Production (Synthesis) and Rheological Properties of Poly Lactic Acid (PLA) for Food Packaging and Biomedical Application

Govind Sahu[1], M. S. Rajput[1], Udit Narayan Sahu[1], S. P. Mahapatra[2]

[1]Department of Mechanical Engineering, National Institute of Technology Raipur, Chhattisgarh - 492010, India
[2]Department of Chemistry, National Institute of Technology Raipur, Chhattisgarh - 492010, India

Abstract

Biomaterial is gaining more importance in medical and packaging applications compared to conventional petro based polymer since last few decades. Biodegradable polymers are those materials which degrade into the simple compounds through hydrolysis that can be easily metabolised. Among the available biopolymers, Poly lactic acid (PLA) possesses excellent material properties for the biomedical application, including sutures, fixation screws, and clips for ligament reconstruction and 3Dimensional scaffolds for bone tissue regeneration. It is because PLA and its degraded compound, namely water and carbon dioxide are neither toxic nor cancer-causing to the human body. In this study, the poly-lactic acid was prepared by simple dehydration of lactic acid and refined through ring opening polymerization by using a Tin catalyst (Stannous Octoate). Fourier transform infrared spectroscopy (FTIR) and rheology characterization of the PLA was performed to observe its feasibility for medical and food packaging applications.

Keywords: Poly Lactic Acid (PLA), Fourier Transform Infrared Spectroscopy (FTIR), Rheology.

1. INTRODUCTION

In recent days, the biomass based plastics (Bio-plastic) gaining more importance because of many economic factors that are (i) degradation or incineration of plastic for environmental concern (ii) depletion of petroleum resources increases the cost of production of conventional plastics. Bioplastic has the ability to reduce the environmental carbon emissions because it is produced (synthesised) by without using the fossil fuel or petroleum resources, which plays important role in global warming. Some times in very small quantities of fossil fuels are used when we produce in large scale as compared to conventional plastic. However, bioplastic is used in limited quantities because its production cost is 5–10 times greater than conventional plastic [1]

Another drawback of conventional polymers is the high capital cost of their recycling and toxicity of their monomers or oligomers. Mechanical recycling (grinding, washing, separating, drying, re-granulating and compounding), and sewage and composting and incineration are the possible alternatives for the plastic waste management but they have several disadvantages as to economic, health and environmental aspects [2].

In the case of Biopolymer, the above-mentioned issues are reduced up to certain level regarding biodegradation process. Biodegradation is the phenomenon in which the polymers degrade in natural environments including changing chemical structure, loss of mechanical, physical and structural properties and breaking down in the simple compounds like water, carbon dioxide, minerals and humus materials. The rate of degradation depends upon various factors like temperature, moisture, pH and O_2 presence in the natural environments [3].

Now a day's biomaterials are also gaining more attraction toward the field of biomedical to treat and repair the loss of tissue and organs from injury and disease. Among all the available biomaterial PLA possesses superior biocompatibility and its degradation compound (CO_2 and water) are non-toxic

which makes it very useful in biomedical application, such as drug delivery system and because of its mechanical strength it is widely used in orthopaedic applications, biomedical implants (including sutures, screws and clips for bone fixing and ligament reconstruction and 3Dimensional scaffolds for bone tissue regeneration). Due to its mechanical properties compared to other many some polymers and its environmental friendly make it very useful in the field of food packaging application. Furthermore, PLA is synthesized from lactic acid obtained from renewable resources (sugar cane and corn starch). The rate of degradation of PLA also depends upon its molecular weight, index of dispersion and chain structure [4].

The PLA was produced by direct poly condensation of lactic acid under vacuum without catalyst, solvents and initiators. Condensation processes the simplest, safe as well as compact, but water removal was the major difficulty associated with the condensation process. Hence synthesis of PLA is usually done by ring opening polymerization (ROP) of lactide, by using compounds of tin, zinc, aluminium and lead as a catalyst. Including Stannous octoate ($Sn(Oct)_2$), tin carboxylates and aluminium alkoxides many of this are toxic or flammable [5]. This paper reports the synthesis of PLA by direct polymerization without catalyst at180 ºC polymerization temperature, under the vacuum condition for 100 hr. PLA was also synthesized by ring opening polymerization (ROP) for comparison of properties of final products obtained.

