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Studies on Blending Properties of Poly Lactic Acid and Starch with Methylene Diphenyl Diisocyanate

Dineshkumar Myilsamy[1], **Sudhan Gowtham**[2], **Janani Saravanakumar**[3], **Durgadevi Rajendran**[4]

Department of Petrochemical Engineering, SVS College of Engineering, Coimbatore, India[1,2,3,4]

*Corresponding author: Mr. Dineshkumar M

Abstract: Poly Lactic Acid (PLA) is a biodegradable polymer. PLA can be prepared by two chemical reaction, ring opening or direct condensation polymer. In order to increase the biodegradability of polymer and to decrease its high cost, an effect have been made to blend with starch, due to the low cost of starch. This blending has an effect of fully biodegradable material. By contrast, few bends have poor mechanical properties. In this analyze, starch is blended with low level of MDI (Methylene Diphenyl Diisocyanate).As it could be a good coupling agent between starch & PLA. The emphasizing of this blend with MDI was to determine its mechanical &thermal properties. Scanning Electron Microscope (SEM) on the observation of blend was also performed. No significant difference in water absorption occurred between the blend with or without MDI. Results revealed that the strengthening of blends in the development of biodegradable plastics.

Keywords: Biodegradable Blend; Poly(Lactic Acid)/Starch; Methylene Diphenyl Diisocyanate; Coupling Agent

I. INTRODUCTION

Recent concerns about petroleum polymers in the environment have stimulated interest in the development of biodegradable plastics from renewable resources. Starch is a readily available and renewable agricultural resource that is susceptible to biological and oxidative attacks. To increase the biodegradability of petroleum polymers, efforts have been made to blend starch with selected thermal plastics, such as low density poly ethylene, poly (vinyl alcohol), and polystyrene [1]. Poly Capro Lactone (PCL) and Poly Ethylene Vinyl Alcohol (EVOH) have been of great interest for blending with starch and starch derivatives to impart full biodegradability [2-4]. However, PCL and EVOH are fossil fuel-derived plastics that increase carbon dioxide in the environment and stimulate the greenhouse effect. A thermo plastic polymer from a renewable source would be better for the development of a biodegradable plastic [5-8].

Poly Lactic Acid (PLA) is polyester made from L- or D-lactic acid. A desired stereoisomer oflactic acid can be made commercially through carbohydrate fermentation technology. PLA can be prepared through two chemical reactions, ring opening or direct condensation polymerization [9-12]. Ring opening polymerization starts with lactide, a cyclicdimer of lactic acid, as a monomer, so the product is commonly called polylactide. PLA made from the direct condensation polymerization of lactic acid is called poly lactic acid. The PLAs derived from these two pathways have similar mechanical properties [2, 13-15]. Pure PLA can degrade slowly to carbon dioxide, methane, and water in the environment to over a period of several months to 2 years, compared with 500 –1000 years for petroleum plastics. It has many properties comparable to those of polyethylene, polypropylene, polystyrene, and polyethylene terephthalate, such as stiffness, tensile strength, and gas permeability. In the past few decades, the applications of PLA as a biodegradable have mainly been in the biomedical field [4, 8, 16-19]. However, it has also been fabricated into a wide variety of consumer products, including compostable bags for waste, table utensil films, and paper coatings, and has been spun into fiber and cloth.

Natural starch exits in a tiny, rigid, granular form. The introduction of low-cost starchasafiller to PLA would result in a fully renewable biodegradable material [5]. However, some blends have poor mechanical properties, especially at high starch concentrations, because of weak interfacial attractions between starch granules and the PLA matrix. Generally, the mechanical properties of a blend can be improved by the strong interfacial tension between the filler and matrix being overcomes [20-22]. Reducing the interfacial tension and strengthening the interaction between polymer phases can transfer the internal stresses from the filler to the matrix and, consequently, enhance the strength of the blend. Strong interfacial adhesions can be achieved with the addition of a coupling agent to the blend system. A good coupling agent should have functional groups that react with both the matrix and filler [14, 18]. Methylene Diphenyl Diisocyanate (MDI), which is highly reactive with both hydroxyl and carboxyl groups to form urethane linkages, could be a good coupling agent between starch and PLA. Residues of untreated MDI are not expected in a blend because of the high reactivity of its isocyanate groups. In addition, the small amount of urethane linkages in the blend could be attacked by some fungi and absorbed by soil. The objective of this study was to determine the effects of MDI on the mechanical behavior, thermal dynamic mechanical properties, crystallization, microstructure, and water absorption of a PLA/starch blend.

