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Polylactides: Properties and Prospects of an Environmentally Benign Plastic from Renewable Resources

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SUMMARY: Pressing environmental and economic concerns dictate the need to develop new synthetic macromolecules based on renewable resources. The vast majority of existing materials are based on non-renewable fossil resources that will eventually be extinguished. Manufacturing synthetic polymers and disposal by incineration produces CO_2 and contributes to global warming. For these reasons, poly(lactic acid) (PLA) polymers are of increasing commercial interest because they are derived from a renewable resources, sequester significant quantities of carbon dioxide relative to petrochemical based materials, conserve energy, and easily degrade. The mechanical properties of PLA are compared to other commodity plastics and it is shown that PLA closely resembles polystyrene. The effects of blending linear and branched chain architectures are discussed and it is shown that this provides a convenient method for controlling the elasticity and viscosity of the composite material without affecting mechanical or permeation properties. The melt rheology of high L content linear PLAs shows two unique features; they may be drawn to large Hencky strains without breaking and they exhibit considerable strain hardening. As a result, PLA is easily processed into fiber form. Due to the excellent combination of mechanical, rheological, and environmental properties, the prospects for widespread commercialization of PLA are excellent.

Introduction

Nearly all polymeric materials are currently based on non-renewable fossil resources. Incineration of these materials makes a net contribution to atmospheric CO_2 and plastics currently account for in excess of 20 % by volume of the landfills in the United States. In addition, many widely used materials, notably polystyrene and poly(vinyl chloride), are made from noxious or toxic monomers. There is a need to employ green chemistries in developing renewable commodity plastics that don't involve toxic and noxious compounds in their

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manufacture. However, for acceptance in the marketplace these materials must be competitive on a cost-performance basis.

Significant issues of sustainability exist in the plastics industry based on its current structure. All major commodity plastics are presently based on petroleum resources. Proven petroleum reserves are about one trillion barrels. Depending on the assumptions made regarding the rate of industrialization in the third world and growth in the developed world, this supply may last for as long as a few hundred years or for as little as fifty years. As the supply of petroleum depletes, its cost will again rise and the present low cost of fossil based plastics will not be possible. Thermoplastic production in the United States has approximately doubled every ten years for the past three decades. Present US consumption of 80 billion pounds per year can be expected in increase. [1] It is evident that a doubling of fossil based plastics consumption each decade in light of declining petroleum reserves is not sustainable

It should also be noted that plastic materials represent a serious solid waste disposal problem. The US Environmental Protection Agency estimates that 20% by volume of municipal landfills are occupied by plastics. This is an even greater concern in Europe and Japan where landfill space is not as available as in the United States. One solution adopted is to recover energy content through combustion of solid wastes thus reducing landfill needs.

However, another issue of sustainability faces the plastics industry. Namely, emission of carbon dioxide is considered as a potential threat in the form of global warming. As is the case for all industrial processes, the energy input required normally results in the production of carbon dioxide. While not unique to the plastics industry, if the threat of global warming is to be taken seriously steps must be taken to reduce CO_2 emissions. Burning plastics to recover the energy content contributes to carbon dioxide emissions. The use of plastics must be scrutinized for potential CO_2 savings.

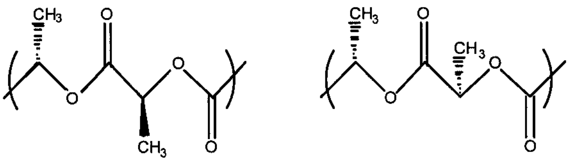
Polylactides (PLA) are a family of degradable plastics based on a monomer produced by the fermentation of corn. An independent evaluation of the process economics performed at the Argonne National Laboratory has found that advances in fermentation and separation technologies allow the manufacture of lactic acid for twenty-five cents per pound and that poly(lactic acid) (PLA) is an economically feasible material. [2] Recently construction has started on a plant in the United States to produce 300 million pounds per year of PLA.

