. Surface morphology, structural, mechanical, optical and antibacterial properties of the prepared NC films were investigated. Scanning electron microscopy revealed the rough surface while X-Ray diffraction established the presence of amorphous phase in the prepared NC films. The NC films showed an increase in tensile strength of up to 52% and elastic modulus by 44% while the elongation at break decreased compared to the neat PLA films. Loading of MgO NPs into PLA also enhanced the antibacterial and ultraviolet screening properties in the films. However, the transparency value decreased with the incorporation of MgO nanofiller in the neat PLA. The net effect of incorporating nanofillers into PLA paves a path for its use as a sustainable packaging material.

1 INTRODUCTION

Increased demand for packaged food has driven the packaging industries to utilize petroleum-based polymers over papers, metals or ceramics. This is due to their superior properties including flexibility and light-weight along with reasonably good mechanical and barrier properties. This, in sequence, has accelerated the production of non-degradable litter around the globe and stirred the researchers to look for renewable and biodegradable substitutes for traditional petroleum-based packaging materials. In the past few years several biopolymers, for example, polylactide, chitosan, polyhydroxy alkanoates, starches etc. have extensively been studied owing to their suitability as a sustainable packaging material. Among the diverse range of the investigated biopolymers, PLA has emerged as the most promising biopolymer, owing to its superior mechanical strength, renewability and biodegradability [1]. In spite of these distinct attributes, PLA falls short in few key areas like plasticity, thermal stability and barrier properties along with hydrophobic nature which confines its utilization in various packaging applications [2]. These shortcomings of PLA can be mitigated by incorporating nanofillers to make use of its renewable and biodegradable properties for sustainable packaging.

Recently, metal oxide nano-fillers loaded into different polymers have been reported for their possible utilization as a packaging material. Metal oxides like ZnO, TiO_2 and MgO possess good antibacterial

properties and their nano-order reinforcement into polymers enables longer shelf life of packaged food by suppressing pathogenic activity along with improved mechanical properties, thermal stability and permeability [3]. U.S. Food and Drug Administration (FDA) generally recognizes the use of MgO as safe for food application. MgO occurs naturally as a colorless, crystalline mineral periclase and is reproducible as well as economical for large-scale production [4]. These features make MgO suitable candidate for reinforcement in biopolymers like PLA. To the best of our knowledge, there is no study already reported on the application of PLA/ MgO nanocomposites for the packaging applications. In this study, flexible films of PLA reinforced with MgO NPs up to 4 wt% were prepared and investigated for their mechanical strength, optical properties, and antibacterial efficacy. The PLA/MgO NC films were prepared using the solvent casting method and their microstructural properties evaluated using XRD and Field Emission Scanning Electron Microscopy (FE-SEM) techniques.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

The PLA-4043D resin used in this study is commercially available in pallet form NatureWorks LLC, USA. The MgO nanopowder with average particle size of 60 nm and 99.9% purity was procured from Nanoshel LLC, USA. The chloroform used as a solvent for preparation of the films was supplied by Fisher Scientific (India) Pvt. Ltd., Mumbai, India.

2.2 Preparation of nanocomposite films

In this study, the PLA and PLA/ MgO NC films were prepared by the solvent casting method. In order to remove any traces of absorbed moisture, the PLA granules were dried at 65°C for 24 hrs. before dissolving into chloroform. The pristine films were prepared by dissolving PLA granules (5 g) into 60 ml of chloroform with continuous stirring at room temperature. For the NC films MgO NPs were accurately weighed in the desired proportions and separately dispersed in chloroform using ultrasonication and then poured into PLA dissolved in chloroform solution with continuous stirring of 1-2 hrs. The obtained solution was evenly spread on a glass plate using a 700 µm, bar type, manual film applicator to obtain uniform film thickness. The chloroform was allowed to evaporate at room temperature for 3 days. The resultant films were peeled from the glass plate and conditioned at 50° C for 24 hrs. in a vacuum oven to remove residual solvent which may act as a plasticizer. The thickness of the films was measured using a handheld electronic micrometer and found to be in between 35-45 µm.

