



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

<sup>1</sup>\*Karimi, A., <sup>2</sup>Garmabi, H., <sup>3</sup>Javadi, A.

<sup>1</sup> Master of Science holder, Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, 424, Hafez Ave., Tehran, Iran

<sup>2</sup> Professor, Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, 424, Hafez Ave., Tehran, Iran

<sup>3</sup> Assistant Professor, Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, 424, Hafez Ave., Tehran, Iran

\*(corresponding author: amir\_karimi@aut.ac.ir)

**Abstract-** The aim of this study is to improve the melt strength of Poly(lactic acid) (PLA) using methylmethacrylate-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 poly(lactic acid) (PLA) in internal mixer at different weight fractions including 0, 6 and 8% as chain extender to modify the rheological behavior. 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 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. Generally speaking, our results showed that Poly(MMA-g-GMA) is an effective chain extender for PLA.

**Keywords** – PLA, rheological and mechanical properties, reactive blending, P(MMA-g-GMA)

### I. 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]. 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 [2].

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 [3]. 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 [3].

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.

### II. EXPERIMENTAL

#### Materials

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.

### Sample preparation

First of all the copolymers was produced and obtained in solution and melting method 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.

TABLE I: COPOLYMER'S CONTENTS

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

TABLE II: PLA BLENDS' CONTENTS

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

## III. RESULTS AND DISCUSSION

### 1. Rheological Properties

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

From Figure1, a significant increase of the complex viscosity,  $\eta^*$ , in the low frequencies region, is firstly observed with the addition of acrylate copolymers into PLA.

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 happened 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.

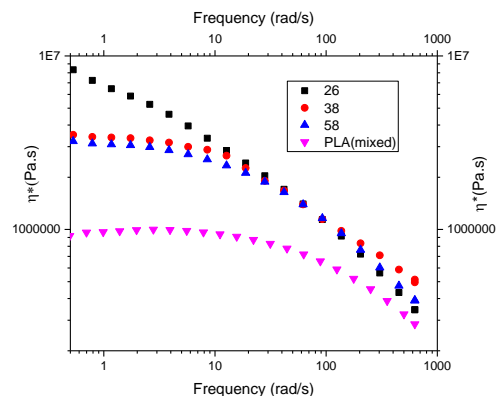


Fig. 1: Frequency versus complex viscosity

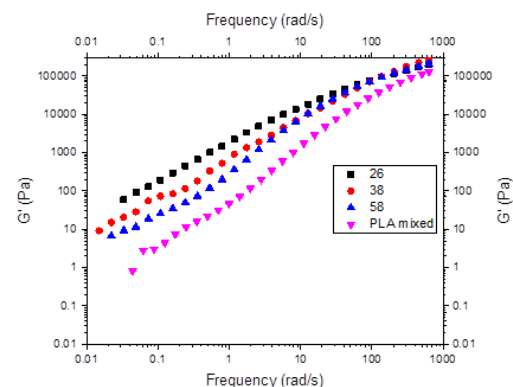


Fig. 2: Frequency versus storage moduli

### 2. Thermal Properties

The thermal properties was measured by DSC and it was determined 3 point first of all, according to the Tg that is shown in the Figure 4 these blends are single phase and are compatible after that crystallinity temprature (Tc) changed and increased maximum about 15°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.

## IV. 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 melt strength and storage moduli and complex viscosity will be improved too. This reaction make little changes in crystallization percentage, crystallization temperature and glass transition temperature.

## REFERENCES

- [1]. R. E. Drumright, P. R. Gruber, and D. E. Henton, Poly(lactic Acid Technology), *Adv. Mater.*, 2000, 12(23), 1841-1846.
- [2]. N. Whiteman, *Polymers, Laminations and Coatings Conference*, Chicago, IL, 2000, 631.
- [3]. J. Tuominen, J. Kylmä, J. Seppälä. Chain extending of lactic acid oligomers. 2. Increase of molecular weight with 1, 6-hexamethylene diisocyanate and 2, 2-bis(2-oxazoline). *Polymer* 2002; 43: 3-10