The advantages of PLAs are numerous and include: 1) production of the lactide monomer by fermentation of a renewable agricultural source (corn), 2) fixation of significant quantities of carbon dioxide, the leading greenhouse gas, 3) significant energy savings 4) the ability to recycle back to lactic acid (a non-toxic, naturally occurring metabolite) by hydrolysis or alcoholysis, 5) the capability of producing hybrid paper-plastic consumer packaging that is compostable, 6) reduction of landfill volumes, 7) improvement of farm economies, and 8) the all important ability to tailor physical properties through material modifications. [3]

Figure 1 shows the L and D enantiomers of lactic acid along with two dimer rings formed via reactive distillation of an aqueous lactic acid solution. [4] Since the L-lactic acid is available from fermentation, the LL-lactide is of greatest industrial interest. However, some racemization occurs during the distillation to produce the LD-lactide (the meso structure). Control of the ratio of the L to D content is an important molecular feature of PLAs. Mixing of these monomeric forms produces a polymer in which the strict strereoregularity is disrupted.

L-lactic acid D-lactic acid

LL-lactide meso-lactide



Syndiotactic PLA linkage Isotactic PLA linkage

Fig. 1: Chemical structure of PLA and its constituents.

This paper discusses the properties of PLAs with a particular emphasis on the melt rheological properties so important to successful processing. The effects of blending linear and branched chain architectures are discussed and it is shown that this provides a convenient method for controlling the elasticity and viscosity of the composite material without affecting mechanical or permeation properties. The melt rheology of high L content linear PLAs shows two unique features; they may be drawn to large Hencky strains without breaking and they exhibit considerable strain hardening.

Materials and Methods

The PLA samples used in this study were provided by Cargill-Dow Polymers (Minnetonka, Minnesota USA) and were melt synthesized using stannous octoate as a catalyst. Materials were received as granular pellets. PLA pellets were held in a vacuum oven at 40±1 ^{0}C for at least 48 hours prior to manipulation. For some tests, chemical stabilization of the PLA samples was accomplished by adding tris(nonylphenyl) phosphite (TNPP). This was done by mixing PLA pellets with different amounts of TNPP in a Haake Rheodyne 5000 mixing bowl at 180±1 ^{0}C until a constant torque was observed (i.e. for about 12 min). The samples were then immediately compression molded at 180 ^{0}C to get disks having a diameter of 25 mm and a thickness of approximately 2.5mm. These disks were held in a vacuum oven at 40±1 ^{0}C for at least 48 hours prior to testing. For extensional testing, bars of 60mm x 8mm x 1.5 mm were compression molded in the same fashion. Tensile testing bars were also prepared in the same fashion.

Shear rheometry has been carried out on a Rheometrics RMS-605 mechanical spectrometer using standard 25mm parallel plates and 0.1 radian cone and plate configurations. Capillary measurements were performed in a Kayeness LCR5000 capillary rheometer. A capillary die having an L/D of 30 was employed and the Rabinowitsch correction was applied to the data. Elongational measurements were performed on a Rheometrics RME instrument. Tests were performed at a temperature of 180 ^{0}C and at an extensional elongation rate of $\dot{\varepsilon} = 0.1\ s^{-1}$ using rectangular shaped samples. These data were corrected according to the results of a round-robin evaluation of the performance and accuracy of this instrument. [5]

Tensile testing was performed using an Instron tensile testing apparatus. ASTM standards were followed: the rate of deformation was 2 in./min. and five specimens of each sample were tested. Averages and standard deviations for modulus and strain at break were recorded.

Permeation properties were measured using a cross-flow geometry in a Millipore membrane cell. PLA films were cast from solution in methylene chloride using a Gardner casting blade onto a glass plate. After solvent evaporation and annealing in a vacuum oven, films were notched and thicknesses determined using an alpha-step profilometer. Films were subsequently floated off the glass in a water bath, recovered, dried overnight at 40 °C, and then placed in the membrane cell. Detection was accomplished by gas chromatography (SRI).

Molecular weight and its distribution were measured by gel permeation chromatography (GPC) calibrated with light scattering measurements. These experiments were performed at 35^0 C in chromatography grade tetrahydrofuran (THF) using 3XPLgel 10um columns at a 1 ml/min flow rate.

Results and Discussion

Figure 2 presents a comparison of the physical properties of PLA to other commodity thermoplastics. [6] From this comparison, it is seen that PLA compares favorably with polystyrene, a widely used plastic based on non-renewable resources. It should be noted though, that PLA has a glass transition temperature that is significantly lower, $T_g \approx 59$ °C, than polystyrene, $T_g \approx 100$ °C. This translates into a lower heat distortion temperature and limits the applicability of PLA for certain applications requiring better heat resistance. Despite this limitation, it is clear that PLA can be employed for many applications presently utilizing less environmentally friendly materials.