3 CHARACTERIZATIONS

The crystallographic properties of the prepared NC films were studied by XRD analysis performed using a 3kW Rigaku Smart lab apparatus. The samples were scanned in the 2θ range of 5 to 65° at a rate of 5° per minute. The surface morphology of the prepared films was captured using Nova Nano SEM 450, a field-emission scanning electron microscope. The representative samples of the prepared films were coated with gold for 2 minutes using Emitech SC7620 mini sputter coater in order to make them detectable by SEM.

The essential mechanical properties of the flexible packaging films were studied using a Tinius-Olsen Universal Testing Machine (UTM). The UTM was equipped with a 250 N load cell and rubber lined flat grips to avoid any slippage during the test.

In vitro antibacterial efficacy of the prepared films was examined against foodborne bacteria culture by the Fluorescence Activated Cell Sorting (FACS) technique using a BD ACCURI C6 Flow Cytometer. FACS is considered to be one of the best modern technique for cell sorting known for the rapid and reproducible results compared to other techniques [5].

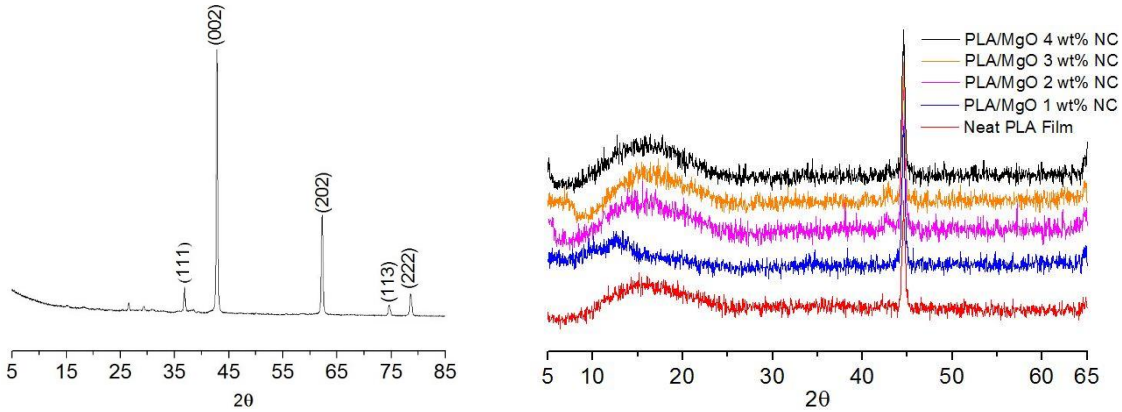
The optical properties of the films were analyzed by recording the percent transmission spectra from UV-visual spectrophotometer (Model - Shimadzu UV-3600 Plus, Japan) in the ultraviolet and visual range.

4 RESULTS

4.1 XRD Analysis

Properties of polymer nanocomposites depend considerably on the crystalline arrangement of the molecules. Understanding crystallographic properties helps in the prediction of physical, mechanical, barrier and thermal stability properties of the films. The XRD was carried out at ambient conditions and the results are presented in Fig. 1. XRD pattern of the MgO nanopowder shows characteristic peaks at 2θ values of 36.78, 42.76, 62.16, 74.56 and 78.5° which are indexed as shown in Fig. 1 (a) [6]. The diffractogram of PLA film exhibits a broad peak around 2θ=16.5° corresponding to amorphous phase of the PLA as presented in Fig. 1 (b). The peak at 44.5° in all the XRD patterns belong to the specimen holder plate and therefore it was excluded from consideration.

For PLA/MgO NC films, a small increase in the diffraction intensity around 2θ=42.7° in 2, 3 and 4 wt% NC films corresponding to (002) crystal plane of MgO NPs can be observed. This confirms the presence of MgO NPs in the prepared composite. The peaks at 16.5° corresponding to the PLA and 42.7° corresponding to MgO NPs occur at same 2θ values in all the compositions, indicating that the solvent casting process did not alter the structure of MgO and confirms its presence in the matrix [7].