2. EXPERIMENTAL

2.1. Materials

DL-lactic acid was procured from a standard supplier by Thermo Fisher Scientific India Pvt. Ltd. 403-404 with acidimetric 88-92%, Wt./ml at 20 ºC 1.20-1.22g, molecular wt. 90.08 and stannous octoate from Triveni chemicals India limited, was used as a catalyst for ring opening polymerization

(ROP). Rheology analysis was performed in by rotational Rheometer: MCR 102.

2.2 Apparatus and procedure.

Synthesis of PLA was conducted in 3 necks round bottom flask fitted with mechanical stirrer and condenser also connected with a vacuum pump. Thermocouples were attached at the various locations on the flask to measure and a heater was installed control temperature at each location. The pressure inside the flask was controlled by a vacuum pump and by measuring the pressure by a transducer and monitored by a computer through data acquisition system.

250 ml of DL lactic acid was kept into the flask, and synthesis of PLA was carried out in the following steps

(i)   Lactic acid was heated to the distillation temperature of 160 °C and maintained at this temperature for 4 to 5 hours ie. for oligomerization at 1 atmospheric pressure.

(ii)   The pressure inside the flask was slowly reduced to the vacuum condition 125 Pa and temperature at 170 °C maintained at this temperature and pressure (i.e.at polymerization temperature and pressure) 100 hour of time. The distilled water was removed from condenser trap after every 30 minutes and at the end of polymerization the product (PLA) was poured into the petri dish and allowed it to come to room temperature.

2.3. MEASUREMENTS

2.3.1. Rheological properties

The melt rheological properties of the PLA were investigated using a rotational Rheometer (MCR 102 Rheometer, Anton Paar Physica). The measurements were performed in the steady state shear and dynamic oscillatory shear mode by using 25 mm diameter parallel plate with maintaining the gap of about 0.9 mm between the plates. The temperature during rheological measurements was kept constant at 180°C in a nitrogen atmosphere.

The test sample was prepared with a thickness of 0.9 mm and a diameter of 2.5 mm by compression moulding. Steady state shear rotational mode measurements were carried out within 0.1-100 s^{-1} shear rate. The dynamic oscillatory shear measurement was carried out within the angular frequency range of 0.1-100 rad/sec under the constant (within 5%) strain value. In addition, the linear viscoelastic response of PLA was examined by measuring their storage modulus (G') and loss (G'') modulus at 180°C.

3. RESULT AND DISCUSSION

Fig. 1 shows the steady state shear viscosity and shear stress as a function of shear rate for the PLA at the constant temperature at 180 °C. Fig. 1 shows the variation of shear stress with the shear rate which revealing that shear stress is directly proportional to the shear rate, indicates similar to all thermoplastic polymer, PLA showed the Newtonian behaviour at the low shear rates below (< 1S^{-1}). After that start following the power law i.e $\tau = \beta \gamma^{n}$ indicating the non- Newtonian behaviour at the high shear rates above i.e. (> 1s-1). Where τ = shear stress, γ = shear rate and β = constant and n = non-