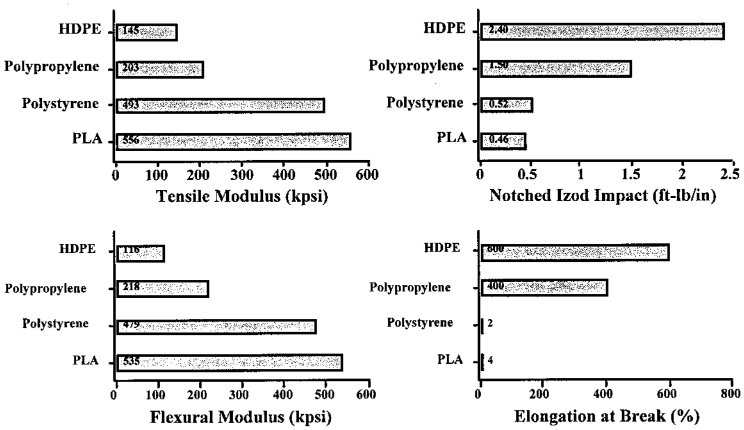


Fig. 2: Physical properties of PLA compared to other common plastics.

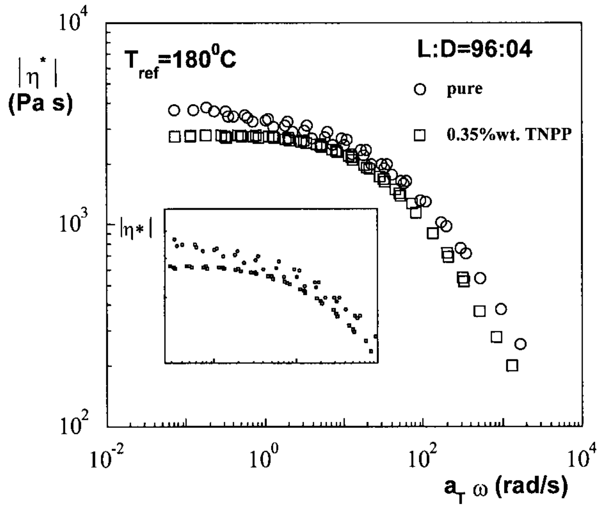


Fig. 3: Complex viscosity of PLA versus reduced frequency for a material having an L:D ratio of 96:04 and a M_w of 110k (g/mol). The inset shows the improvement in superposition achieved upon stabilization using TNPP.

Measurement of the melt rheological properties of PLA is complicated by degradation effects. A comparison between the measured complex viscosity, η^*, versus reduced frequency, $a_T\omega$, of pure PLA and PLA stabilized with 0.35 % wt. tris(nonylphenyl) phosphite

(TNPP) is presented in Figure 3. These master curves are referenced to 180 °C and are constructed from isothermal curves obtained at three different temperatures (160 ^{0}C, 180 ^{0}C and 200 ^{0}C). While time-temperature superposition appears to be roughly obeyed for both samples, this is not the case. The detail shown in the inset of the graph reveals that superposition is not obeyed for the unstabilized sample. However, the stabilized sample shows excellent superposition within the temperature window explored thus demonstrating that the use of TNPP as a stabilizer does lead to a thermorheologically simple material response.

In order to customize processing properties, it is often desirable to manipulate the rheological properties of a polymer material through blending. In particular, the addition of some branched material to a linear base often has the effect of increasing the elasticity. If this can be accomplished without increasing the viscosity greatly, certain processing operations are made easier.

Table 1 presents molecular weight data for a series of PLA blends consisting of linear and branched components. The branched material was produced by peroxide modification in a twin-screw extrusion operation. [7] The samples were subsequently produced by compounding varying weight percentages in a subsequent twin screw operation. All samples were exposed to the same temperature history. Headings in the table refer to the as received samples (Virgin), samples after processing in the Haake mixer to add TNPP (Stabilized), and samples recovered after rheological testing (Post-testing). Even with stabilization there is an apparent trend suggesting a decreasing weight averaged molecular weight with increased thermal exposure.

Table 1. Molecular weights of PLA blends.

