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Mechanical Properties ofPoly Lactic Acid:An Accelerated Destructive Degradation Test

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ABSTRACT : *Research in renewable products with the potential to replace fossilized matter as raw materials for energy and materials use is at the forefront of modern science and engineering. Materials (i.e., Poly lactic acid) have been researched by industry and academia showing great interest in the degradation process typically represented by degradation models. The accuracy of these models is a complex task to accomplish. It requires the quantification of the degradation rate of the materials with different variables. In this paper, tensile testing is used to characterize the lifetime of PLA material. Over 60 specimens were manufactured under ASTM standard, followed by 2,000 hours of accelerated destructive degradation testing. The results demonstratea significant statistical effectin the mechanical properties of the material. The variables that made adifference on the degradation rate weretemperature, humidity rate, UV light.*

KEYWORDS –*PLA, accelerated destructive degradation, repeated measures, tensile*

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I. INTRODUCTION

Poly lactic acid (PLA) is a bio-based biodegradable polymer that can be produced from renewable resources including starch from corn and potatoes, sugar from beets, and sugar cane among others. PLA and its copolymers have attracted significant attention in environmental, biomedical, and pharmaceutical applications and as alternatives to petrol-based polymers. Packaging is the primary application as an alternative to petrol-based polymers [1]. Most commercially available poly L-lactic acid (PLLA) materials are used for automobile interiors, electronics chassis, and other consumable products. However, some applications require a higher mechanical performance and resistance to hydrolytic/thermal degradation.Poly lactic acid is a well-behaved thermoplastic with a reasonable shelf life for most single-use packaging applications and, when disposed properly, it will hydrolyze to harmless, natural products. It could be a technical and economic solution to the problem of the eventual disposal of the very large amount of plastic packaging used in this U.S.A [2].

PLA has become one the most attractive biodegradable polymer in the past 20 years. Biotechnological lactobacillus process is the most common process to obtain PLA. High strength and thermos-plasticity allow this biopolymer to be used to manufacture a great variety of products. This material is easily processed by traditional techniques including injection molding, blow molding, extrusion, and thermoforming. Gupta & Kumar commented that depending on the use of PLA, most people prefer to use PLA for its low molecular weight to shorten degradation [3]. Garlotta [2] described a complete study of PLA, mechanical properties, analysis of different variables (i.e., molecular weight). Furthermore, PLA degradation process depends on several factors such as molecular weight changes observed under different crystallizationtemperature.PLA application in manufacturing process has increased in the last years, more specifically in the design and manufacturing of short-life-time products and waste disposal bags. This application requires to have a specific time of degradation of PLA. Therefore, various authors havecharacterized and studied PLA under three different types ofdegradation:photodegradation, hydrolysis, and thermal degradations with the purpose of determining lifetime of PLA [4].

It is well known that some polymers and composites based on polymeric matrix experience photodegradation, this degradation usually comes from the combination of heat, light, oxygen and water. The level of degradation of a composite depends on its ability to absorb UV light. The presence of catalyst residues (hydro peroxide and carbonyl groups) are responsible for UV light absorption, which are present in the polymer manufacturing process [5].

Another type of degradation that is known to affect biopolymers is thermal degradation. Different kinds of degradation reactions may be induced thermally: depolymerization and substituent reactions. Depolymerization happens when the main polymer chain bonebreaks into smaller chains until monomer or indistinguishable material remains. In substituent reactions, a part is attached to the main polymer chain bone and this attachment alters the chemical nature of the material. Moreover, organic polymers burn if the temperature is high enough. Theirdegradation process involves the oxidation of molecules as part of the depolymerization of the material. Exposure to temperature, the polymers undergo to a certain level of degradation rate, no matter the stage of the material, common results of degradation by temperature are loss of weight and color changes [6]. In addition, when degradation by hydrolysis takes place, long polymer PLA chains are converted into short ones, subsequently, oligomers and monomers are created as a result of the water solubility of the polymer [7].

This paper presents a research in the degradation rate of poly lactic acid (PLA), based on the three types of degradations explained above photodegradation, hydrolysis and thermal degradations. Tensile strength was evaluated as the mechanical property affected by the degradation rate. In general, when characterizing the mechanical properties of materials, molecular weight, chain structure, molecular orientation, crystallinity, and material morphology are considered. Essabir (2013) mentioned that the worldwide increment use of biopolymers in recent years has been mainly due low cost, low density, biodegradable characteristics, and especiallygood mechanical properties. It is well known that mechanical properties, such as tensile strength of biopolymers depends on several factor including but not limiting to molecular weight, dispersion/distribution state, morphology, and degradation rate. Recent studies have turned the attention to improve degradation durability in material that involves biopolymers such as PLA [8].