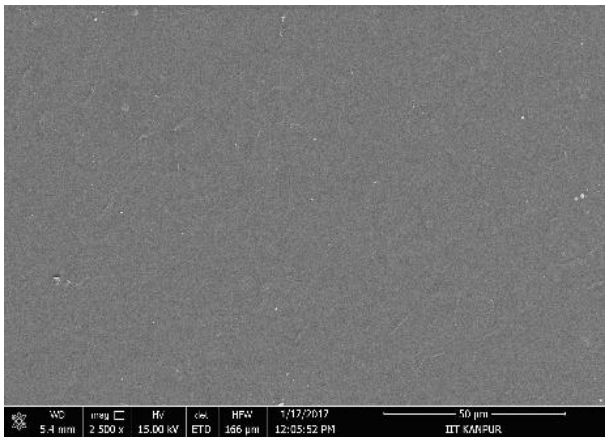


(a) (b)

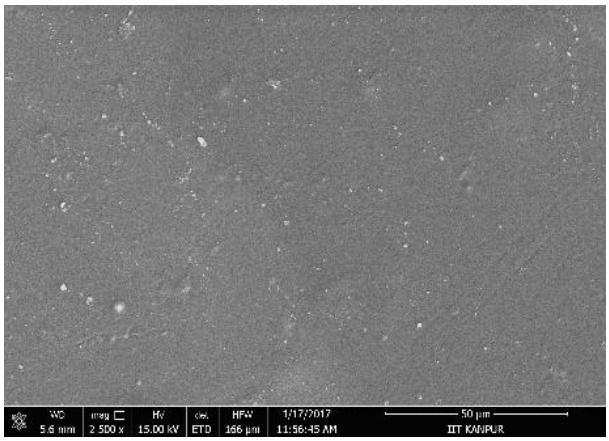
Figure 1: XRD Diffractogram of (a) MgO nanopowder and (b) PLA/MgO nanocomposite films

4.2 SEM Analysis

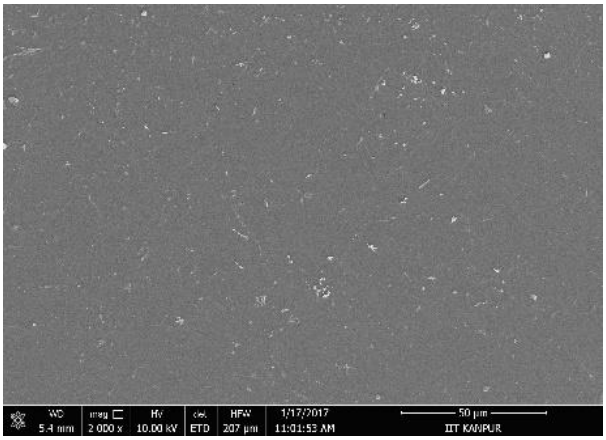
The FE-SEM micrographs are illustrated in Fig. 2. The images depict that the pristine PLA film has an even and compacted surface while the surface of the nanocomposite films consist of roughness and bumps due to presence of the NPs in the matrix [7]. As captured in the SEM surface micrographs, the NPs are homogeneously distributed with agglomerated masses at different locations. A similar surface morphology was also observed in [3]. The surface analysis also reveals the embedded clusters of MgO NPs in PLA projected on the surface of the NC which hints at retention of antibacterial properties. The uniform distribution of nanoparticles in PLA chains is also reflected as an improvement in mechanical properties. Surface analysis of the prepared samples evidences no physical defects like scratches, micro-cracks or pin holes due to solvent evaporation, which suggests successful preparation of NCs by using the solvent casting method.