	Virgin			Stabilized			Post-testing		
% Linear	**Mn**	**Mw**	**pdi**	**Mn**	**Mw**	**pdi**	**Mn**	**Mw**	**pdi**
0	55,000	155,000	2.8	50,000	145,000	2.9	50,000	135,000	2.7
20	60,000	160,000	2.7	45,000	140,000	3.1	50,000	130,000	2.6
40	50,000	140,000	2.8	55,000	140,000	2.5	50,000	125,000	2.5
60	60,000	140,000	2.3	55,000	130,000	2.4	45,000	120,000	2.7
80	60,000	120,000	2.0	50,000	120,000	2.4	55,000	115,000	2.1
100	60,000	120,000	2.0	55,000	115,000	2.1	55,000	110,000	2.0

Figure 4 presents the results of tensile testing on the Virgin blends. It is easily seen that with in the standard deviation of the test results, there are no differences in the mechanical properties of the linear-branched blends.

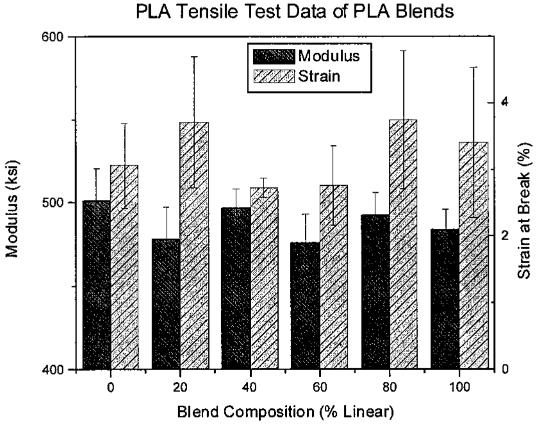


Fig. 4: Tensile testing results for the blends of Table 1. Error bars represent one standard deviation obtained from testing 5 specimens.

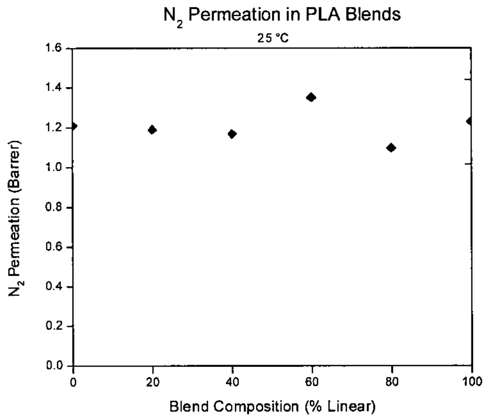


Fig. 5: Permeation of nitrogen through films of the blends described in Table 2.

Figure 5 presents the results of permeation studies on the blends. Permeability of nitrogen measured at 25 °C is shown, again it is evident that blending of the different chain architectures does not affect this important property. This finding is not surprising as the usual solution-diffusion mechanism of transport for small molecules through a polymer film should depend on the nature of the monomeric groups (which dictate solubility) and the small scale segmental motions (which dictate diffusivity). [8]

In contrast, Figure 6 presents zero shear viscosities determined for each of the blends. Here a clear trend is observed that follows a logarithmic mixing rule,

$$\text{Log}(\eta_o) = \sum_i w_i \,\text{Log}(\eta_{o,i}) \tag{1}$$

where η_o is the zero shear viscosity and w_i is the weight fraction of the linear or branched component. [9] Correspondingly, in Figure 7 the first normal stress difference, a key indicator of elasticity, is displayed as a function of blend composition. The normal stress difference is determined from the low frequency asymptote of the dynamic data according to Equation 2,

$$\psi = \frac{\sigma_{11} - \sigma_{22}}{\dot{\gamma}^2} = 2\lim_{\omega \to 0}\left(\frac{G'(\omega)}{\omega^2}\right) \tag{2}$$

where ψ is the first normal stress coefficient, σ_{ij} represents the ij^th^ component of the stress tensor, $\dot{\gamma}$ is the shear rate, $G'(\omega)$ is the dynamic storage modulus, and ω represents the frequency. Again, it is clear that a monotonic increase in the blend elasticity is achieved through blending. These results demonstrate that it is possible to profoundly alter the rheological behavior of PLA without compromising its mechanical or permeation properties.

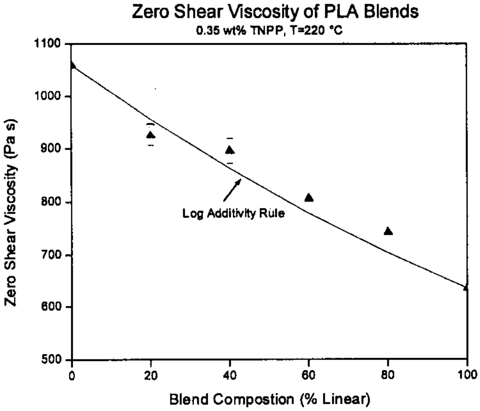


Fig. 6: Zero shear viscosity, η_o, as a function of blend composition.

