



Development of high performance sealable films based on biodegradable/compostable blends



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ABSTRACT

In this study, the seal behavior of toughened blends of poly(lactic acid) (PLA) and polycaprolactone (PCL) was investigated in details. The blended samples were prepared using melt blending in a twin-screw extruder and were processed in the form of cast films of about 30 μm in thickness. Scanning electron microscopy (SEM) study of the morphology of the blends shows that laminar morphology develops in blends of 20% and 40% dispersed phase. Analysis of the thermal behavior of the blends using DSC thermograms reveals significant effect of blending on hindering the crystallization of PCL, resulting in lower crystallinity for samples with high PLA content. Latter provide blends with more amorphous phase and chain mobility, which help lowering the Seal and Hot-tack initiation temperatures. Blending is shown to decrease Seal and Hot-tack initiation temperatures up to 30 °C compared to neat PLA. In addition, this technique is proven to be successful to increase the Hot-tack strength of the blends to a comparative level to commercially available seal grade resins at about 1100 g/25.4 mm for PCL content of 40%. The results indicate that elongation at break increases from about 4% for pure PLA to almost 150% for the blend of 40% PCL and over 400% when PCL content reaches 60%. Higher toughness is an important property for a flexible package and prevents defects caused by its handling and storage conditions.

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1. Introduction

Consumption of significant amounts of polymers in packaging applications has caused many concerns in waste management areas. Although plastics account for about 11% of total municipal waste in United States and Canada, their stability in landfill and their high CO₂ footprint have raised many environmental concerns (Bohlmann, 2004). On the other hand, many research works have investigated the capability of bio-based and biodegradable plastics to provide promising research area for various applications (Sinclair, 1996; Jiang et al., 2005; Park et al., 2000; Pakravan et al., 2011). The new approach to replace petroleum based resins with the bio-based and biodegradable materials have given rise to the need for the improvement of the available biodegradable polymers through conveniently inexpensive processes such as melt blending (Jiang et al., 2005; Park et al., 2000; Garlotta, 2001; Mohanty et al., 2000).

Poly(lactic acid) (PLA) is aliphatic polyester, which shows biodegradable properties and has been the focus of interest of many studies in recent years. In many applications, PLA resin has attracted

researchers due to its high tensile strength and modulus. PLA can be a suitable bio-plastic for its ease of processing and temperature range similar to conventional plastics in packaging industry. However, the brittleness of PLA has always been a draw back in many applications (Sinclair, 1996; Garlotta, 2001; Oyama 2009; Liu et al., 2010; Nampoohiri et al., 2010; Theryo et al., 2010). In this work, we are looking for a technique that can make PLA suitable for flexible packaging applications and, specifically, as a seal layer grade material. Considering the thermal and mechanical properties of PLA and the potential of its toughened blends, it is believed that by adjusting the content of modified PLA, a range of flexibility and thermal behaviors can be achieved. The focus on heat-sealing process is because it is an essential step in order to obtain a reliable performance from a flexible multilayer food packaging film structure (Mazzola et al., 2012; Mueller et al., 1998; Leong et al., 2007; Hashimoto et al., 2006).

In Seal applications, two interfaces of the same film may come in intimate contact with each other. Then two heated jaws, will heat, press the two films surfaces together and keep them for a given time (dwell time) and in partially molten state till the seal is formed (Mazzola et al., 2012; Mueller et al., 1998; Hashimoto et al., 2006; Najarzadeh and Ajji, 2014). Measurement of Seal and Hot-tack initiation temperatures and the plateau strengths obtained through sealing process are the main aspect of interest in this study.

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Likewise any physical process there is a limit to the maximum temperature, minimum time and the maximum plateau strength that can be achieved through heat-sealing process which are dependent of thermal and mechanical and melt behavior of used resins (Qureshi et al., 2001; Wool, 1995). The Hot-tack strength and Hot-tack initiation temperature are also functions of the above-mentioned behaviors. The main difference is that the strength, one achieves through Hot-tack is mostly related to the melt behavior of the resin, but in seal the solid mechanical behavior plays more significant role. To the knowledge of the writer there are very few works on the investigation of the Hot-tack initiation and strength of the pure and blended resins (Mazzola et al., 2012; Najarzadeh and Aji, 2014; Hashimoto et al., 2006). Published research works have tried to improve the seal properties of conventional petroleum based resin and existence of detailed study on this behavior for degradable resins is of essential importance. The focus of this work is to show the capabilities of PLA blends to perform as seal layer in packaging in wide range of temperatures and compositions.

