Potential Polylactic Acid /Alginic Acid Films Reinforced With Molybdenum Disulphide for Packaging Purposes

Kalyani Sreekumar, B Bindhu

Abstract— The Polymer composites with enhanced properties have widely gained the interest of researchers. Polymers play a crucial role in many of the industries and the limitations of the synthetic polymers like waste disposal management, makes researchers to rely on biopolymers from renewable resources. Polylactic acid and alginic acid are two biopolymers that are being widely used. In this paper we are reporting the preparation of exfoliated molybdenum disulphide reinforced polylactic acid/alginic acid composite films, synthesized via solvent casting method. The optimized addition of filler particles are seen to have effects in the polymer matrix. The water permeability along with photoluminescence makes these composite an excellent candidate for packaging applications.

Index Terms— Alginic Acid, Biomaterials, Fillers, Molybdenum Disulphide, Packaging, Polymer composites, Polylactic acid

1 INTRODUCTION

The growing concern on environmental issues had resulted in substitution of petroleum based conventional materials by biomaterials/polymers. These materials are usually composed of various organic/inorganic materials that can be extracted from renewable natural resources. Hybrid materials with two or more components are being studied extensively due to their unique properties that can be made used in various applications. These materials can be tuned with the addition or modification of other materials to meet the property requirements. Polylactic acid and alginates are categorized as eco friendly polymers. Both PLA and AA have properties like biodegradability, biocompatibility[1], non toxicity[2], and renewability[3]. PLA is synthesized from renewable resources such as corn and sugar beets [4], whereas AA is extracted from brown seaweeds[5]. Lactic acid (2-hydroxy proponoic acid) is the building block of PLA. Depending on the proportion of optically active D- and L- enantiomers of lactic acid(2-hydroxy proponoic acid), PLA with different properties can be obtained[6]. AA is linear copolymer comprised of β-(1-4)-linked D-mannuronic acid and α-(1-4)-linked L-glucuronic acid units[7]. Various materials like hydroxyapatite[8][9], chitosan[10][11], starch[12][13], cellulose[14][15] have been incorporated with PLA and AA. 2D layered materials like MoS_2 acts as an excellent host to polymer matrix due to its intercalation property when isolated into monolayer [16].

Through this paper we are reporting preparation of novel composites formed of PLA/AA/MoS_2. The composite films were synthesized via solution casting method with chloroform as the solvent.

2 EXPERIMENTAL

2.1 Materials Used

Alginic acid from brown algae [(A7003); Sigma Aldrich(formula weight= 176.10 g/mol). Chloroform ($CHCl_3$) [Merck Specialities, India]., Molybdenum Disulphide [HPLC, LR; MW: 160.06], 6-Aminohexanoic acid [Sigma Aldrich, Fluka Analytical, NT; MW:131.17], Lithium Hydroxide (Monohydrate) [Molychem, GR; MW:41.96], N-Methyl-2-Pyrrolidone [RFCL, MW:99.13], Polylacticacid [resin grade (Ingeo-4043D) Supplied by Nature work LLC].

.

2.2 Preparation of Composites

Exfoliation of MoS_2 was carried out as per reference[17],[18]. The PLA/AA was taken in 1:1 ratio, and different concentrations of MoS_2 were loaded. Required amount of alginic acid and MoS_2 was dispersed in chloroform using a magnetic stirrer. This solution was then mixed with solvated PLA in a magnetic stirrer followed by ultrasonication about 2 min, taking the degradation of polymers into consideration. The solution was casted in a level surface and was left to evaporate.

3 RESULTS AND DISCUSSION

The prepared films were peeled off from the surface and were characterized to study the properties. The optical microscopic images of the prepared composites are shown in fig.1. All the composites showed better dispersion rate and few agglomeration was seen in higher loading of MoS_2. The film thickness measured with the micrometer on average of five different parts of the sample was calculated as (~0.079mm)

- *Kalyani Sreekumar, Department of Physics, Noorul Islam Centre for Highrh education, Thuckalay , kalyani.sreekumar@gmail.com*
- *B Bindhu Department of Physics, Noorul Islam Centre for Highrh education, Thuckalay , bindhu.krishna80@gmail.com*

