

Hybrid Polylactide Blends

Subjects: Biochemistry & Molecular Biology | Materials Science, Biomaterials

Contributor: Anna Kowalewska

Conformation of polylactide macromolecules can be adjusted by interactions with some specific additives (arylamides, hydrazides, 1,3:2,4-dibenzylidene-d-sorbitol, orotic acid, humic acids, fulvic acids, nanocellulose, and cyclodextrins) due to the formation of hydrogen bonds or host-guest complexes. This “soft templating” may enhance nucleation of polymer crystals and influence the properties of polylactide blends.

Keywords: polylactide ; composites ; crystallization ; supramolecular interactions ; hydrogen bonding ; host-guest complexes ; organic nucleators ; cyclodextrins ; nanocellulose ; humic acids

1. Introduction

Polylactide (PLA) is a biodegradable semi-crystalline polymer that has attracted enormous attention over recent years as a biocompatible and environment-friendly material ^{[1][2][3]}. It has been approved by the U.S. Food and Drug Administration for biomedical applications and contact with body fluids, e.g., as bioresorbable artificial ligaments or drug delivery systems ^[4]. PLA is also one of the most important thermoplastic materials for 3D printing ^[5]. It is easily processable, although its brittleness prevents tensile drawing. The tensile modulus and strength of neat PLA can be increased and the strain at break can be reduced when the polylactide matrix contains a significant amount of crystalline fraction ^[6]. The crystallinity degree also governs the barrier properties of polylactide ^[6]. The crystallization behaviour of polylactide has been extensively investigated (details can be found in comprehensive reviews, e.g., ^{[6][7][8]}). Two optically active forms (L and D) exist due to the presence of an asymmetric carbon atom in molecules of lactic acid. The commercially available PLA is usually rich in the L-structures, but is not isotactic. D-units that separate longer L-isotactic sequences in statistical copolymers disturb chain order and the morphology of PLA crystals.

In general, the type of crystal structure depends on the crystallization conditions. The most common orthorhombic α' - and α -crystals that have similar 10_3 helical chain conformations and belong to the same crystal system are formed in melt and solution crystallizations. The less ordered α' -form is obtained exclusively at crystallization temperatures below 100 °C, or as an admixture coexisting with the α -form, when PLA is crystallized isothermally at temperatures below 120 °C. The presence of α' crystals in PLA results in higher elongation at break but also lower modulus and barrier properties than those of samples containing more tightly packed α crystals. A less thermally stable β -form of a frustrated structure (three polylactide chains of 3_1 helical conformation are randomly oriented up and down in a trigonal cell) is obtained by stretching the α -form at high draw ratios in the hot-drawing of melt- or solution-spun fibres. The γ -form was obtained by the epitaxial crystallization of PLA on hexamethylbenzene. In this form two polymer chains of 3_1 helical conformation are oriented antiparallel in the crystal cell.

2. Applications and Development

Considerable attention was given to the improvement of crystallization kinetics (nucleation and crystal growth) that can be enhanced by nucleators and/or plasticizers. Numerous potential nucleating systems have been examined in the literature, including “green” nucleating agents. PLA-based polymer composites and nanocomposites containing nanoclays ^{[9][10][11]}, nanosilicas ^{[12][13]}, carbon nanotubes ^{[14][15]}, or graphene ^[16] are well known. Another class of additives for polylactide that can improve its crystallization rate are species that exploit supramolecular phenomena, e.g., hydrogen bonding or host-guest effects, to interact with PLA macromolecules (“soft templating”). Hydrogen bonding is also important for the formation of poly(l-lactide)/poly(d-lactide) (PLLA/PDLA) stereocomplex structures (SC) ^{[17][18][19][20]}. The specific C-H...O=C interactions between the paired stereoisomeric PLLA and PDLA chains play a very important role in the formation of SC crystals. It was found that the racemic ($3_2/3_1$) helical conformation of the pair of macromolecules starts to emerge in the melt of a racemic blend, and the formed structures subsequently act as nucleating sites upon cooling ^[21]. Thus, the conformation of the polylactide chains may be changed by intermolecular interactions with neighbouring macromolecules. It means that the crystallization of the PLA matrix can also be adjusted by hydrogen bonding species, even before the true

crystal nuclei emerge. Hydrogen bonding between polylactide and nucleating agents has been postulated, e.g., for PLA blends with amino acids or poly(amino acids) [22], carbon nanotubes [23], phthalimide [24], bisurea derivatives [25], or d-gluconic acid derivatives [26]. PLA was also modified with macromolecular nucleators, such as linear polysilsesquioxanes [27][28][29] or their cyclosiloxane analogues [30] with side substituents acting as donors/acceptors of hydrogen bonds ($\text{-OH}\cdots\text{O}=\text{C-}$; $\text{-COOH}\cdots\text{O}=\text{C-}$; and $\text{-C-F}\cdots\text{H}_3\text{C-}$) to/from the polyester backbone.

