4-24-2014

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Recommended Citation

Pickthorn, Sean, "Classification of biorenewable multiblock copolymers" (2014). *Celebrating Scholarship & Creativity Day*. 25.
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Classification of Biorenewable Multiblock Copolymers

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Recent advances in polymer production sciences have led to an increase in research in sustainable practices. Our efforts intended to produce a toughened biorenewable multiblock copolymer. Polylactide has been noted to be produced by sustainable practices but is limited because of the fragile structure. To improve the brittle behavior of polylactide, preparation of polylactide-b-polybutadiene-b-polylactide multiblock copolymers were synthesized with a fixed weight of dihydroxyl polybutadiene (~3000 and ~2000g/mole series) and variable volume percent (50-90%) of both semicrystalline poly(L-lactide) and amorphous poly(D,L-lactide). Producing a multiblock copolymer intended to strengthen the mechanical properties by bridging and gapping over several domains. Initially, triblock polymers were catalyzed with a ring opening polymerization and characterized. Toluene diisocyanate (TDI) and terephtaloyl chloride (TCL) were used to couple the triblock copolymers to form multiblock structures. Characterization of these products was accomplished by differential scanning calorimetry, small angle X-ray scattering, ^{1}H-NMR spectroscopy, size exclusion chromatography, dynamic mechanical analysis, and tensile testing, leading to an extensive set of thermal and mechanical properties of both the triblock and multiblock copolymers. The data collected indicated a controlled product with a clear enhancement of mechanical properties of polylactide. Trends were associated with the weight percent of polylactide and this can be used in future work as we explore other aspects of this material. This research can be continued by experimenting with other blending options, measuring other aspects of the toughness of the material, and investigating other coupling agents to initiate the multiblock synthesis. *[This research was supported by funding from the NSF, awarded to the Center for Sustainable Polymers, University of Minnesota, Minneapolis, MN]*

Introduction

Sustainable polymers are the materials which are bio-based, biodegradable, or both. There are two main advantages of sustainable polymers compared to conventional polymers: They save fossil resources and reduce greenhouse gas emissions.[1] Especially in the present day state of earth, we need to be conscious about the long term effects of the chemistry that we have the capabilities to perform. One example is Polyethylene being used in most high density and high impact polymers, as well as thin films. Polyethylene is, unfortunately, derived from unsustainable sources, and is costly and difficult to recycle into a re-moldable form of polyethylene. With that being said, efforts have been focused on ways that we can make our current processes greener, or use bio-derived and biodegradable sources to lessen our long term impact on the environment. Polylactide is a representative sustainable polymer, as it is procured from corn and is also biodegradable.[2] It is currently in use for small disposable cups, medical devices, and packaging where the homopolymer is useful but unable to withstand high impacts or temperatures. The downside, however, is it currently has a crucial limitation because of its extremely brittle mechanical behavior when subject to sstronger forces.[3] To enhance the tough mechanical properties, multiblock copolymers with polylactide and polybutadiene were investigated due to the likely event of crossing-over and bridging between respective matrixes. Multiblock copolymers containing a large number of blocks are expected to have unique morphologies and mechanical properties relative to conventional triblock copolymers. [4-6]

To investigate the effects of adding brittle components to a mutiblock, two different stereochemistries were used for this analysis. Namely D,L-lactide and L-lactide. D,L-lactide holds a more amorphous structure whereas L-lactide is more semicrystalline.[7] Varying stoichiometric amounts of lactide was used to create a different ratio of lactide to polybutadiene in the ABA triblock prepolymers. The ratio ranged from 20 to 80% lactide.

The starting triblock prepolymers, denoted in this work as LBL-triblocks (D,L-lactide-*b*-butadiene-*b*-lactide) and (L-lactide-*b*-butadiene-*b*-lactide), were synthesized using a ring opening polymerization (ROP). A summary of the overall reaction scheme is shown in Figure 1. The nomenclature for the triblocks is:

LBL-(stereochemistry used)(weight percent lactide)
Ex: LBL-DL50

The LBL-triblocks were further polymerized to create multiblock copolymers, denoted as mLBL-DL or mLBL-L [Poly(D,L-lactide-*b*-butadiene) and poly(L-lactide-*b*-butadiene)].

Ex: mLBL-DL50 These multiblock copolymers, created from starting triblocks with a differing ratio of lactide and butadiene, were then analyzed to observe the rigidity and strength trends.