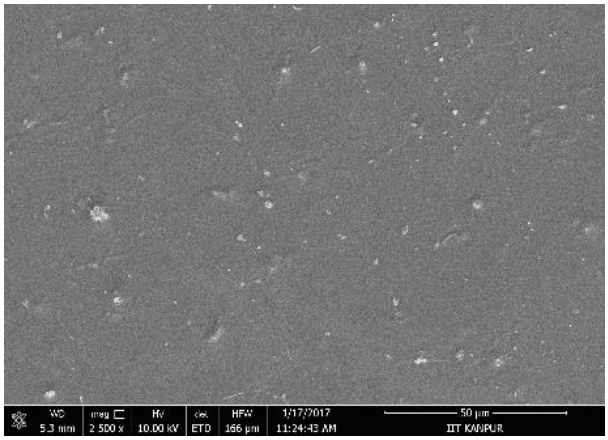
(a) Pristine PLA



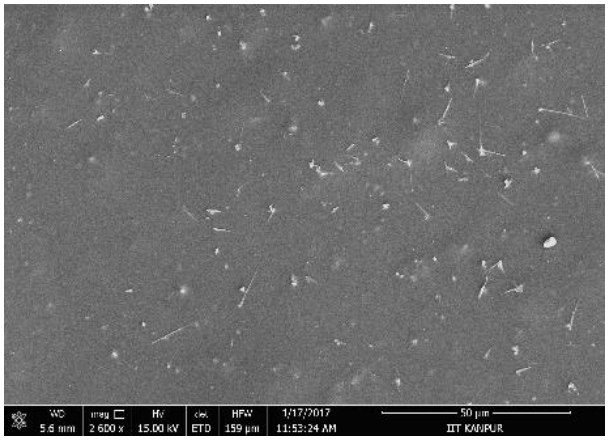
(b) PLA/ 1% MgO NC



(c) PLA/ 2% MgO NC



(d) PLA/ 3% MgO NC



(e) PLA/ 4% MgO NC

Figure 2: FE-SEM micrographs of prepared PLA/MgO nanocomposite films

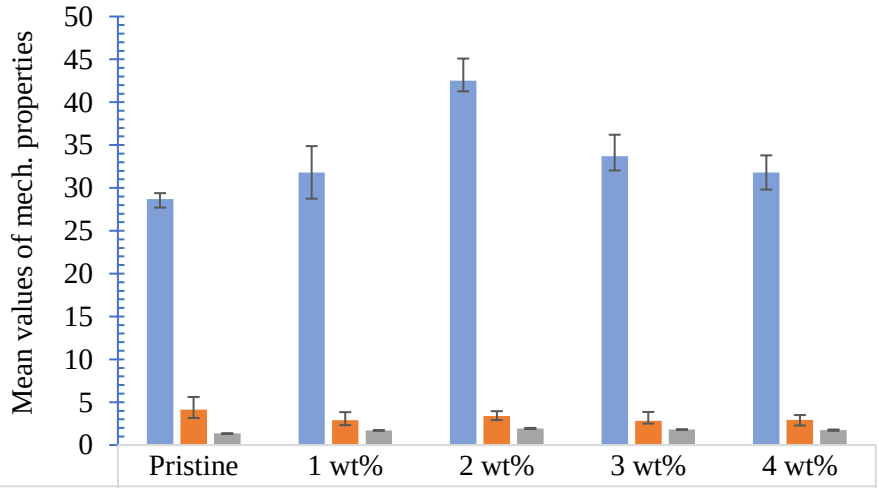
4.3 Mechanical Properties

Foremost mechanical properties desired for flexible film packaging applications, like Tensile Strength (TS), Elastic Modulus (EM) and Elongation at Break (EAB) were found out of the NC films at 70% RH and

20° C surrounding conditions. The specimens were cut into rectangular strips of 150 x 10 mm size following the ASTM D882-2002 standard. The tensile tests were conducted at a strain rate of 10 mm/min. Total 5 specimens of each composition were tested and an average of the thickness measured at 5 different locations along the length of the specimens was used to compute the stress values. The mean values of the mechanical properties along with the range are presented in Fig. 3.

Mechanical properties of the PLA biopolymer were significantly altered by incorporation of MgO nanofiller. The tensile strength of the NC films increased by nearly 52% for the 2 wt% composition, as compared to the pristine PLA film. The trend of the tensile test results infers that mechanical properties of prepared NC increase up to 2 wt% loading of the NPs. Further loading of the nanofillers increased the tendency of agglomeration, which in turn, deteriorated the expected properties.