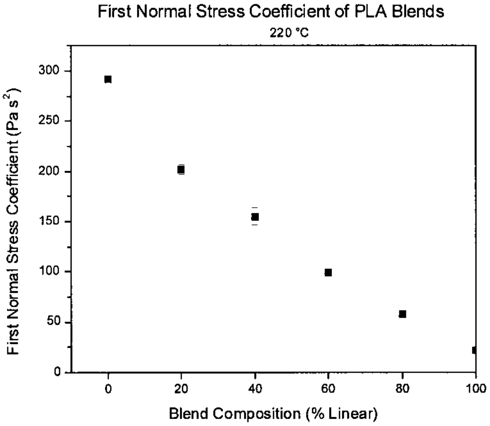


Fig. 7: First normal stress difference as a function of blend composition.

Extensional deformations are of practical importance in many industrially relevant flows. Figure 8 presents extensional data for two different linear PLAs (nominal L:D values of 98:02 and 96:04 and corresponding weight averaged molecular weights of M_w = 115,000 and M_w = 110,000 g/mol, respectively).

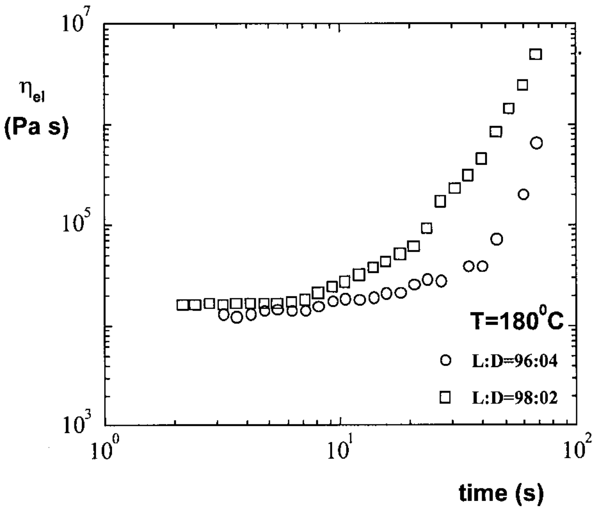


Fig. 8: Elongational viscosity of two PLAs of high L-content measured at an extensional rate of $\dot{\varepsilon}$ = 0.1 1/s. Significant strain hardening is accompanied by large deformability.

The most striking feature of the response is a strong strain hardening (the extensional viscosity increases by two orders of magnitude). The literature suggests that extension thickening is exhibited when the rate of deformation considerably exceeds the rate of molecular relaxation (i.e. when $\lambda_{longest} > 1/\varepsilon$). This effect is normally most significant when long chain branching is present because such branching introduces very long relaxation times. However, a distinction to be noted for PLA is its extensibility; Hencky strains in excess of 10 were reached in these experiments. Further details of the rheological behavior of PLA including non-linear rheological response are available elsewhere. [10, 11]

Conclusions

Environmental and economic concerns call for the development of synthetic macromolecules based on renewable resources. The vast majority of existing materials are based on non-renewable fossil resources that will eventually be extinguished. Manufacturing synthetic polymers and disposal by incineration also produces CO_2 and contributes to global warming. For these reasons, poly(lactic acid) (PLA) polymers are of increasing commercial interest. These polyesters are derived from a renewable resources, sequester significant quantities of carbon dioxide relative to petrochemical based materials, conserve energy, and easily degrade.

Studying the melt rheology of PLA is difficult due to degradation effects. Stabilization using tris(nonylphenyl) phosphite (TNPP) provides a method of overcoming this problem. PLA stabilized using TNPP exhibits the usual thermorheological simplicity associated with most thermoplastics.

Blending linear and branched chain architectures provides a convenient method for controlling the elasticity and viscosity of this class of polymers without affecting mechanical or permeation properties. Accordingly blends may be developed for a wide variety of applications presently filled by less environmentally friendly plastics.

The melt rheology of high L content linear PLAs shows two unique features; they may be drawn to large Hencky strains without breaking and they exhibit considerable strain hardening. As a result, PLA is easily processed into fiber form. Due to the excellent combination of mechanical, rheological, and environmental properties, the prospects for widespread commercialization of PLA are excellent.

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