3.1 X-ray Diffraction Analysis

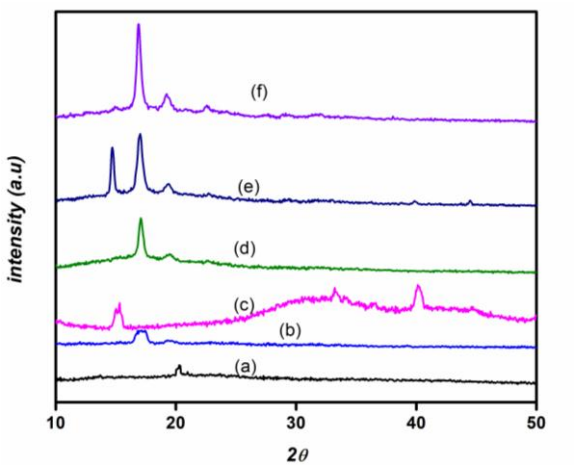


Figure 2. The Xrd spectrum of (a) V.AA; (b) neat PLA; (c) $LiMoS_2$; (d) PLA/AA1wt%MoS_2; (e) PLA/AA/3wt%MoS_2; (f)PLA/AA/4wt%MoS_2

The Xray diffraction spectrum of the samples are given in fig.2. The characteristic peaks of VAA, PLA and $LiMoS_2$ occurs at 2θ= 20.04 A^0, 17.11 A^0, and 15.14 A^0 respectively. It is seen from the spectra that the characteristic peaks of V.AA, PLA and $LiMoS_2$ are seen in PLA/AA with 3wt% MoS_2 loading (fig.2e) which indicates better binding of all the three components together. The absence of peak at 2θ= 15.14 A^0, for PLA/AA1MoS2 and PLA/AA3MoS2, which is well defined for PLA/AA/3Mos2, indicates that the optimized concentration of MoS2 was well dispersed in the polymer matrix. The crystallite size was calculated from Scherrer formula

$D = k\lambda/\beta\cos\theta$

Where,

k is a constant to be taken 0.9 and λ, β and θ are the X-ray wavelength (= 1.54056Å), full width at half maximum and Bragg angle respectively.

The neat PLA used in this work has d-spacing 5.17A^0 at 2θ=17.11^0. The Xrd pattern of PLA/AA/1mos2, PLA/AA/2Mos2, PLA/AA/3mos2 has the d-spacing of 5.15 A^0, 5.47 A^0, 5.16 A^0 respectively. The increase in crystallite size for PLA/AA/3MoS_2 indicates well orientation of filler particles in PLA/AA matrices.

3.1 Photoluminescence

The photoluminescence spectrums of the samples are given in fig.3. The neat PLA shows no predominant peaks in the spectrum. A strong photoluminescence was found in the PLA/AA/3MoS_2 with an emission maximum at 363nm with a reduced band gap of 3.42eV compared with that of PLA/AA/4MoS_2. The B1 direct excitonic transitions at K point of the Brillouin zone are seen in the emission peaks at ~520nm and is attributed to the emergence of photoluminescence when the layers of MoS_2 are isolated into few or two layers[19]. In the bulk form, bands are formed by a bunch of adjacent energy levels of large number of atoms and molecules, but when isolated into single or few layers, the overlapping energy levels decreases in number, forming bands of lower widths, which in turn results in a high energy gap between valence band and conduction band. Strong photoluminescence occurs due to an indirect to direct band gap transition in the d-electron system of MoS_2[20]. Since the neat PLA dosent show any traces of luminescence, the emergence of photoluminescence in PLA /AA/MoS_2 composites can clearly be attributed to the action of exfoliated MoS_2 in the composites.