An improvement in tensile strength and elastic modulus indicates the good compatibility of the filler and polymer matrix. The presence of nano-sized filler in the polymer network facilitates improved interaction between the filler and polymer chain which consequently facilitates the transfer of stress from the matrix to nano-filler and vice versa. On the other hand, the presence of nanoparticles in the polymer network also restricts the free movement of polymer chains which in turn decreases the EAB significantly [8]. Among the prepared NCs the 2 wt% film has the best mechanical properties including the highest EAB which can be endorsed to the uniform dispersion of NPs in the PLA matrix, as also observed in surface analysis through FE-SEM.



	Pristine	1 wt%	2 wt%	3 wt%	4 wt%
TS (MPa)	28.7	31.8	42.5	33.7	31.8
EAB (%)	4.1	2.9	3.4	2.8	2.9
EM (GPa)	1.351	1.707	1.946	1.817	1.735

Figure 3: Mechanical properties of the prepared films

4.4 Antimicrobial Efficacy

The metal oxides are known for their superior antibacterial efficacy [3] their reinforcement in polymer matrix imports bactericidal properties in the NC films which is desired essentially in food packaging applications. To ensure retention of antibacterial efficacy of MgO NPs in the PLA/MgO NC, the prepared films were evaluated against food borne bacteria by using the FACS technique. We adopted the methodology suggested by Das & Shukla [9] to grow the E. Coli culture and prepare of the FACS sample.

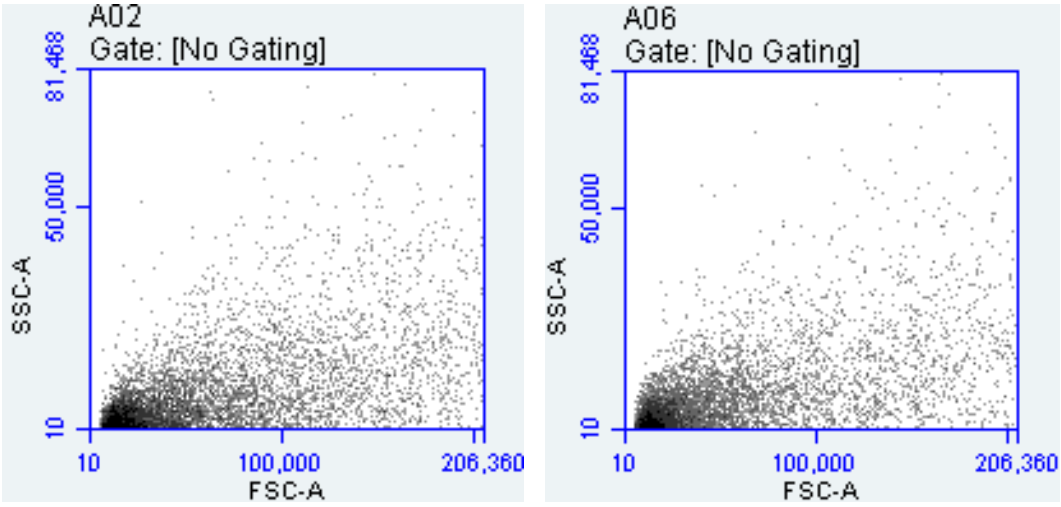
The test protocol comprises growth of E. coli culture in Luria-Bertani broth followed by treatment of microbial inoculum with 5 x 5 cm^2 size of PLA and PLA/MgO NC films. The treatments were performed in an incubator-shaker at 35ºC for 7-8 hrs. The treated culture was then centrifuged to obtain pellets and washed with phosphate buffered saline (PBS) solution. The bacterial cells were finally diluted into PBS and sorted by the FACS cytometer. In total 10,000 events were analyzed for each sample. BDC6 sampler software package was used to interpret and present the results.

FACS was performed for three sets of each composition and results were obtained in terms of average forward scattering (FSC) and side scattering (SSC) corresponding to neat PLA and its NC films as summarized in Table 2.

