

Improvement of rheological and mechanical properties of PLA by reactive blending with Poly(MMA-g-GMA)

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Abstract:

The aim of this study is to improve the melt strength of Polylactic acid (PLA) using methylmethacrylate-g-glycidylmethacrylate copolymers, Poly(MMA-g-GMA), that was synthesized by reactive blending at different weight fractions of GMA from 6 to 10 %. Copolymers were blended with polylactic acid (PLA) in internal mixer at different weight fractions from 0%, 6% and 8% as chain extender to modify the rheological behavior. The properties of neat PLA and modified PLA were characterized by Differential Scanning Calorimetry (DSC) and Rheometric Mechanical Spectrometer (RMS). The balanced torque was increased by increasing the fraction of copolymer chain extender. The results showed that Poly(MMA-g-GMA) is an effective chain extender for PLA. The glass transition temperature of PLA was also changed by blending with the synthesized copolymer. The blending affected the cold crystallization behavior and melting behavior of PLA, as well. Dynamic moduli also showed higher viscosities that can lead to higher melt strength.

Keywords: PLA; rheological and mechanical properties; reactive blending; P(MMA-g-GMA)

Introduction:

Degradable plastics have attracted increasing attention in recent years because of environmental reasons. Among degradable polymers, poly (lactic acid) or polylactide (PLA) is one of the most important biodegradable and biocompatible polymers [1-3]. Unfortunately, it is difficult to obtain PLA polymers with high molecular weight, which affects the melt viscosity, mechanical properties and thermal properties of the polymer [4]. Up to now, the simplest process to synthesize PLA is direct melt condensation polymerization, which the cost is low. But it is difficult to obtain a high molecular weight in a solvent-free system [5]. Another way to achieve PLA with high molecular weight is to use ring-opening polymerization; however, the cost is very expensive [6].

Using chain extenders to achieve high molecular weight polymers is an effective way. Chain extender has two or more functional groups, which link the low molecular weight pre-polymer into a polymer with higher molecular weight [7]. Typical chain extenders for polyesters, which contain -OH and -COOH groups, are diisocyanates, diepoxides, bisoxazolines, dianhydrides and bisketeneacetals. Diepoxides react with both carboxyl and hydroxyl end groups. However, excessive contents of chain extender can lead to branching or even crosslinking. Various kinds of chain extenders were used for polyesters[7-11].

In this work, Poly methyl methacrylate-co-glycidyl methacrylate (PMMA-co-GMA) copolymer synthesized by continuous bulk polymerization was used in polylactide in melt blending process. The rheological properties and thermal of mixed PLA and modified samples were investigated.

Experimental:

Material:

The copolymer, poly methyl methacrylate-co-glycidyl methacrylate, was synthesized by two method continuous bulk polymerization in the laboratory and grafting the glycidyl methacrylate monomer on Poly methyl methacrylate (that was supplied by LG Acrylic EG920) in a reactive blending process (that is explained the results in the other Poster). And the content of glycidyl methacrylate in the polymer chain extender is about 4%-10% wt. Poly (lactic acid) (PLA) (INGEO 2003D) was supplied by Natureworks LLC.

Preparation of samples:

First of all the copolymers was produced and obtained in solution and melting method (that is completely explained the results and methods in the other Poster), then the copolymers and PLA pellets were dried in a vacuum oven at 55°C and 20mmHg for 24 hours. After that PLA and copolymers that was made in melting method were mixed to same weight percent (8%) and one of the copolymers that was synthesized in solution method was mixed at 6wt%. Then the mixture was blended in a chamber of Brabender internal mixer at 185°C and 60 rpm. The blends were then compress molded into sheets with the dimension needed for Rheological, Mechanical and thermal characterization at 190°C. The data of copolymer's content preparation are in Table 1 and the data of blends' contents are declare in Table2.