Newtonian index. Indicates similar to all thermoplastic polymer, PLA showed the Newtonian behaviour at the low shear rates below (< 1S^{-1}). The shear viscosity of the PLA is almost constant at the low shear rate (1S^{-1}) and starts decreasing with increase in shear rates, revealing shear thinning behaviour as shown in Fig 1. The degree of shear thinning allows the PLA to flow readily at high shear rates. Similar behaviour was also observed in case of all biodegradable polymers like poly caprolactone [6], and biodegradable aliphatic polyester (BAP) [7].
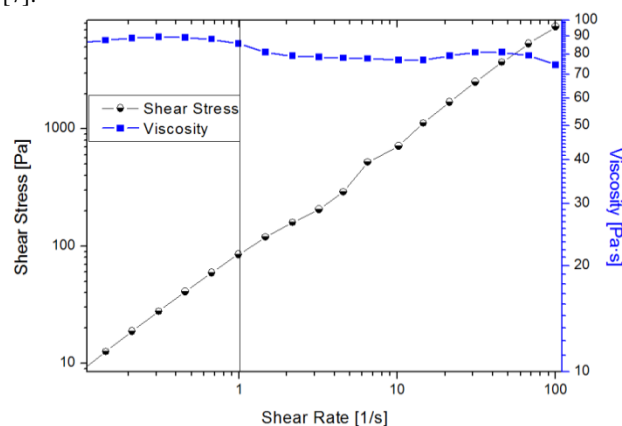

Fig.1 Variation of steady state shear viscosity and shear stress with respect to applied shear rate for the PLA.

Besides of steady shear viscosity, the complex viscosity was also examined by measuring in the dynamic oscillation mode. Fig. 2 shows the variation of complex viscosity of PLA as a function of the angular frequency within the range of 0.1-100 rad/sec. The complex viscosity of PLA exhibited newtonian plateau regions in the low-frequency range, up to 0.4 s^{-1}and slightly shear thinning behaviour when frequencies increases.
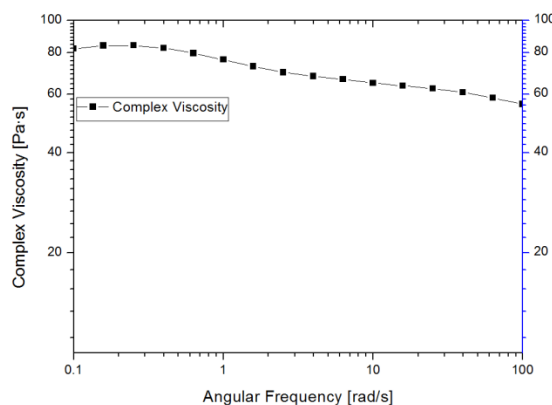

Fig.2 Complex viscosity versus angular frequency of the PLA.

The frequency sweep test was carried out to examine the viscoelastic nature of PLA with in a constant deformation of (5%) at 180 °C. The storage modulus (G') represents elastic response and loss modulus (G'') represents the viscous response of the polymer respectively. Fig. 3 shows the variation of G' and G'' of the PLA with respect to the Angular frequency within 0.1-100 rad/sec range. Fig. 4 represents that loss modulus (G'') dominates the storage modulus (G') of the PLA at all frequency ranges.

By applying force to the polymer which is greater than the force between the polymers, its microstructure starts collapsing. The rotational energy given to the polymer is dissipated to change its microstructure and polymer starts flowing and G'' shows larger value than the G'
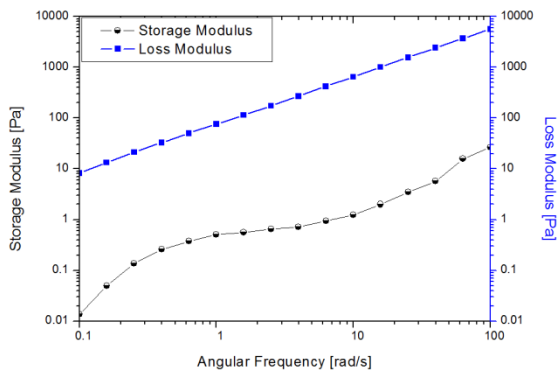

Fig.3 Variation of storage modulus (G') and loss modulus (G'') of the PLA as a function of Angular frequency.

5. CONCLUSION

The rheological properties, such as shear viscosity, complex viscosity, shear stress, loss modulus and storage modulus of the PLA, were investigated using both steady-shear and oscillatory shear mode measurements. The rheological study concluded that PLA showed newtonian behaviour at low strain rate and at low-frequency range similar to all thermoplastic and shear thinning behaviour at higher strain rate and frequency in the measured range similar to the biodegradable polymer.

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