The specimens or sampleswere fabricated using extrusion and injection molding process based on ASTM procedures. NatureWorks PLA 3100HP was the material used in the experimentation. This PLA is used in crystalline engineered formulations; however, it is sold as neat resin. 3100HP biopolymer can be processed on most conventional injection molding equipment.The extrusion machine is a 15cc twin co-rotating screws by Xplore model DSM 15 cc capacity and the injection molding machine was a Xplore DSM 12 cc heating chamber, model Micro 12 cc IMM.

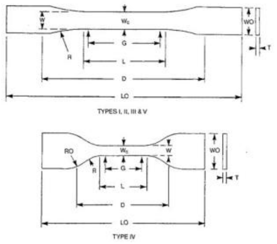
II. RESEARCH METHOD

In this paper, the research process is described based on accelerated degradation testing and repeated measures. Nelson [9] said that accelerated degradation tests (ADT’s) are concerned with models and data analysis for degradation of product performance over time at overstress and designed conditions. In accelerated degradation testing, a common objective of the experimentation is to estimate a particular quantile of the failure time distribution at use-conditions [10].

Repeated measures or repeated measurements analysis designs are defined by measures taken on each participant (sample unit) under each of several conditions; conditions could refer to a situation or to different points in time [11]. Repeated measures allow conducting a valid experiment when limited units or samples are available. In repeated measures, the researcher has the chance to explore the changes through passage of time (usually), this could be in long or short term, depending on the condition designed and established by the experiment. The repeated measure analysis tends to reduce the variance of estimates of treatment-effects, allowing to do statistical inferences with limited samples in the experiment [12].

The ASTM D638 -10 standard test method for tensile properties of plastics discusses the determination of the tensile properties of unreinforced and reinforced plastics in the form of standard dumbbell-shaped test specimens when tested under defined conditions of pretreatment, temperature, humidity, and testing machine speed. Test data obtained by this test method are relevant and appropriate for use in engineering design. This test method is designed to produce tensile property data for the control and specification of plastic materials. These data are also useful for qualitative characterization and for research and development. The Type IV specimen should be used when direct comparisons are required between materials in different rigidity cases (that is, no rigid and semi rigid). Fig. 1 presents the Type IV specimen used for testing no rigid plastics with a thickness of 4 mm (0. 16 in.) or less.

Tensile measurement of neat resin properties E_m and $S_{m1}^{(+)}$



ASTM D638-10 Type I, II, III, IV and V neat resin tensile specimen geometries. (From ASTM Standard D638-10. Copyright ASTM International. Reprinted with permission).

Fig.1 ASTM tensile standard

The manufacturing process to fabricate specimens for testing includes two sequential processes; extrusion and injection molding process.Poly lactic acid samples were tested for accelerated degradation using the weatherometer ATLAS Ci5000 Xenon Weather-Ometer. This test last for 2,000 hours (approximately 3 months). The set-up parameter for the accelerated weathering conditions were set according to the ASTM D2565-1. Cycle #1 is selected, and it is described as follows: 102 minutes of light exposure only followed by 18 min of light with water spray (102/18) cycle. Temperature of exposure is 63±2°C; the irradiance is 0.35 ±0.02 W/m2 at 340 nm.

Table 1. Experimental sample distribution

	Time	**Tensile test**
Control	0/ control	T0
Hours	250	T1
	500	T2
	1000	T3
	1500	T4
	2000	T5

The experimental plan for this research is described in the table 1. The experiment includes 10 replications on each test/code, the ASTM's standard recommended at least six specimens to validate the experiment and it was decided to include 10 to minimize the chances of ending up missing important information. Sample fabrication included a total of 60 tensile samples including 10 samples fabricated to be tested as control samples.

III. RESULTS AND DISCUSSIONS

The accelerated weathering was conducted for a total of 2000hours, samples were exposed to the ASTM cycle of degradation and the results are presented in this section. It is important to point out that the distribution expected for this material was not a normal distribution, however, statistical testing suggests that the distribution that most accurately fits the degradation path of the PLA is Weibull distribution. Fig. 2 presents theMinitab output that suggests that there might be other distributions that can be considered suitable for the material degradation rate.