Table1. copolymer's content

| Sample | GMA wt.% | PMMA (MMA) wt.% | Copolymerization method |
|--------|----------|-----------------|-----------------------------------|
| PGMS10 | 10% | 90% | Solution Radical Copolymerization |
| PGMM10 | 10% | 90% | Melt grafting Copolymerization |
| PGMM6 | 6% | 94% | Melt grafting Copolymerization |

Table2. PLA blends

| Sample | Copolymer type | Copolymer wt.% |
|-----------|----------------|----------------|
| PLA | - | 0% |
| PLA26(26) | PGMS10 | 6% |
| PLA38(38) | PGMM10 | 8% |
| PLA58(58) | PGMM6 | 8% |

characterization

Differential scanning calorimeter (DSC) measurements were performed with a Mettler DSC under an ultrahigh-purity nitrogen atmosphere. The equipment was calibrated with Aluminum standards. Samples were heated from 25°C to 200°C at a nominal rate of 10°C min⁻¹ and held for 2 min to erase all previous thermal history and then was cooled to 25°C at the rate of 10°C min⁻¹. The samples were again heated at the same rate up to 200°C at the heating rate of 10°C min⁻¹.

Rheological Mechanical Spectroscopy (RMS) measurements were performed with a Antoon Paar MCR302 Parallel Plate Rheometer under an ultrahigh-purity nitrogen atmosphere. Samples were heated to 185°C and dynamic frequency sweep test (strain: 5%; frequency: 0.01 to 600 rad/s and temperature at 190 °C) were subsequently performed to determine the dynamic properties of the materials, using a parallel-plate geometry with 25 mm of diameter.

Results and Discussion:

Rheological properties:

Shear rheological properties of pure PLA and stable blends (up to reaction completion) were measured and compared in terms of complex viscosity modulus *versus* angular frequency as shown in Figure 1.

From Figure 1, a significant increase of the complex viscosity, η^* , in the low frequencies region, is firstly observed with the addition of acrylate copolymers into PLA. This evolution can be analyzed by the chemical reaction which can happen between PLA with the chain extender.

In fact, since acrylate copolymers has single or multiple reactive end groups, several polymer chains could be chemically bounded with one or more copolymer. In this way, a chain extended and branched structure could be developed and gelation may be happen but Figure 2 is shown that there is no solid like structure according to G' (Storage moduli) versus frequency specially at low frequencies so there is no gelation.

Secondly, a pronounced shear thinning behavior was detected. An increase of the long chain branching amount, a broadening of the molar mass distribution and a shift of the chains relaxation time for PLA to higher values were resulted. The modified PLA exhibited thus a typical feature of a mixture of linear and randomly branched polymers.

According to other papers and results of them we can conclude that the Elongational viscosity is increased in this situation and in order to that we can find out the melt strength of extended polymer is improved.