II. EXPERIMENTAL

Materials: PLA with a weight-average molecular weight of 120,000 Da made mainly from $_{\mathrm{L}}$-lactic acid waspurchased as chips (2.7 mm × 2.7 mm × 2 mm) from Shimadazu (Japan). Wheat starch (Midsol 50, Midwest Grain Products, Inc., Kansas City, KS) with an amylose content of 23–28% and a particle size distribution of 17.95–18.09(95%conFident limits) was used. It was dried in a convection oven at 130°C for 2 h according to AACC Method 44-15A to about a 0.5% moisture content. Wheat starch consists of two kinds of granules: large, disc-shaped A-granules and small, spherical B-granules. The B-granules are about 30% of wheat starch by weight. Polymeric MDI (Rubinate1840) was obtained from ICI Polyurethanes (Geismar, LA) and contained about 45% 4,4'-methylene diphenyl diisocyanate in a dark brown, viscous, liquidform.

Blend Preparation: The PLA chips were ground through a 2-mm screen in a laboratory mill (model 4 Laboratory Mill, Thomas–Wiley Co., Philadelphia, PA). The ratio of PLA to dried starch was 55 to 45 by weight, and MDI was added at four concentrations, 0.25, 0.5, 1, and 2 wt %, based on 100parts of the blend. Each blend, including PLA and starch without MDI, was mixed in an intensive hot mixer (Rheomix 600, Haake, Paramus, NJ) equipped with two corotating rollers with a gap. Blends were hot mixed at 180°C and 135 rpm for 4 min. Pure PLA also was treated under the same mixingconditions.

Tensile Testing: Blends from the mixer were compression molded into tensile bars (type IV) according to ASTM Method D 638-91 with a Carver hot press (mod- el 3890, Auto “M”, Carver Inc., Wabash, IN) at 176°C and 4.2 MPa for 9 –15 min. The molded specimens were cooled to 65°C before removal from the mold and then preconditioned at 50% relative humidity and 25°C for 48 h beforetesting. The tensile strength and elongation at break were determined with an Instron testing system (model 4465, Canton, MA) according to ASTM D 638-91 with a crosshead speed of 5 mm/min and a 25-mm gauge length. Six replicates were tested for eachtreatment.

Morphology: The microstructure of a blend was observed with scanning electron microscopy (SEM; Hitachi S-3500N, Hitachi Science Systems, Ltd., Japan). Each specimen from a tensile test was mounted on an aluminum stub, and the fractured surface was coated with a mixture of 60% gold particles and 40% palladium with a sputter coater (DeskII Sputter/Etch Unit, NJ) beforeobservation.

Water Absorption: The broken specimens (30mm×15mm×2mm) after tensile testing were used for a waterabsorption test. They were dried at 50°C for 24 h and cooled to room temperature. The dried specimens were immersed in distilled water at 25°C for specific intervals, removed from the water, blotted with tissue paper to remove excess surface water, and then weighed. Three replicates were tested for each treatment. The water absorption was calculated on a drybasis.

III. RESULTS AND DISCUSSION

Morphology: Figure 1(A) shows the SEM micrograph of the tensile fracture surface of the 55/45 (w/w) PLA/starch blend without MDI.

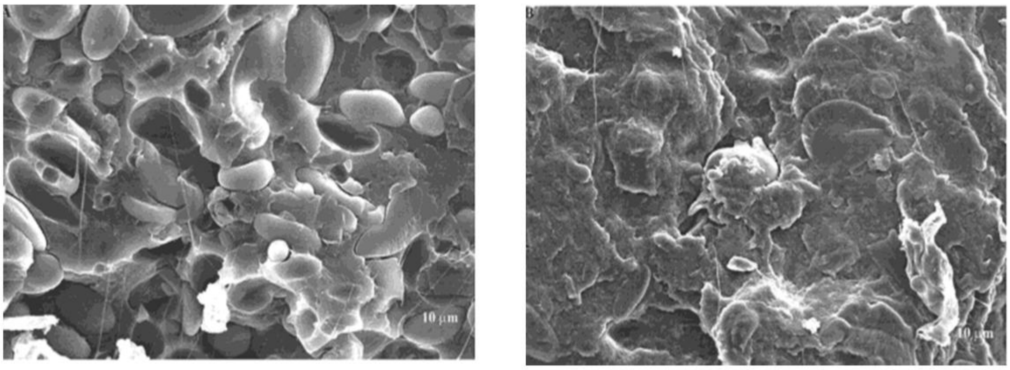

Figure.1: SEM micrographs of the tensile fracture surface of PLA/starch blends (55/45 weight ratio) (A) without MDI and (B) with 0.5% MDI

Two phases can be seen clearly, and in the fracture process, many starch granules were pulled out from the matrix, with large voids thereby being created. Also, gaps between remaining starch granules and the PLA matrix are visible. These results indicate poor interfacial adhesion between PLA and granular starch. Figure 1(B) shows the micrograph of a blend after compounding with 0.5wt% MDI. Few individual starch granules can be observed, and those that are distinguishable appear to be coated with matrix PLA. Moreover, fracturing of the blend occurred through the starch granules rather than at their interface.