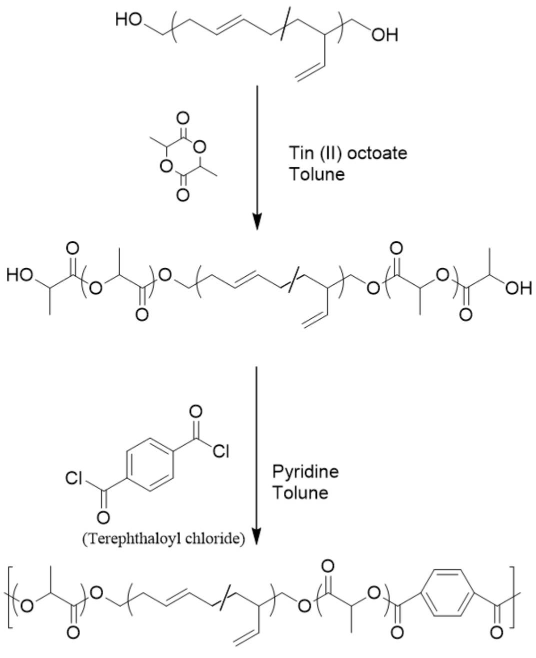


Figure 1. Synthetic scheme of mLBL multiblock copolymers. First step involves the ring opening polymerization (ROP) of D,L or L-lactide from a dihydroxyl terminated polybutadiene macroinitiator. This was followed by a polycondensation reaction with terephthaloyl chloride (TCl)

Experimental Section

Synthesis and Characterization of LBL-triblocks

Synthesis of multiblock copolymers first required the synthesis of poly(D,L-lactide-*b*-butadiene-*b*- D,L-lactide) (LBL-DL) and poly(L-lactide-*b*-butadiene-*b*- L-lactide) (LBL-L) triblocks. The methods were adapted from a combination of previous studies[8-9] to form the LBL-triblocks and this was initiated with a commercially available polybutadiene (Kresol), of which we used two distinct molecular weights (M_N=3300g/mol and 2200g/mol). The polybutadiene was weighed out in a pressure vessel and was slowly stirred and connected to a vacuum line overnight. They were then transferred to an argon glovebox where tin (II) octoate and the appropriate amount of D,L or L-lactide were added. The vessel was then sealed and transferred to a hot oil bath at 70^{O}C and stirred for 1 hour. Then the bath was ramped to 110^{O}C and continued to stir for 3 hours. The vessel was then cooled to room temperature and the polymer was precipitated in methanol. It was then collected and dried under vacuum to be characterized using a combination of ^{1}H NMR spectroscopy, SEC, and DSC.

Synthesis of Multiblock Copolymers

The triblock prepolymers were further synthesized into the final Multiblock copolymers by using terephthaloyl chloride (TCl). The reaction with TCl showed better coupling efficiency compared to previously done reaction trials. The specific LBL-triblock polymer was dried overnight in a pressure vessel connected to a vacuum line. In an argon glovebox, the vessel was filled with a stoiciometrically appropriate amount of terephthaloyl chloride (TCl), pyridine, and toluene. The vessels were sealed, removed and stirred at 100^{O}C for 12 hours and then cooled to room temperature. Any formed salts were removed via filter paper and the multiplock polymers were precipitated and dried by the same procedure as the triblock polymers.

Reaction Validation and Molecular Weight Analysis

Precise molecular weights for the triblocks were obtained to ensure adequate polymerization. This was done by using H^1NMR Spectroscopy to identify the precise starting and ending molecular weights of the samples.[10] First, the samples were dissolved in deuterated chloroform ($CDCl_3$). The examination was conducted on a Varion Inova 500 at room temperature and analyzed by MestReNova software. Characteristic peaks were also analyzed to confirm reaction completion.

Molecular Weight Comparison

Once the LBL-triblocks were verified for reaction completion, they were put through automated size exclusion chromatography (SEC) testing to be able to compare relative molecular weights based on polystyrene standards. The testing was executed with THF at room temperature through three 5 mm Phenomenex Phenogel columns.

Differential Scanning Calorimetry (DSC)

Triblock samples were subjected to temperature analysis. This was done using DSC testing to verify the T_C and T_M, depending on the chirality of the lactide, to be used as reference in the tensile testing melting process. Also, this test would give insight into the morphology and order of the polymer matrix. The samples were loaded in aluminum hermetically sealed DSC round pans. The procedure for all tested materials would heat the sample to 125°C, then cool to -115°C, and reheat to 125°C at a rate of 10°C/minute.