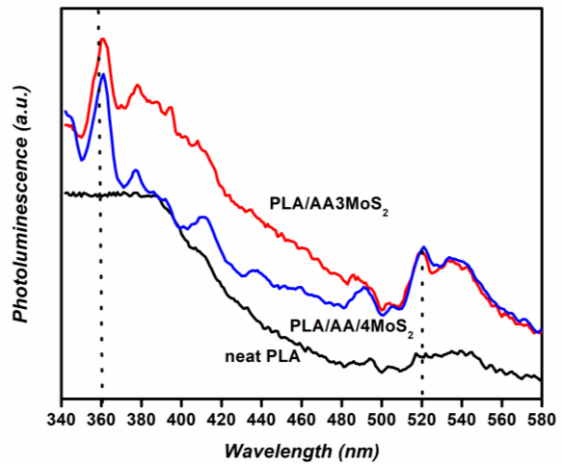


Figure 3. Photoluminescence spectrum of PLA and PLA/AA/MoS_2 composites

3.2 Barrier property studies

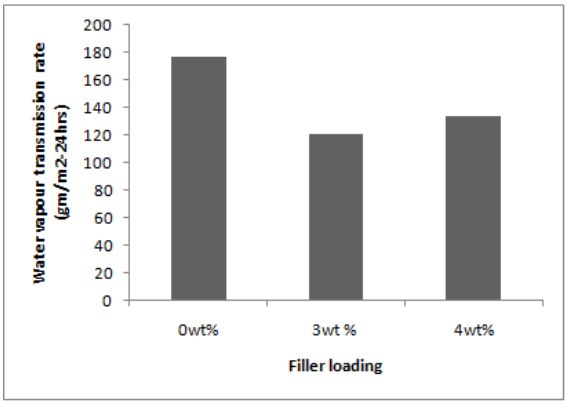
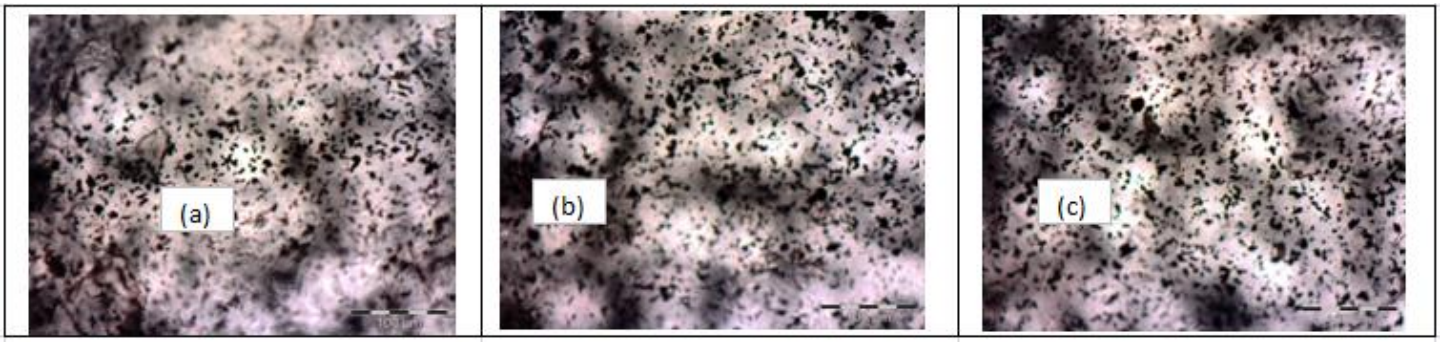


Figure 4. Water vapour transmission rates of PLA/AA with filler loading

Figure 1. optical images of PLA/AA with (a) 1wt%MoS_2; (b) 2wt%MoS_2; (c) 3wt%MoS_2



The water vapour transmission rates of the samples in water vapour transmission rates of the samples are shown in the fig4. The water vapour permeability of the samples were studied using water vapour transmission rate tester (ASTM F1249). The readings were taken as an average of three samples of each constitution. The films with optimized filler loading (3wt%MoS_2) proved to be better moisture barrier. This can be attributed to tight binding of components forming a layer by layer structure in the composite, which obstructs the path of other moisture or vapour contents.

4 CONCLUSION

Exfoliated MoS_2 has been successfully incorporated into the PLA/AA matrices in an optimized concentration. The composite films were casted via solution casting technique. The filler particles are found to have effect on the composite structure. After an optimized addition of fillers, agglomeration and inhomogenity was seen in the composite films, which can be attributed to the weak bindings with higher filler concentrations. The increase in crystallite size for PLA/AA/3MoS_2 indicates well orientation of filler particles in PLA/AA matrices. An emergence of photoluminescence was seen for PLA/AA/MoS_2 composites. MoS_2 when isolated into few or single layers have photoluminescence properties, and the addition of exfoliated MoS_2 into the PLA/AA matrix made the composites to have photoluminescence. This property of the composite along with the enhanced water permeability can be made use in packaging industries.

REFERENCES

[1]. I. Vroman and L. Tighzert, "Biodegradable polymers," *Materials*, vol. 2, no. 2. pp. 307–344, 2009.

[2]. L. K. Narayanan, P. Huebner, M. B. Fisher, J. T. Spang, B. Starly, and R. A. Shirwaiker, "3D-Bioprinting of Polylactic Acid (PLA) Nanofiber–Alginate Hydrogel Bioink Containing Human Adipose-Derived Stem Cells," *ACS Biomater. Sci. Eng.*, vol. 2, no. 10, pp. 1732–1742, 2016.

[3]. N. Najafi, M. C. Heuzey, and P. J. Carreau, "Polylactide (PLA)-clay nanocomposites prepared by melt compounding in the presence of a chain extender," *Compos. Sci. Technol.*, vol. 72, no. 5, pp. 608–615, 2012.