2. Experimental

2.1. Materials

The seal grade polylactic acid (PLA) obtained from Natureworks, Cargill Dow LLC, USA, is a copolymer of D&L lactic acid with high D-monomer content and no crystal content (amorphous grade). Also a film grade PLA resin 4032D, from Natureworks as well, has been used for lamination applications. The polycaprolactone (PCL) was purchased from Solvay LLC USA. Some of the material's characteristics are listed in Table 1. Film sample of pure material as well as their blend in a wide range of concentrations 20% to 80% have been used to cover wide operation window in term of mechanical and seal properties. All the samples have been processed in twin-screw extruder (Leistritz model ZSE 18 HP co-rotating) and were made into films using a cast film die. All the films have been drawn from the melt to a thickness of 30 μm for further analysis.

The temperature profile in the twin-screw extruder along the barrel was set at 170/180/190/190 and the die was set to 190 °C. Different blend compositions have been used to prepare the samples. Table 2 give the PLA/PCL ratio in each blend's cast film.

2.2. Rheological characterization

Rheological characterization was carried out using parallel-plate geometry by a constant strain rheometer (MCR 301 Anton Paar, Austria). The experiments were performed in the dynamic mode at 190 °C under nitrogen atmosphere in the range of 0.1 to 100 Hz. The viscosity η^* and storage modulus G' of the polymers were measured and are shown, as a function of frequency. The time sweep test, show thermal instability of PLA resin after 20 min of shearing at 190 °C. The frequency sweep test is taking long intervals for measurements at lower frequencies about 0.01 Hz, which leads to PLA being sheared for more than said 20 min before the instrument measures data at 1 Hz and above. This will cause thermal degradation of the less stable PLA resin in measurement time. To obtain more reliable data points, the test was carried out from higher frequencies to lower frequencies. Latter would let us have more accurate data at higher frequencies. (i.e. The higher number of data point will be measured before we reach the limiting time of around 20 min explained above.)

2.3. Differential scanning calorimetry

TA instrument differential scanning calorimeter (DSC) Q 1000 was used to analyze the thermal behavior of the blends. The heating cycle starts from room temperature and the samples were heated

to 170 °C at a heating rate of 10 °C/min. the samples were kept at 170 °C to remove previous history then cooled to room temperature afterward at the same rate of 10 °C/min and heated again to 170 °C. The changes in melting point of the blends samples were compared to their neat data and their melting behavior was followed for different composition.

Crystallinity values, reported in the graphs, are calculated using a heat of fusion of 136 J/g for fully crystalline poly[ϵ]-caprolactone (Guo and Groeninckx, 2001).

2.4. Scanning electron microscopy (SEM)

The blends samples were molded in epoxy resin then microtomed using an ultra-microtome equipped with a diamond knife at -100 °C and then coated with platinum vapor. The films were Cryo-microtomed in both Machine Direction (MD) and transverse (TD) directions. A high resolution Hitachi S-4700 microscope operated at 2 kV accelerating voltage was employed for FEG-SEM.

2.5. Thermal lamination

To prepare samples for the Seal and Hot-tack experiments, all the samples needed to be protected by a film layer of higher melting material than that of the experimental temperature window. The film chosen for this application was semi-crystalline PLA film, which has a melting point of 168 °C, higher than the maximum sealing temperature of 115 °C. The lamination was carried out using Lab scale thermal laminator (BJ Creation Inc.).

2.6. Mechanical tests

Tensile test were performed to determine the mechanical behavior of the blends. Testing was carried out in accordance to the ASTM D882 on an Instron (Norwood, MA) 3365 universal testing machine with a 500 N load cell. The Young modulus, stress and strain at yield, and stress at break were measured. In order to determine mechanical properties, a crosshead speed of 12.5 mm/min was used.

2.7. Seal and Hot-tack

Lab scale SL100 Lako-Tool instrument was utilized to investigate seal and Hot-tack behavior of the prepared samples. The tests were performed under specifications mentioned in the ASTM F88 and F2029 experimental methods. Metallic jaws covered by Teflon were used and the sealed area was 19.1 mm \times 25.4 mm on sample strips 25.4 mm width \times 330.2 mm length. An average over at least five experiments for each sample was used for each specific temperature. The pressure was set to 0.5 N/mm² and the dwell time fixed for all samples at 1 s. These conditions will allow us to measure the seal properties more precisely for PLA resin, which is not forming very strong bonding through sealing at low dwell times.

3. Results and discussions

3.1. Viscoelastic behavior analysis

Blending of two thermoplastic resins is directly influenced by, their melt viscosities and viscosity ratio ($\lambda = \eta_d/\eta_m$) as well as their interfacial interactions. In blends of poly(lactic acid) and Polycaprolactone, likewise an immiscible blend, final blend properties depend on the morphology of the blend. The final morphology of blend, as will be explained in Section 3.3, is indivisible of their melt rheology and interfacial tension. The melt shear viscosity of PLA and PCL was measured at 190 °C and is illustrated in Fig. 1. Due to PLA thermal degradation, the data below 0.1 Hz are not reported

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