Film type	Average FSC	Average SSC
Pristine Film	134,402	13,064
1 wt. % NC Film	117,397	11,966
2 wt. % NC Film	110997	11373
3 wt. % NC Film	107,773	10,897
4 wt. % NC Film	100,858	10,772

Table 2: FACS analysis results

The flow cytometry dot plot obtained from FACS is presented for the 2 wt% NC film possessing the best mechanical properties. Fig. 3(a) illustrates the FACS results (FSC = 139861, SSC = 13714) for the neat PLA film which was used as the control, while Fig. 3 (b) presents the result of the 2 wt% NC treated sample (FSC = 108630, SSC = 10995). A decrease in the values of FSC and SSC was found which indicates a reduction in size and granularity of the E. coli microorganisms, confirming the death of bacteria [5]. The FACS study also reveals the retention of anti-bacterial properties in the prepared NC films.



(a) (b)

Figure 4: FACS flow cytometry dot plots of (a) Pristine PLA (control) and (b) 2 wt% PLA/MgO NC

4.5 Optical Properties

The optical properties of PLA and its NC films were analyzed by recording the percentage transmission spectra in the 200-700 nm wavelength range. The films were loaded in the spectrophotometer cell and the transmittance spectra were recorded with respect to air. The results of the study are presented in Fig. 5 and illustrate the dominant screening of incident radiation in the UV range compared to the visual range. It can be seen, from the graph, that the prepared films allow around 86% of the incident light to be transmitted which reveals adequate transparency properties.

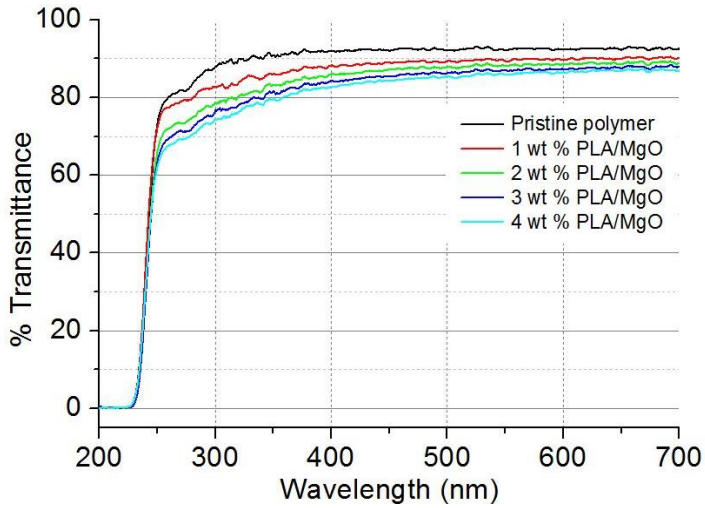


Figure 5: Percent transmission spectra of PLA and its NC films

The transparency value of the NC films was also computed using equation given below [10]:

$$TV = \{-\log(T_{600})\}/x \quad (1)$$

where *TV* is the transparency value, T_{600} is the fractional equivalent to percentage transmission and *x* is the film thickness in mm. The lowest value of *TV* corresponding to the neat PLA film indicates high transparency of the film. However, with higher loading of the filler, the transparency of the films decreased continuously.

Film type	% Transmission		Transparency Value (*TV*)
	Wavelength (280 nm)	Wavelength (600 nm)	
Pristine Film	83.3	92.4	0.72
1 wt% NC film	78.9	89.7	0.87
2 wt% NC film	74.5	88.6	0.96
3 wt% NC film	72.5	87.5	1.03
4 wt% NC film	71.1	86.8	1.09

Table 3: UV barrier, visual light transmission and transparency values of the prepared NC films

The presence of the metal oxide nanofiller in the polymer matrix enables dominant screening of UV radiation over visual light. Long exposure to UV radiation deteriorates the food constituents such as vitamins, fats, flavors etc. due to photo-oxidation [11]. The ability of the packaging film to block the UV radiation hence turn out to be an important attribute for food packaging applications.