Extremely efficient nucleating systems are based on arylamides and arylhydrazides that may self-organize in the polymer melt. Unfortunately, not all supramolecular nucleators are biodegradable, bioabsorbable, or nontoxic. The potential problems with some of those organic compounds can be a significant concern in the biomedical field. Therefore, polylactide matrices have been also blended with harmless biobased nucleating agents (e.g., orotic acid, humic acids, fulvic acids, nanocellulose, and cyclodextrins). The key feature of those additives is their capability for "soft templating". In this review, the research progress on PLA nanocomposites containing both groups of nucleating agents has been evaluated in the context of their biomedical applicability.

3. Conclusions

Polylactide nanocomposites, composites, and blends containing specific organic compounds (arylamides and arylhydrazides, 1,3:2,4-dibenzylidene-d-sorbitol, or orotic acid), humic and fulvic acids, nanocellulose, and cyclodextrins have been reviewed. Supramolecular interactions operating in those blends play a very important role in the properties of those novel hybrid materials. They differ from other PLA-based hybrids containing inorganic additives or composites of PLA and graphene or carbon nanotubes.

Aryl nucleators containing amide or hydrazide linkages are capable of crystallization in the polylactide melt. The formation of nanofibrils/nano-objects upon the self-organization of these moieties exploits two recognition motifs: hydrogen bonds and π - π interactions between the molecules taking part in the formation of supramolecular structures and intermolecular hydrogen bonds linking those formations and the polyester backbones. Macromolecular nucleators (humic/fulvic acids and nanocellulose) not only help in the formation of crystal nuclei but also improve the mechanical properties of the PLA. Host-guest effects in blends containing inclusion complexes of PLA and ($\alpha/\beta/\gamma$)-cyclodextrins change the mobility of the polyester chains. The formed structures may also enhance the polylactide crystal growth, but they have much larger potential. Treading cyclodextrins onto PLLA backbones may be used for the design of biocompatible molecular rotors. Interestingly, chiral recognition was observed for the PLLA/PDLA mixtures and α -CD.

The performance of PLA can be improved because of those specific interactions that modify the organization of the polymer matrix. The "soft templating" may change the conformation of segments in PLA chains and influence the nucleation of polymer crystals, thus enormously enhancing the crystallization process. Despite the templating, the type of crystal structure is not changed, except that the well-organized α -crystals are more easily formed in such systems. The influence of supramolecular nucleators is of exceptional importance, as the crystallinity of PLA plays a significant role in its mechanical and barrier properties, biodegradability, and thermal stability. Many supramolecular systems described in this review are biocompatible and can be used for biomedical purposes.

References

1. Gross, R.A.; Kalra, B. Biodegradable polymers for the environment. *Science* 2002, 297, 803–807.
2. Nair, L.S.; Laurencin, C.T. Biodegradable polymers as biomaterials. *Progr. Polym. Sci.* 2007, 32, 762–798.
3. Lasprilla, A.J.R.; Martinez, G.A.R.; Lunelli, B.H.; Jardini, A.L.; Maciel Filho, R. Poly-lactic acid synthesis for application in biomedical devices—A review. *Biotechn. Adv.* 2012, 30, 321–328.
4. Tyler, B.; Gullotti, D.; Mangraviti, A.; Utsuki, T.; Brem, H. Polylactic acid (PLA) controlled delivery carriers for biomedical applications. *Adv. Drug Deliv. Rev.* 2016, 107, 163–175.
5. Poh, P.S.P.; Chhaya, M.P.; Wunner, F.M.; De-Juan-Pardo, E.M.; Schilling, A.F.; Schantz, J.-T.; van Griensven, M.; Hutmacher, D.W. Polylactides in additive biomanufacturing. *Adv. Drug Deliv. Rev.* 2016, 107, 228–246.
6. Saeidlou, S.; Huneault, M.A.; Li, H.; Park, C.B. Poly(lactic acid) crystallization. *Progr. Polym. Sci.* 2012, 37, 1657–1677.
7. Liu, G.; Zhang, X.; Wang, D. Tailoring crystallization: Towards high-performance poly(lactic acid). *Adv. Mater.* 2014, 26, 6905–6911.
8. Lan, Q.; Li, Y. Mesophase-Mediated Crystallization of Poly(l-lactide): Deterministic pathways to nanostructured morphology and superstructure control. *Macromolecules* 2016, 49, 7387–7399.