The SEM results are consistent with the formation of a block or graft copolymer of starch/PLA joined by urethane bonds formed during reactive compounding with MDI. The same SEM evidence was found when 3% starch graft PCL increased interfacial adhesion in a 70/30(w/w) starch/PCL blend. Starch graft PLA coupled by ester bonds probably formed during the reactive extrusion of a30/70(w/w) blend of starch/lightly maleated PLA because SEM showed increased interfacial adhesion with respect to a blank of starch/PLA.

Water Absorption: Starch is hydrophilic because it contains an abundance of hydroxyl groups, but PLA is a hydrophobic polymer. When starch is soaked in excess water at 25°C, it can take up to about 50% water on a dry basis. Therefore, the theoretical maximum water content absorbed by the blend containing a 45% starch phase is about 23% when submerged in excess water at 25°C. The water absorption for both blends with or without MDI increased greatly during the first 15 days and then leveled off at about 14% (Fig. 5). No significant difference in water absorption occurred between the blends with and without MDI. The water absorption for raw PLA also had the same tendency as that of the blend with starch but leveled off at about 1%. These results indicated that starch content was the major factor affecting the water absorption of the PLA/starch blends.

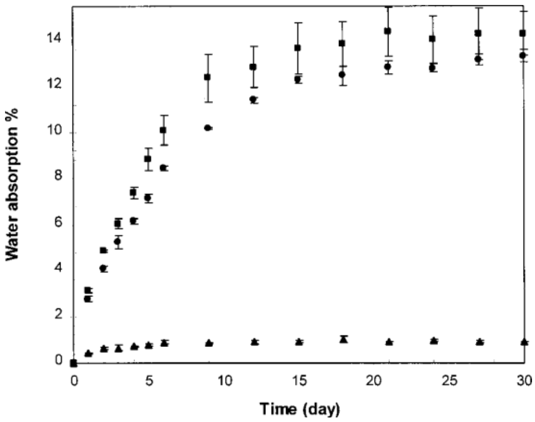

Figure 2 Water absorption versus time for PLA and PLA/starch blends (55/45 weight ratio): (Œ) raw PLA, ( ) blend without MDI, and (F) blend with 0.5 wt %MDI.

CONCLUSION

A low concentration (0.25–0.5wt%) of MDI during the hot mixing of approximately equal weights of dry granular starch and PLA dramatically improved the strength and elongation properties in the blend. With this one-step method, the ingredients PLA, starch, and MDI could be added into an injection-molding machine or extruder to produce shaped pieces. The blends slowly absorbed liquid water, making them suitable for molding into degradable single use items. The higher water absorption after a long time would probably lead to better biodegradability. The completeness of the reaction of MDI in the blend should be determined, as well as the fate of the methylene diphenyl urethane linkage groups during biodegradation. Further study on extrusion and injection molding should be conducted.

REFERENCES

[1]. C. H. Cui et al., “A high heat-resistance bioplastic foam with efficient electromagnetic interference shielding,” Chem. Eng. J., vol. 323, pp. 29–36, 2017.
[2]. V. Bátori, D. Åkesson, A. Zamani, and M. J. Taherzadeh, “Anaerobic degradation of bioplastics : A review,” vol. 80, pp. 406–413, 2018.
[3]. Y. Deng and N. L. Thomas, “Blending poly(butylene succinate) with poly(lactic acid): Ductility and phase inversion effects,” Eur. Polym. J., vol. 71, pp. 534–546, 2015.
[4]. Y. Aso et al., “Continuous production of D-lactic acid from cellobiose in cell recycle fermentation using β-glucosidase-displaying Escherichia coli,” J. Biosci. Bioeng., vol. xx, no. xx, pp. 1–6, 2018.
[5]. S. Kumar, S. Singh, S. Senapati, A. P. Singh, B. Ray, and P. Maiti, “Controlled drug release through regulated biodegradation of poly(lactic acid) using inorganic salts,” Int. J. Biol. Macromol., vol. 104, pp. 487–497, 2017.
[6]. F. R. Beltrán, V. Lorenzo, J. Acosta, M. U. de la Orden, and J. Martínez Urreaga, “Effect of simulated mechanical recycling processes on the structure and properties of poly(lactic acid),” J. Environ. Manage., vol. 216, pp. 25–31, 2018.