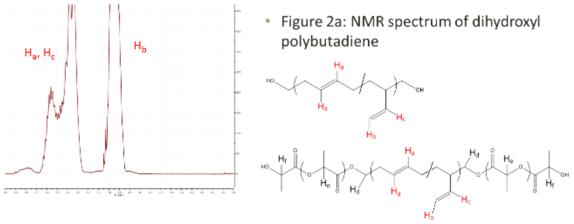
Tensile Testing

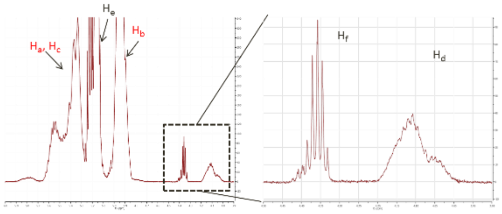
The final product multiblocks were ultimately subjected to mechanical testing on a RSA G2 Solids Analyzer. Polymers were first molded into a thin film using a hot polymer press and the T_C or T_M to ensure uniform polymer films of approximately 0.2 mm thickness. The films were then cut into dog-bone shaped objects, to be used in the RSA G2, by a punch and arbor press. The dimensions were ideally a length of 25mm, gauge length of 6mm, cross sectional area of 3.2mm, and thickness of .2mm. These specific dimensions were put into an analysis software on the RSA G2, and it was used to measure the Young's modulus of the specific multiblock copolymer. The results from this testing were compiled into a graph for ease of viewing across a diverse sample range.

Results and Discussion

LBL-Triblock Synthesis and Classification

The main concern for this segment of the research was the development of a homogenous polymer with a low polydispersity and a high efficiency in the polymerization. The NMR data was used to analytically observe the degree of polymerization by recognition of the respective peaks and using ratios to determine the completion of the polymerization. First, the starting polybutadiene was analyzed first to measure a precise weight to be used in future analysis. The formed LBL-triblocks were then analyzed with respect to the starting weight of polybutadiene to determine the weight percent of polylactide.


- Figure 2a: NMR spectrum of dihydroxyl polybutadiene



- Figure 2b: NMR spectrum of LBL2-DL60

We found approximately a 70% completion of the polymerization, with a slightly lower result from the samples attempting a higher percentage of lactide. This analysis was also used to confirm the specific sample consisted of the desired percentage of lactide to butadiene. The end hydroxyl groups were also tested with Trifluoroacetic anhydride (TFAA) to ensure that they were clean and reactive for the future multiblock polymerization step.

Molecular Weight Comparison

The next characterization was the continuous flow SEC which measured the molecular weight relative to polystyrene standards. This was simply used to measure the polydispersity of the sample, and as another verification step to measure the extent of polymerization completion in the triblocks and multiblocks, and to be used as a benchmark to compare across our samples of the triblocks and future multiblocks. Using NMR analysis to observe the extent of multiblock completion would result in a complexity of peaks with difficult and imprecise values. The original triblock SEC data was compared to the final multiblock data to easily observe the extent of reaction.

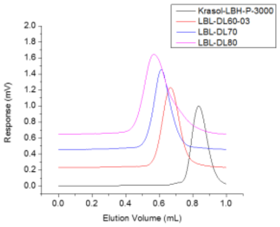


Figure 3a: SEC comparison of the starting polybutadiene and LBL triblocks

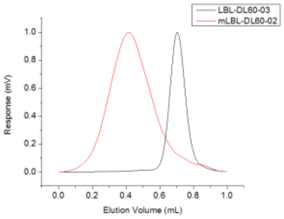


Figure 3b: SEC comparison of LBL-DL60-03 and its resulting multiblock

We observed a low polydispersity for our starting triblock polymers which indicated good starting material for the synthesis of multiblocks, and also noted the differences in molecular weight across samples with different weight percent polylactide. The polydispersity of the multiblocks was suspected to increase, and was confirmed by this data. It is clear that the multiblocks were able to significantly increase their molecular weight from their triblock counterparts. This shows that the multiblock reaction was successful at significantly increasing the molecular weight.

Differential Scanning Calorimetry (DSC)

DSC was used to identify some of the characteristics of the triblock polymers and their inherent structure, but was mainly used for analysis of the multiblock copolymers and their T_g and T_c for L-lactide samples, T_m for DL-lactide samples. Due to the differences in stereochemistry, there are alterations in solid structure. L-lactide has a more crystalline microstructure and therefore analysis of T_g and T_c must be pursued, and DL-lactide has an amorphous microstructure meaning that a T_c is not present. The T_g and T_m will be used when pressing the material to insure that the material melts and is able to fill into a thin film, but does not heat to the point of degredation.[11]

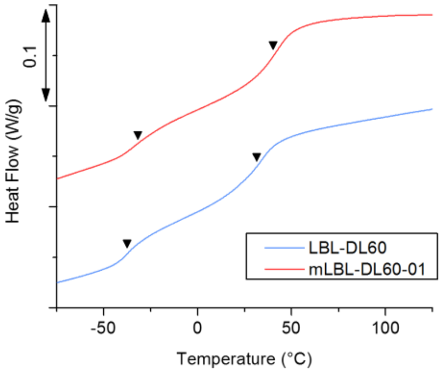


Figure 4: DSC data for a variety of triblocks and their respective multiblocks

Tensile Testing

The final, and most significant test was to identify the toughness and elasticity of the multiblock polymer.[12] The data taken from the previous DSC identified the optimum temperature for pressing into a thin film, and these films were punched with a dog-bone shaped cutout to be used in the tensile testing machine. The samples were loaded and the Young's modulus was measured to give results in a graphical form of Stress vs. Strain. Looking at the slope of the response line gives insight into the modulus of the material and can be compared to other polymers. The area underneath the curve is used to measure the toughness of the product.

