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Thermal and ionizing radiation induced degradation and resulting

formulation and performance of tailored poly(lactic acid) based hot

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ABSTRACT

Polylactic acid (PLA) was studied for variation in material properties after step-wise thermal degradation at 255 °C in air. It was found that melting temperature, T_{m} , and enthalpy of fusion, ΔH_f , decreased systematically with corresponding decreases in molecular weight. Radiation induced degradation via Co-60 (1.17 and 1.33 MeV γ -photons) produced equivalent but not the same trends for T_m and ΔH_f . For both degradation pathways, differential scanning calorimetry (DSC) revealed a clear transition from one welldefined melting peak in the control case, to two separate regions growing broader with increased exposure resulting in the polymer becoming almost completely amorphous after one hour. PLA based formulations with and without plasticizers as hot melt adhesives were devised for deriving tailored properties. Comparable to, or superior performance to an EVA based industry benchmark adhesive was attainable in terms of hardness, elasticity, shear strength, set time, viscosity, and fiber tearing on corrugated cardboard. In a novel, in-situ application mode using quenched-annealed PLA to join steel dowels, bond strengths of 42.9 MPa (6200 psi) were attainable; potentially offering the community a new method for joining structures.

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1. Introduction

Polylactic acid (PLA) is a biopolymer which can be derived from dextrose, and in its high polymer form is characterized as a rigid thermoplastic which can be produced in amorphous or crystalline forms depending on stereochemistry. [1] It has been studied as early as 1932 in which PLA was produced from the cyclic dimer of lactic acid, lactide. [2] Due to the environmental benefits throughout the product life cycle and a generally broad range of applications, PLA has since become the most widely produced biodegradable polymer in the global market. [3,4].

PLA's ability to be synthesized from renewable resources and to degrade readily into low toxicity byproducts, namely carbon dioxide and water, also provides added value. [4,5] In North America the feedstock is primarily corn, however sugar beets, sugar cane, and wheat could all be used in the same manner. [6,7] The essential raw material which one needs to obtain is dextrose,

http://dx.doi.org/10.1016/j.ijadhadh.2016.08.010 0143-7496/© 2016 Elsevier Ltd. All rights reserved. and in North America corn is a widely available source of this raw material.

A significant current producer of PLA in that market is NatureWorks[®] which has an advertised production capacity of 150,000 metric tons per annum and recently has shown interest in expanding globally with a responsibly diversified feedstock. [4,8,9] With these attributes and large scale production in place, PLA has become of interest with hopes to replace petrochemical derived counterparts in many applications. We believe that one application of particular potential based on our research is the adhesive market, the subject of this manuscript. [10].

For hot melt adhesives (HMAs) knowing the dynamic response under static heating is essential; even more so for use in high temperature applications. As such, thermal degradation was studied by us and is reported in this manuscript in order to predict the useful adhesive lifetime while exploring the limits of PLA bond strengths at elevated temperatures. Analogous means for attaining similar states using high energy gamma photons were also studied, for which results are reported in this manuscript. In addition, PLA-based formulations of HMAs and their abilities to join materials in traditional and novel (non-traditional) applications regimes are also presented.

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2. Materials used, property tailoring and measurement methods

This section presents information on materials used for this reported study along with thermal and ionizing radiation based methods for helping to tailor the PLA polymer to attain desired HMA properties. Radiation methods are routinely used in various industrial applications such as for medical sterilization and other applications such as for polymer cross-linking and food preservation, the interested reader may wish to refer to *Radiation and Modern Life*. [11] Irradiation when performed appropriately does not leave the target objects radioactive. As such, radiation induced degradation was presented by us for comparison as a possible engineering-scientific alternate option of PLA polymer processing for deriving desired properties for hot melt adhesives as well.

2.1. Materials

PLA resin as used for this reported study, was obtained from NatureWorks[®] in the form of a semi-crystalline film and sheet grade (4043D, $T_g = 55-60$ °C, $T_m = 155-170$ °C, MFR = 7 g per 10 min at 210 °C).

2.2. Thermally tailored properties

PLA tailoring using thermal degradation was conducted with 30.0 g batches of resin beads in a temperature controlled oil bath. Resin was heated in glass ignition tubes measuring 2.5 cm \times 25 cm outer dimensions and placed into a 255 \pm 2.5 °C (high smoke point) oil reservoir exposed at the free liquid surface to room air. Upon removal the samples were cast into PTFE molds and reclaimed for testing. The temperature of \sim 255 °C was chosen because it was the highest temperature enabling rapid polymer degradation without significant charring and/or burning of the PLA resin.

2.3. Gamma photon based tailored properties

Samples were irradiated in a *Nordion GammaCell 220TM* Co-60 (emitting 1.17 and 1.33 MeV photons) irradiator. Dose rates on the order of 4 kGy per day were attainable using spacers to maximize dose uniformity. Samples were irradiated in the presence of room air in resin form.

2.4. Differential scanning calorimetry (DSC)

A Perkin Elmer Jade Differential Scanning CalorimeterTM equipped with intercooling unit was utilized to assess for thermal property variations. A ramp rate of 5 °C per minute was deployed under nitrogen purge. Nominal sample mass was ~5 mg. Data were analyzed with a composite trapezoidal sum method in order to calculate enthalpy of crystallization, enthalpy of fusion, glass transition temperature and melting temperature variations.

2.5. Molecular weight determination

Molecular weight was measured via gel permeation chromatography (GPC) using a *Polymer Laboratories GPC-20*TM with tetrahydrofuran (THF) as the solvent and at a sample concentration of $\sim 2 \text{ mg ml}^{-1}$. Narrow polystyrene standards were used for calibration.

2.6. Hardness testing

Shore D hardness was measured with a handheld durometer, capable of readouts in increments of 0.5 HD. Measurements were taken at 1 ± 0.3 s to provide an apparent hardness value.

2.7. Hot melt viscosity variations with temperature

A Brookfield[®] RVT rotating viscometer was used in conjunction with a programmable Vulcan[®] 3-550 high temperature oven to derive data on viscosity variations with temperature. The viscometer was calibrated with high temperature Brookfield[®] viscosity standards using a number 6 spindle at 100 RPM, and sample volumes of ~20 ml. Thermocouples were acquired from Omega[®] engineering with special limits of error (greater of 1.1 °C or 0.4% measured value).

2.8. Mechanical strength testing

Strength measurements were made using an *Instron* 5566ATM load frame, in tension with a fixed extension rate of 1.3 mm per minute until failure.

2.9. Surface characterization

Atomic Force Microscopy (AFM) was used to characterize the surface of substrate specimens when using the novel, in-situ method of PLA application (discussed in Section 3.12). The instrument deployed was a *Veeco Dimension* 3100^{TM} in tapping mode, with *TAP300GD*TM gold plated probes.

3. Results and discussion

3.1. DSC response for thermally tailored PLA

DSC curves for various PLA samples (ranging from unmodified 4043D to states produced after thermal processing at 255 °C from 30 to 80 min depicted as PLA-30 to PLA-80, respectively) are shown in Fig. 1. Thermal processing as performed produced a clear difference starting from a single well defined melting dip for 4043D resin into two broadened dips for specimens PLA-30 through PLA-80. This is attributed to degradation-induced formation of cyclic and linear oligomers. [12] Crystallization peaks



Fig. 1. DSC results for thermally tailored 4043D resin, naming convention of PLA - time [min] for thermal exposure in a 255 $^\circ$ C oxidative environment.

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