9. Paspali, A.; Bao, Y.; Gawne, D.T.; Piester, F.; Reinelt, S. The influence of nanostructure on the mechanical properties of 3D printed polylactide/nanoclay composites. *Compos. B Eng.* 2018, 152, 160–168.
10. Mihai, M.; Ton-That, M.-T. Novel bio-nanocomposite hybrids made from polylactide/nanoclay nanocomposites and short flax fibers. *J. Compos. Mater.* 2019, 32, 3–28.
11. Rojas-Lema, S.; Quiles-Carrillo, L.; Garcia-Garcia, D.; Melendez-Rodriguez, B.; Balart, R.; Torres-Giner, S. Tailoring the properties of thermo-compressed polylactide films for food packaging applications by individual and combined additions of lactic acid oligomer and halloysite nanotubes. *Molecules* 2020, 25, 1976.
12. Odent, J.; Raquez, J.-M.; Thomassin, J.-M.; Gloaguen, J.-M.; Lauro, F.; Jérôme, C.; Lefebvre, J.-M.; Dubois, P. Mechanistic insights on nanosilica self-networking inducing ultra-toughness of rubber-modified polylactide-based materials. *Nanocomposites* 2015, 1, 113–125.
13. Hao, X.; Kaschta, J.; Schubert, D.W. Viscous and elastic properties of polylactide melts filled with silica particles: Effect of particle size and concentration. *Composites B Eng* 2016, 89, 44–53.
14. Lee, J.H.; Park, S.H.; Kim, S.H.; Ito, H. Replication and surface properties of micro injection molded PLA/MWCNT nanocomposites. *Polym. Test.* 2020, 83, 106321.
15. He, S.; Bai, H.; Bai, D.; Ju, Y.; Zhang, Q.; Fu, Q. A promising strategy for fabricating high-performance stereocomplex-type polylactide products via carbon nanotubes-assisted low-temperature sintering. *Polymer* 2019, 162, 50–57.
16. Prasitnok, K.; In-noi, O. Functionalized graphenes as nanofillers for polylactide: Molecular dynamics simulation study. *Polym. Composites* 2020, 41, 294–305.
17. Tsui, H. Poly(lactide) stereocomplexes: Formation, structure, properties, degradation, and applications. *Macromol. Biosci.* 2005, 5, 569–597.
18. Tsuji, H. Poly(lactic acid) stereocomplexes: A decade of progress. *Adv. Drug Deliv. Rev.* 2016, 107, 97–135.
19. Jiang, L.; Shen, T.; Xu, P.; Zhao, X.; Li, X.; Dong, W.; Ma, P.; Chen, M. Crystallization modification of poly(lactide) by using nucleating agents and stereocomplexation. *e-Polymers* 2016, 16, 1–13.
20. Michalski, A.; Makowski, T.; Biedroń, T.; Brzeziński, M.; Biela, T. Controlling polylactide stereocomplex (sc-PLA) self-assembly: From microspheres to nanoparticles. *Polymer* 2016, 90, 242–248.
21. Yang, C.-F.; Huang, Y.-F.; Ruan, J.; Su, A.-C. Extensive development of precursory helical pairs prior to formation of stereocomplex crystals in racemic polylactide melt mixture. *Macromolecules* 2012, 45, 872–878.
22. Carbone, M.J.; Vanhalle, M.; Goderis, B.; Van Puyvelde, P. Amino acids and poly(amino acids) as nucleating agents for poly(lactic acid). *J. Polym. Eng.* 2015, 35, 169–180.
23. Zhou, Y.; Lei, L.; Yang, B.; Li, J.; Ren, J. Preparation and characterization of polylactic acid (PLA) carbon nanotube nanocomposites. *Polym. Test.* 2018, 68, 34–38.
24. He, D.; Wang, Y.; Shao, C.; Zheng, G.; Li, Q.; Shen, C. Effect of phthalimide as an efficient nucleating agent on the crystallization kinetics of poly(lactic acid). *Polym. Test.* 2013, 32, 1088–1093.
25. Xu, Y.; Wu, L. Synthesis of organic bisurea compounds and their roles as crystallization nucleating agents of poly(L-lactic acid). *Eur. Polym. J.* 2013, 49, 865–872.
26. Zheng, X.; Luo, H.; Chen, S.; Zhang, B.; Sun, B.; Zhu, M.-F.; Zhang, B.; Ren, X.-K.; Song, J. Conformation variation induced crystallization enhancement of poly(L-lactic acid) by gluconic derivatives. *Cryst. Growth Des.* 2020, 20, 653–660.
27. Herc, A.S.; Lewiński, P.; Kaźmierski, S.; Bojda, J.; Kowalewska, A. Hybrid SC-polylactide/poly(silsesquioxane) blends of improved thermal stability. *Thermochim. Acta* 2020, 687, 178592.
28. Herc, A.S.; Bojda, J.; Nowacka, M.; Lewiński, P.; Maniukiewicz, W.; Piórkowska, E.; Kowalewska, A. Crystallization, structure and properties of polylactide/ladder poly(silsesquioxane) blends. *Polymer* 2020, 201, 122563.
29. Kowalewska, A.; Herc, A.S.; Bojda, J.; Palusiak, M.; Markiewicz, E.; Ławniczak, P.; Nowacka, M.; Sołtysiak, J.; Różański, A.; Piórkowska, E. Supramolecular interactions involving fluoroaryl groups in hybrid blends of ladder polysilsesquioxanes and polylactide. *Polymer Testing*. (under review).
30. Herc, A.S.; Włodarska, M.; Nowacka, M.; Bojda, J.; Szymański, W.; Kowalewska, A. Supramolecular interactions between polylactide and model cyclosiloxanes with hydrogen bonding-capable functional groups. *eXPRESS Polym. Lett.* 2020, 14, 134–153.

