TURI
TOXICS USE REDUCTION INSTITUTE
University of Massachusetts Lowell

Preliminary Studies on the Plasticization of Polylactic Acid

The Toxics Use Reduction Institute
Academic Research Program

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Roger Boggs, Director of Research, Center for Green Chemistry
Rahul Garhwal, MS Candidate, Department of Biological Sciences
Daniel Brooks, BS Candidate, Plastics Engineering
University of Massachusetts Lowell

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, 600 Suffolk Street, Wannalancit Mills – 5th Floor, Lowell, MA 01854

Academic Research Program

The Academic Research Program is a project of the Toxics Use Reduction Institute (TURI) at the University of Massachusetts Lowell.

The program taps the research capabilities of the University of Massachusetts to advance the investigation, development and evaluation of sustainable technologies that are environmentally, occupationally and economically sound. The program provides research funding to UMass faculty from all campuses, annually, on a competitive basis and encourages faculty/industry partnerships and cross-campus collaboration. Industry partners provide guidance, propose applications for new technologies and, in some cases, evaluate and/or adopt processes and technologies resulting from research.

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Introduction

Polylactic acid was first prepared in 1932 by Wallace Carothers at Dupont who developed a condensation process of lactic acid in various solvents under high vacuum. Carothers abandoned this polymer (PLA) as being too brittle for fibers and textile applications and moved on to prepare and develop nylon which was quickly commercialized. After further refinements, a patent for PLA was obtained by Dupont in 1954 but large scale commercial development was to wait for many decades.

The United States does not have abundant oil reserves. It does have large agricultural resources. In addition, there is a great desire to develop and use biodegradable plastics. PLA, a thermoplastic, is classified as GRAS (generally recognized as safe) by the FDA.

The goal of the Toxic Use Reduction Institute is to reduce and ultimately eliminate the use of toxic chemicals in the Commonwealth. This project was undertaken to examine the use of biodegradable additives to PLA to modify its properties such that it might eventually be considered as an alternative to certain applications where polyvinyl chloride (PVC) is presently used. Not only is PVC an undesirable oil based plastic, it is often plasticized with fugitive phthalates.

PLA is a relatively difficult thermoplastic with which to work. It is hydroscopic and readily absorbs moisture.[1] In the melt phase this results in the hydrolysis of PLA and a change in the mechanical properties and the quality of the final polymer is compromised. PLA can be hydrolyzed back to lactic acid and repolymerized.

Process, Results and Discussion

It was decided early on to limit the amount of PLA used in this study to reduce the creation of waste, a principal of Green Chemistry. For this reason it was decided to evaluate a series of potential plasticizers by casting films from solvent.[2-4] We encountered a great deal of difficulty in obtaining samples of PLA from commercial sources. This made our solvent casting strategy even more reasonable as the first step in evaluating additives.

We selected the following additives to screen: myristic acid, sebacic acid, palmitic acid, linseed oil, Vikoflex 7190 (epoxidized linseed oil) and Vikoflex 7170 (epoxidized soybean oil). Our methodology was to find a solvent in which PLA was soluble and then to dissolve the additive in the same solvent. These two individually prepared solutions would then be mixed and allowed to evaporate to cast a film of PLA and the additive. We first examined acetone as a solvent but found that we could not dissolve the PLA. We tried a number of methods to crush

or grind the PLA pellets to increase the surface area so as to facilitate dissolution. These efforts failed to enhance the process of dissolving the PLA. In fact, the only solvent which we found to dissolve an appreciable concentration of PLA on a weight/weight basis was chloroform. From a basic science view point, this was a very good solvent in that the literature revealed previous work in PLA films cast from chloroform. In this manner, if we worked carefully, our results could be referenced to previous work at various research universities and our work could be more broadly used by industry in the Commonwealth as a reliable data set.

Of the additives above, linseed oil and the two Vikoflexes gave plasticized films of PLA from chloroform. To be a good plasticizer, the additive must remain in the PLA, that is it must remain dissolved. After allowing our films to stand for several days, it was quickly discovered that the raw linseed oil was not retained in the PLA and formed an oily surface on the cast films.

At this point, our results narrowed the work to a more detailed study of the two Vikoflexes and it was our intent to measure film properties. We first had to bring some precision to our film casting at various loading levels of the two Vikoflexes and we also had to learn how to measure tensile strength and other basic plastic measurements so as to characterize the effects of the levels of plasticizers. Furthermore, we had to establish some rigor with drying the film samples to assure the retained solvent content of the films.

Before doing this however, we stepped back to carefully screen the TURI Cleaner Solution Database.[5] It is of course always better to use less toxic materials whenever possible. Unfortunately, despite a careful examination of this list of solvents we were limited to using chloroform. Our laboratory studies used limited volumes of chloroform and we handled this solvent with the respect it requires. Once again, we would emphasize that casting films from chloroform greatly reduces the amount of PLA waste and will eventually allow our results to be referenced and extended on scientific work in the literature.

In the final stage of this preliminary work, we looked at the level of Vikoflexes plasticizers in PLA and the impact on the film properties. We prepared the films on a volume of solids basis such that all films cast in the same container would provide a film of the same thickness. Experimental results are available in the Appendix.

Conclusions

On the 75th anniversary of its first preparation, polylactic acid has become a widely popular biodegradable thermoplastic. While now in commercial use, it remains a very difficult plastic resin to manufacture, handle and to recycle. The use of additives will continue to greatly expand the properties of polylactic acid and its applications in the coming years. Vikoflex 7190 and 7170 are two attractive plasticizers to be studied more closely. We have established a reliable laboratory method for casting films which will permit formulations to be evaluated quickly with minimum waste.

Acknowledgements

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Notes

1. NatureWorks was once owned by Cargill which was once a joint venture with Dow Chemical. A vast amount of technical and marketing data is available on their website: http://www.natureworksllc.com/product-and-applications/natureworks-polymer/technical-resources.aspx

2. T. Freier, C. Kunze, K.P. Schmitz, "Solvent Removal from Solution Cast Films of Biodegradable Polymers," Journal of Materials Science Letters **20**, *2001*, 1929.

3. J.W. Rhim, A.K. Mohanty, S.P. Singh, P.K.W. Ng "Effect of the Processing Methods on the Performance of Polylactide Films: Thermocompression versus Solvent Casting," Journal of Applied Polymer Science, **101**, *2006*, 3736.

4. N. Ljungberg and B. Wesslen, "Preparation and Properties of Plasticized Polylactic acid Films," Biomacromolecules, **6**, *2005*, 1789.

5. This work was done with J. Marshall of TURI