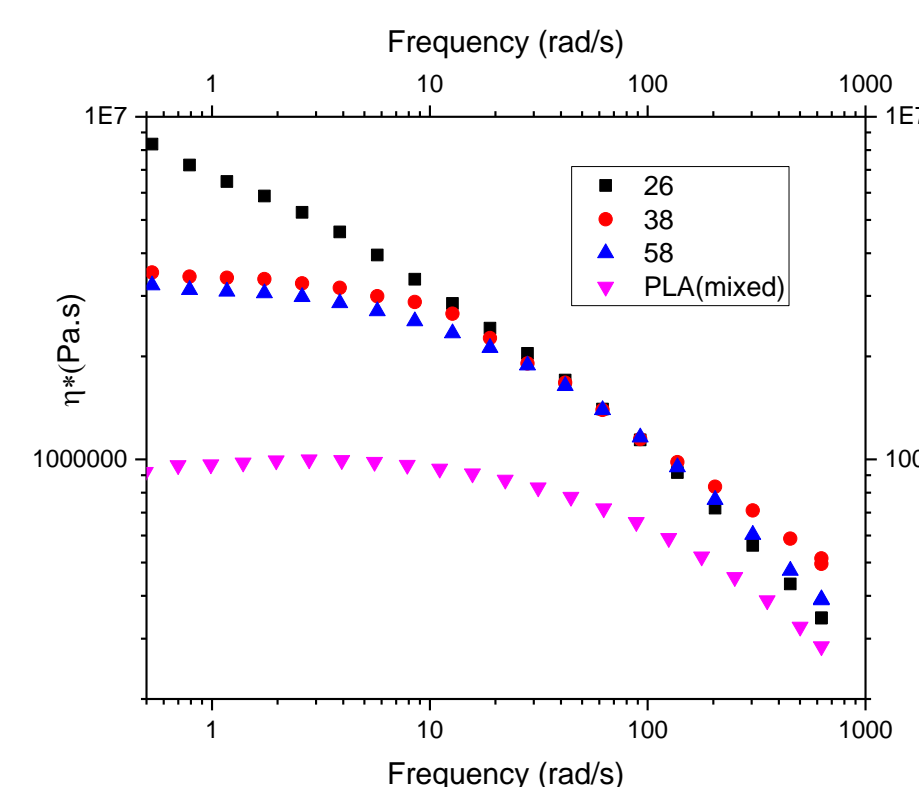


Figure1. Frequency versus complex viscosity

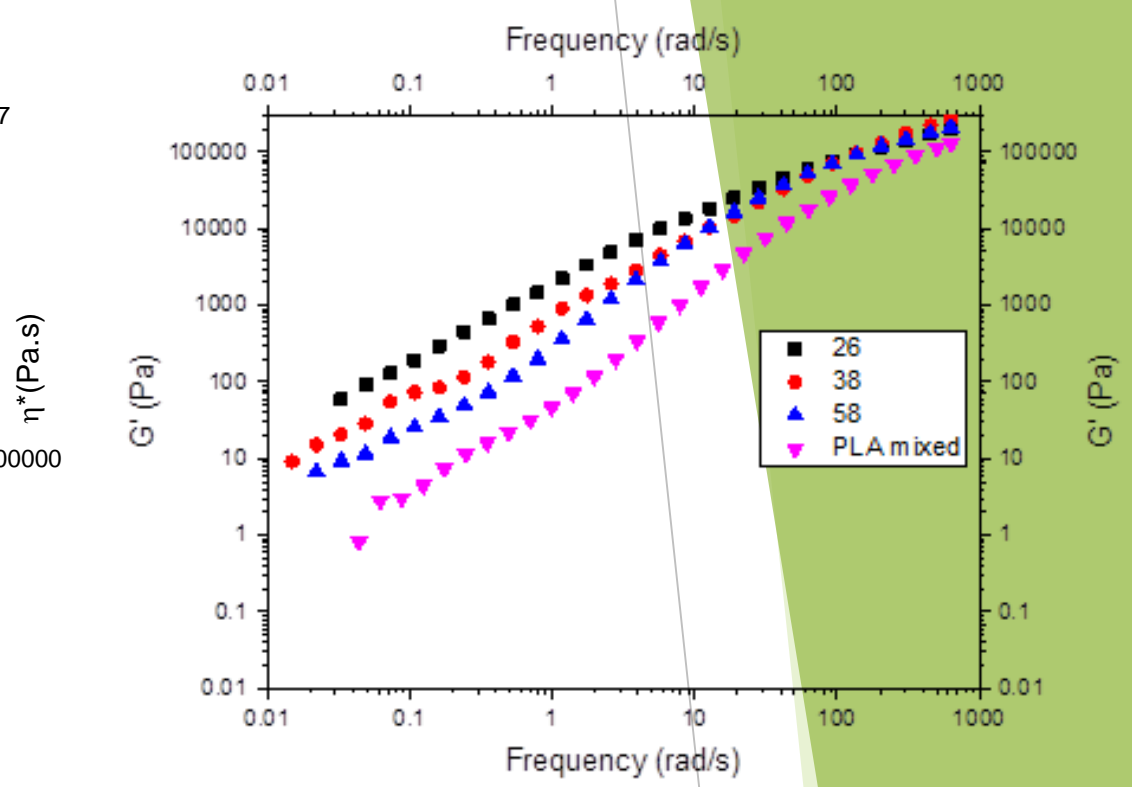


Figure2. Frequency versus storage moduli

Mechanical properties:

The tensile properties of the PLA blends with different content of chain extenders were studied, as shown in Figure 3. It can be seen from Figure 3 that strain of the PLA blend increases obviously with addition of chain extenders while the stress almost keeps constant. Elongation at break was increased more when adding chain extender was synthesized with solution method, Even though the content of chain extender is lower, efficiency of grafting(copolymerization) in this method is very high then long chain branching will be more obvious. The 2nd important subject in Figure 3 is changing the break mechanism from brittle for pure PLA to ductile for the other blends. Though the Elongation at break wasn't increase so much, the toughness proceeding is undeniable.

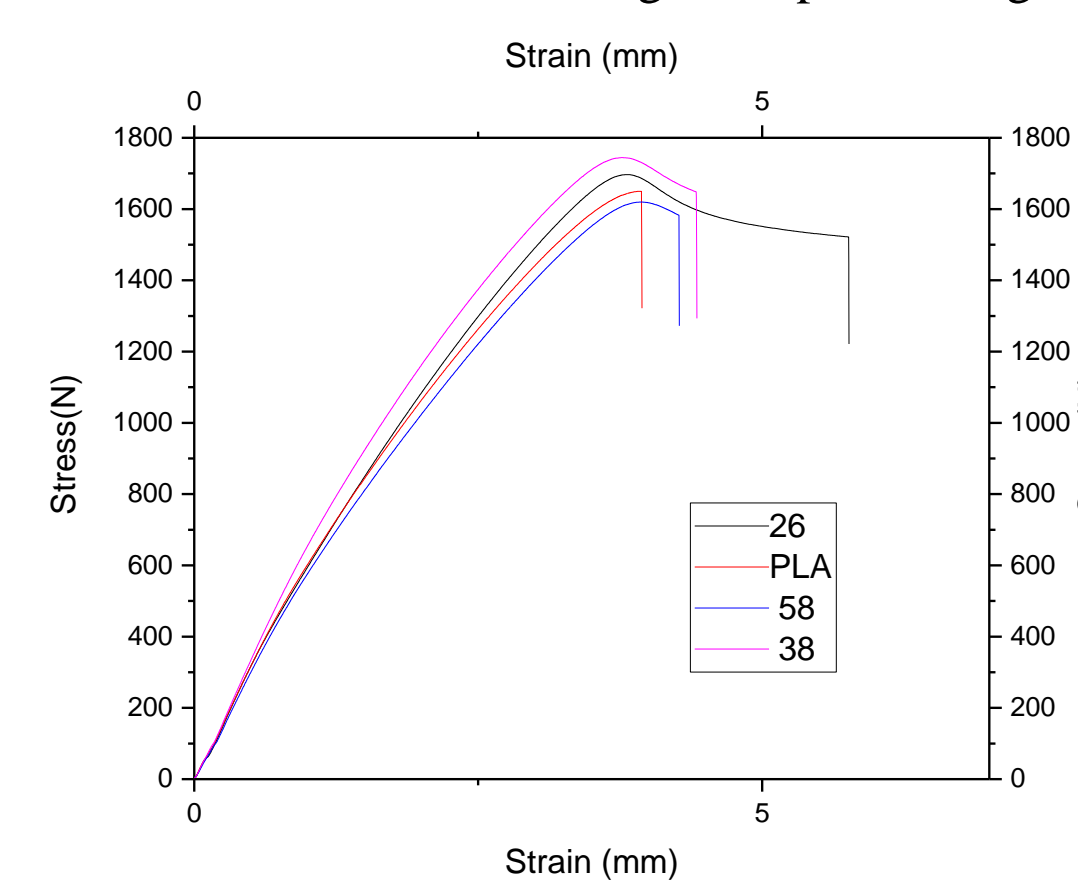


Figure3. Strain-Stress of blends

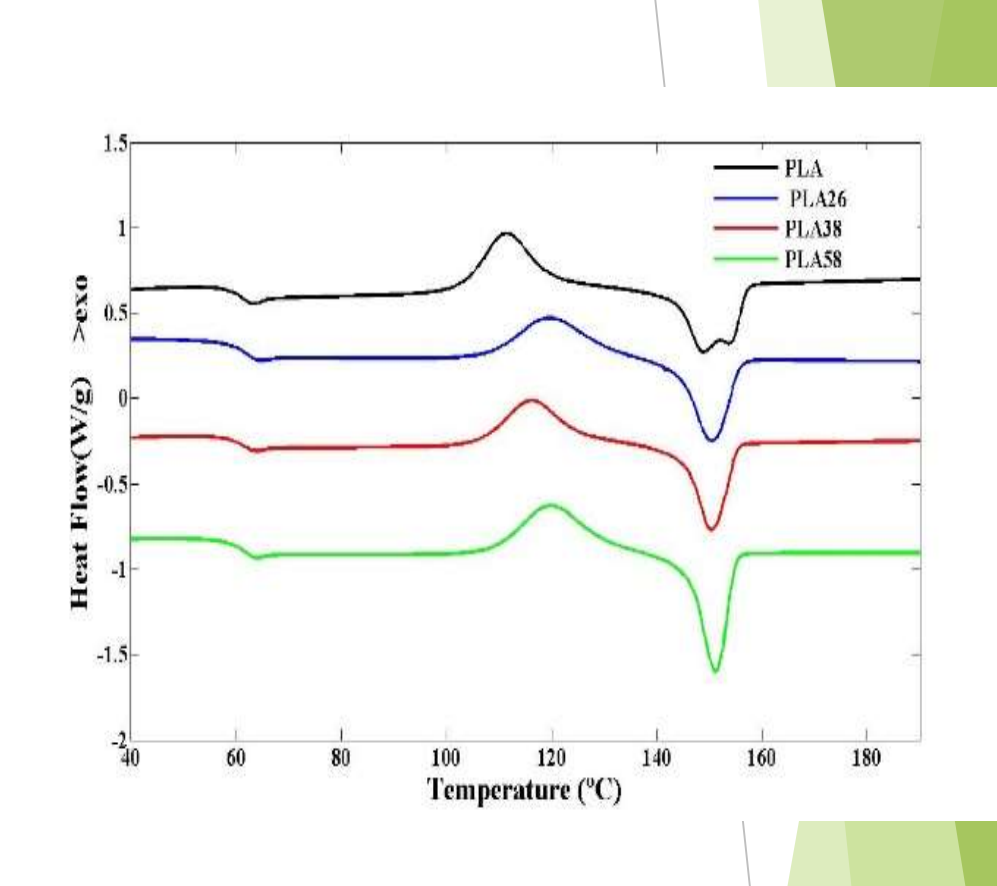


Figure4. DSC heat flow versus temperature

Thermal properties:

The thermal properties was measured by DSC and it was determined 3 point first of all, according to the T_g that is shown in the Figure 4 these blends are single phase and are compatible after that crystallinity temperature (T_c) changed and increased maximum about 15^o C with addition of chain extenders and crystallinity weight percent is decreased because of decreasing of arrangement after the reaction of chain extenders and PLA.

Conclusion:

Bio-based and biodegradable poly (lactide) (PLA) is an aliphatic polyester with notable brittleness, low melt strength and melt properties. The carboxylic end group of PLA can be react with an epoxide group of GMA that is grafted to PMMA and extending of PLA's chain would be happen. This copolymer was produced as chain extender in two different method and then was blended with PLA. The ductility of PLA can be improved by reactive blending with a chain extender. The melt strength and storage moduli and complex viscosity will be improved too. These improvements are more obvious for chain extender that is prepared with solution method because of more efficiency of this method for presence more epoxide group in copolymer (chain extender). This reaction make little changes in crystallization percentage, crystallization temperature and glass transition temperature.

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