[4]. R. E. Drumright, P. R. Gruber, and D. E. Henton, "Polylactic acid technology," *Adv. Mater.*, vol. 12, no. 23, pp. 1841–1846, 2000.

[5]. A. C. S. Alcântara, P. Aranda, M. Darder, and E. Ruiz-Hitzky, "Bionanocomposites based on alginate–zein/layered double hydroxide materials as drug delivery systems," *J. Mater. Chem.*, vol. 20, no. 42, p. 9495, 2010.

[6]. L.-T. Lim, R. Auras, and M. Rubino, "Processing technologies for poly(lactic acid)," *Prog. Polym. Sci.*, vol. 33, no. 8, pp. 820–852, 2008.

[7]. C. L. Bayer, É. P. Herrero, and N. A. Peppas, "Alginate films as macromolecular imprinted matrices," *J. Biomater. Sci. Polym. Ed.*, vol. 22, no. 11, pp. 1523–1534, 2011.

[8]. T. Kasuga, Y. Ota, M. Nogami, and Y. Abe, "Preparation and mechanical properties of polylactic acid composites containing hydroxyapatite fibers," *Biomaterials*, vol. 22, no. 1, pp. 19–23, 2001.

[9]. T. Chae, H. Yang, V. Leung, F. Ko, and T. Troczynski, "Novel biomimetic hydroxyapatite/alginate nanocomposite fibrous scaffolds for bone tissue regeneration," *J. Mater. Sci. Mater. Med.*, vol. 24, no. 8, pp. 1885–1894, 2013.

[10]. Z. Liu *et al.*, "Alginic Acid-Coated Chitosan Nanoparticles Loaded with Legumain DNA Vaccine: Effect against Breast Cancer in Mice," *PLoS One*, vol. 8, no. 4, 2013.

[11]. T. M. Wu and C. Y. Wu, "Biodegradable poly(lactic acid)/chitosan-modified montmorillonite nanocomposites: Preparation and characterization," *Polym. Degrad. Stab.*, vol. 91, no. 9, pp. 2198–2204, 2006.

[12]. S. Benavides, R. Villalobos-Carvajal, and J. E. Reyes, "Physical, mechanical and antibacterial properties of alginate film: Effect of the crosslinking degree and oregano essential oil concentration," in *Journal of Food Engineering*, 2012, vol. 110, no. 2, pp. 232–239.

[13]. S. Zhang *et al.*, "Novel toughening mechanism for polylactic acid (PLA)/ starch blends with layer-like microstructure via pressure-induced flow (PIF) processing," *Mater. Lett.*, vol. 98, pp. 238–241, 2013.

[14]. C. Cemel, "Crossflow Filtration of Iron(III), Copper(II), and Cadmium(II) Aqueous Solutions with Alginic Acid/Cellulose Composite Membranes," *J. Appl. Polym. Sci.*, vol. 115, no. 7, pp. 616–623, 2010.

[15]. A. Iwatake, M. Nogi, and H. Yano, "Cellulose nanofiber-reinforced polylactic acid," *Compos. Sci.*

Technol., vol. 68, no. 9, pp. 2103–2106, 2008.

[16]. K. Zhou, J. Liu, P. Wen, Y. Hu, and Z. Gui, "A noncovalent functionalization approach to improve the dispersibility and properties of polymer/MoS2composites," *Appl. Surf. Sci.*, vol. 316, no. 1, pp. 237–244, 2014.

[17]. B. Bindhu, B. K. Sharu, M. S. Gopika, P. K. Praseetha, and K. Veluraja, "Molybdenum disulfide nanoflakes through Li-AHA assisted exfoliation in an aqueous medium," *RSC Adv.*, vol. 6, no. 26, pp. 22026–22033, 2016.

[18]. K. Sreekumar and B. Bindhu, "Aqueous Exfoliation Of Molybdenum Disulfide Using Ultrasonication," *Mater. Today Proc.*, vol. 5, no. 5, pp. 13152–13156, 2018.

[19]. A. Splendiani *et al.*, "Emerging photoluminescence in monolayer MoS2," *Nano Lett.*, vol. 10, no. 4, pp. 1271–1275, 2010.

[20]. L. Ye, H. Xu, D. Zhang, and S. Chen, "Synthesis of bilayer MoS2nanosheets by a facile hydrothermal method and their methyl orange adsorption capacity," *Mater. Res. Bull.*, vol. 55, no. 2, pp. 221–228, 2014.