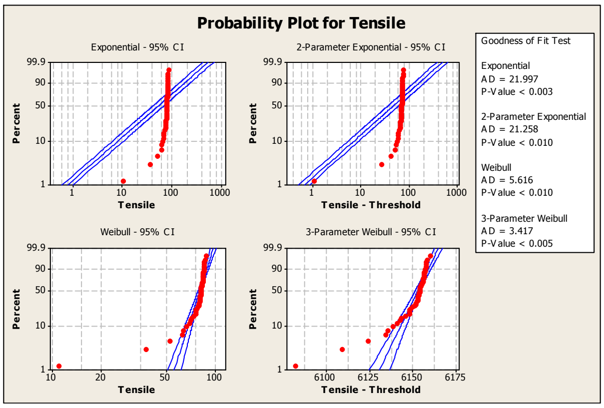


Fig.2 Probability distribution

This paper refers to various authors who have characterized PLA tensile strength by studying processing parameters. For example, Tsuji [13] mentioned that the pure PLA processing temperatures are as follow ~50 °C, ~160 °C ~195 °C and ~100°C, referring to drying, melting in barrel, process and cooling temperature respectively. Their results showed that pure PLA average has a Max tensile strength of 50 MPa and a modulus of 3.4 GPa, elongation break of 2% and the elastic module (E-module) of 3.4 GPa [13, 14].

In this paper, tensile testing was used to evaluate the degradation of this material. The initial (control) averaged ultimate tensile strength (UTS) was approximately 85 MPa, Fig. 3 illustrates the decreasing rate of the UTS through the 6 different times presented in table 1. The maximum strength of this material was slowly decreasing, as expected, affected by the exposure to variables such as UV, humidity, and high temperatures. The degradation presented in the material can be accounted to the combination of the three variables to which the PLA samples were exposed. It can be noted that the most significant decrease occurred after 1500 hours of exposure; 9.5% decrease in tensile strength was accounted to the exposure from 0 to 1500 hours, however, between 1500 and 2000 there was as decrement of approximately 25% in the strength of the material.

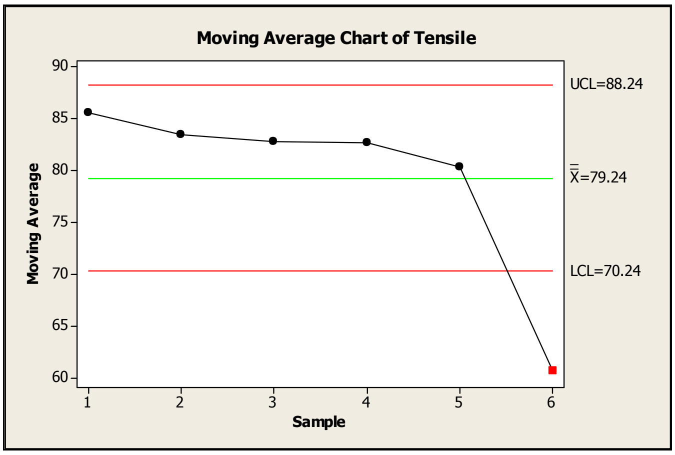


Fig.3 Average UTS

In fig. 4, the output summary of the ANOVA for tensile testing is presented. The results indicated that the model is significant and that there is a statistically significant difference among the groups. A follow-up test was performed to specifically analyze what groups present a difference indicating that group 6 (2000hours) is the group that is statistically different to the rest of the groups. A Tukey comparison test was used to account for this difference. The results presented in the ANOVA table were as expected based on the initial premises of this experiment. The tensile strength of the material decreased rapidly after 1500 hours as pointed out in fig 3.

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One-way ANOVA: Tensile versus Time (hrs)
Source       DF      SS     MS     F      P
Time (hrs)    5  4268.7  853.7  9.57  0.000
Error        54  4819.6   89.3
Total        59  9088.4
Grouping Information Using Tukey Method
Time
(hrs)   N    Mean  Grouping
   0   10  85.576  A
 250   10  83.466  A
 500   10  82.812  A
1000   10  82.596  A
1500   10  80.290  A
2000   10  60.700    B
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Fig. 4 ANOVA and Tukey comparison

IV. CONCLUSION

Based on the mechanical testing results and the statistical analysis,it wasdetermined that PLA has degradation decreasing point after 1,500 hours of accelerated exposure. The total degradation rate of the material was approximately 25 Mpa (30%) after 2,000 hours of accelerated exposure. This information is essential when characterizing any material specifically when selecting materials for product design. The application of biopolymers such as PLA in modern industry is rapidly expanding and understanding the characteristics of this type of material is crucial. Understanding the degradation rate of PLA is useful if the goal is to expand the application of biopolymers, especially given that it is a bio-based material and currently used mainly in the packaging industry.

The present research concludes and studies only one mechanical characteristic of PLA, however, it is necessary to analyze other mechanical properties and even other properties such as visual characteristics of the material, color, appearance and functionality, etc. Future research is proposed to explore other mechanical test such as flexural strength, elongation point, and mass loss as well as visual appearance of the material. The study of these variables may result in a better characterization of this bio-material.

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