[7]. J. I. Gug, J. Soule, B. Tan, and M. J. Sobkowicz, “Effects of chain-extending stabilizer on bioplastic poly(lactic acid)/polyamide blends compatibilized by reactive extrusion,” Polym. Degrad. Stab., vol. 153, pp. 118–129, 2018.

[8]. Y. Hu, W. A. Daoud, B. Fei, L. Chen, T. H. Kwan, and C. S. Ki Lin, “Efficient ZnO aqueous nanoparticle catalysed lactide synthesis for poly(lactic acid) fibre production from food waste,” J. Clean. Prod., vol. 165, pp. 157–167, 2017.

[9]. S. Lv, J. Gu, H. Tan, and Y. Zhang, “Enhanced durability of sustainable poly (lactic acid)-based composites with renewable starch and wood flour,” J. Clean. Prod., vol. 203, pp. 328–339, 2018.

[10]. H. F. Alharbi et al., “Fabrication of core-shell structured nanofibers of poly (lactic acid) and poly (vinyl alcohol) by coaxial electrospinning for tissue engineering,” Eur. Polym. J., vol. 98, pp. 483–491, 2018.

[11]. B. A. Khan, H. Na, V. Chevali, P. Warner, J. Zhu, and H. Wang, “Glycidyl methacrylate-compatibilized poly(lactic acid)/hemp hurd biocomposites: Processing, crystallization, and thermo-mechanical response,” J. Mater. Sci. Technol., vol. 34, no. 2, pp. 324–334, 2018.

[12]. H. Wu et al., “Green and facile surface modification of cellulose nanocrystal as the route to produce poly(lactic acid) nanocomposites with improved properties,” Carbohydr. Polym., vol. 197, no. June, pp. 204–214, 2018.

[13]. Y. Baimark, W. Rungseesantivanon, and N. Prakymoramas, “Improvement in melt flow property and flexibility of poly(L-lactide)-b-poly(ethylene glycol)-b-poly(L-lactide) by chain extension reaction for potential use as flexible bioplastics,” Mater. Des., vol. 154, pp. 73–80, 2018.

[14]. A. Sayadi, T. R. Neitzert, and G. Charles Clifton, “Influence of poly-lactic acid on the properties of perlite concrete,” Constr. Build. Mater., vol. 189, pp. 660–675, 2018.

[15]. F. Vilarinho, M. Andrade, G. G. Buonocore, M. Stanzione, M. F. Vaz, and A. Sanches Silva, “Monitoring lipid oxidation in a processed meat product packaged with nanocomposite poly(lactic acid) film,” Eur. Polym. J., vol. 98, no. November 2017, pp. 362–367, 2018.

[16]. A. Zubov and G. Sin, “Multiscale modeling of poly(lactic acid) production: From reaction conditions to rheology of polymer melt,” Chem. Eng. J., vol. 336, pp. 361–375, 2018.

[17]. K. Suganuma, H. Matsuda, H. N. Cheng, M. Iwai, R. Nonokawa, and T. Asakura, “NMR analysis and tacticity determination of poly(lactic acid) in C 5D5N,” Polym. Test., vol. 38, pp. 35–39, 2014.

[18]. D. Rohindra, K. Kuboyama, and T. Ougizawa, “Pressure dependence of equilibrium melting temperature of poly (lactic acid),” Polym. (United Kingdom), vol. 118, pp. 297–304, 2017.

[19]. M. Tesfaye, R. Patwa, A. Gupta, M. J. Kashyap, and V. Katiyar, “Recycling of poly (lactic acid)/silk based bionanocomposites films and its influence on thermal stability, crystallization kinetics, solution and melt rheology,” Int. J. Biol. Macromol., vol. 101, pp. 580–594, 2017.

[20]. B. Tawiah, B. Yu, W. Y. Cheung, S. Y. Chan, W. Yang, and B. Fei, “Synthesis and application of synergistic azo-boron-BPA / polydopamine as efficient flame retardant for poly(lactic acid),” Polym. Degrad. Stab., vol. 152, pp. 64–74, 2018.

[21]. T. H. Kwan, Y. Hu, and C. S. K. Lin, “Techno-economic analysis of a food waste valorisation process for lactic acid, lactide and poly(lactic acid) production,” J. Clean. Prod., vol. 181, pp. 72–87, 2018.

[22]. S. S. Karkhanis, N. M. Stark, R. C. Sabo, and L. M. Matuana, “Water vapor and oxygen barrier properties of extrusion-blown poly(lactic acid)/cellulose nanocrystals nanocomposite films,” Compos. Part A Appl. Sci. Manuf., vol. 114, no. August, pp. 204–211, 2018.