6 CONCLUSIONS

This study focused on the production and characterization of the PLA/MgO nanocomposite films and investigation of their key attributes for possible food packaging applications. The XRD, SEM and spectrophotometry studies show the physical and structural adequacy of the NC films prepared by the solvent casting method. The XRD study reveals amorphous structure of the prepared films and presence of the MgO NPs has no effect at crystallization process of the films. The mechanical properties of the PLA films were significantly improved by reinforcement with MgO NPs. However, to take maximum advantage of the filler loading, uniform distribution in the network of polymer chains without agglomeration is ideally desired. NPs by virtue of their tiny sizes, have high surface energies and hence they tend to agglomerate which increases with increased particle loading, therefore the desired properties like tensile strength and plasticity deteriorated at higher reinforcement. In agreement with this, the FE-SEM images also revealed prominent agglomeration at higher loading of MgO NPs. The results obtained from the FACS analysis confirmed the retention of antibacterial efficacy of MgO in the polymer matrix. Overall, the ability to block UV radiation without losing transparency, in conjunction with antibacterial characteristics to inhibit degradation of food due to UV radiation and pathogenic activity, yielded promising results encouraging the incorporation of MgO for potential food packaging applications.

ACKNOWLEDGEMENT

The authors would like to acknowledge the testing and characterization facilities of the Centre for Interdisciplinary Research (CIR), Centre for Medical Diagnostic and Research (CMDR), Biotechnology and Applied Mechanics Departments of MNNIT, Allahabad. The authors are also grateful to Indian Institute of Kanpur for extending their FE-SEM facilities. The authors would like to thank the Ministry of Human Resource Development, Government of India for providing financial support.

7 REFERENCES

[1] J.M. Raquez, Y. Habibi, M. Murariu, Philippe Dubois, Polylactic (PLA)-based nanocomposites, *Progress in Polymer Science*, **38**, 2013, pp.1504-152.

[2] Y. Byun, W. Scott, T. Ron, D. Mahalaxmi, H. Jeremy, T.K. Young, The effect of the solvent mixture on the properties of solvent casting polylactic acid (PLA) films, *Journal of Applied Polymer Science*, **124**, 2012, pp. 3577–3582.

[3] A. Marra, C. Silvestre, D. Duraccio, S. Cimmino, Polylactic acid/zinc oxide biocomposite films for food packaging application, *International Journal of Biological Macromolecules*, **88**, 2016, pp. 254-262.

[4] S. Sanuja, A. Agalya, M.J. Umapathy, Studies on magnesium oxide reinforced chitosan bionanocomposite incorporated with clove oil for active food packaging application, *International Journal of Polymeric Materials and Polymeric Biomaterials*, **63**, 2013, pp. 733-740.

[5] A. Paparella, L. Taccogna, I. Aguzzi, C. C. Lopez, A. Serio, F. Marsilio, G. Suzzi, Flow cytometric assessment of the antimicrobial activity of essential oils against Listeria monocytogenes, *Food Control*, **19**, 2008, 1174–1182.

[6] S. Balamurugan, L. Ashna, P. Parthiban, Synthesis of Nanocrystalline MgO Particles by Combustion Followed by Annealing Method Using Hexamine as a Fuel, *Journal of Nanotechnology*, **2014**, 2014, pp. 1-6.

[7] J. Jayaramudu, K. Das, M. Sonakshi, G.S.M. Reddy, B. Aderibigbe, R. Sadiku, S.S. Ray, Structure and properties of highly toughened biodegradable polylactide/ZnO biocomposite films, *International Journal of Biological Macromolecules*, **64**, 2014, pp. 428–434.

[8] J. Ahmed, Y.A. Arfat, E.C. Aguirre, R. Aurus, Mechanical, structural and thermal properties of Ag–Cu and ZnO reinforced polylactide nanocomposite films, *International Journal of Biological Macromolecules*, **86**, 2016, pp. 885-892.

[9] A. Das, M. Shukla, Surface morphology, bioactivity, and antibacterial studies of pulsed laser deposited hydroxyapatite coatings on Stainless Steel 254 for orthopedic implant applications, *Journal of Materials: Design and Applications* (DOI: https://doi.org/10.1177/1464420716663029).

[10] J. H. Han, J. D. Floros, Casting antimicrobial packaging films and measuring their physical properties and antimicrobial activity, *Journal of Plastic Film and Sheet*, **13**, 1997, pp 287-298.

[11] J. Ahmed, M.Z. Mulla, Y.A. Arfat, Thermo-mechanical, structural characterization and antibacterial performance of solvent casted polylactide/cinnamon oil composite films, *Food Control*, **69**, 2016, pp. 196-204.