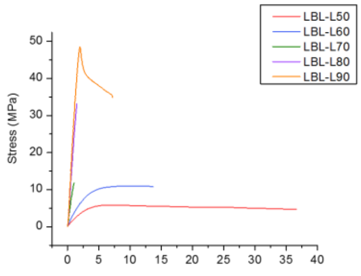


Figure 5a: LBL-L tensile testing

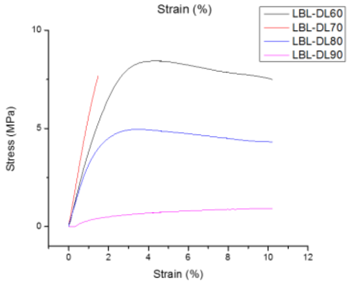


Figure 5b: LBL-DL tensile testing

In the figures 5a and 5b, a comparison between the respective triblocks is drawn. It shows a similar modulus, but differing strain at break based on the stereoisomer of lactide used. Also, the weight percent of lactide made a large difference in both the modulus and strain at break. It can be seen that both materials were successful in achieving some degree of toughness.

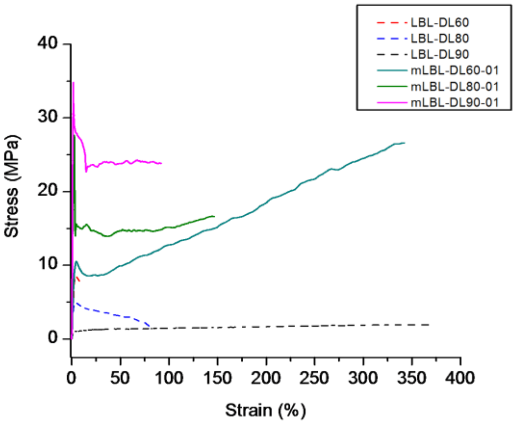


Figure 6: LBL-DL tensile testing and the resulting multiblocks

It is again, clear in the multiblocks, that the differing percent of lactide produced a variety of responses. In the limited time allotted to work on this project, we were just able to finish the results for the 3000g/mol molecular weight polybutadiene, so that is the only official result recorded in this article, but further results can be found in the full journal article.[13] The multiblocks were also able to significantly increase their toughness and their strain at break to produce a significant result. Again, varying dependant on the amount of lactide used.

Other Parameters

Other procedures were conducted by the graduate students in the research group, but helped to identify the wholeness of the material produced and the completion of the intial criteria set forth. These procedures included Small Angle X-ray Scattering (SAXS)[14], which helps to determine the morphology of the polymers synthesized, and rheology to show the order to disorder transition temperature (TODT).

Conclusion and Future Work

The main goal of our project was to synthesize tough and biorenewable multiblock copolymers and I believe it is clear that we were able to enhance the mechanical properties of lactide. Some of our prepared multiblocks are tough, as indicated by the tensile testing. In fact, some were unable to be measured by the RSA-G2 because of the force limit. Even multiblocks with high volume fraction of lactide, a mechanically brittle material, were shown to be tough with a highly increased modulus. Especially noting the increase in modulus as we synthesized from polymer subunits to triblocks to multiblocks. There is still several areas of future action, however, such as continuing to categorize additional areas for the 2000 series. We also ran into problems creating some thin films for our L-lactide derived multiblock series, so solvent casting methods were being pursued.[15-16] We also only reported results for each sample in its own weight percent category. It would be interesting to mix the triblocks and attempt a synthesis of a hybrid multiblock. Perhaps blending a high modulous and a high strain at break triblock to create a polymer that displays even more toughness.

Aknowledgements

A special thanks to Frank Bates, the faculty advisor of the department and Intaek Lee and Tessie Panthani, the graduate students who allowed me to work with them. This was a fulfilling opportunity that challenged me and helped me understand the field of research. I also want to thank the Center for Sustainable Polymers, the department that allowed this research opportunity. This research was supported by funding from the NSF, awarded to the Center for Sustainable Polymers, University of Minnesota, Minneapolis, MN.

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