Determination of Molecular Weight and Molecular Weight Distribution of Poly(lactic acid) by Dynamic Mechanical Properties of Polymer in Melted State

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Abstract

Molecular weight and its distribution of polymers are important factors for polymer processing and mechanical properties. This research aims to determine molecular weight and its distribution of PLA grade 4043D , 3052D and 2003D in melted state by DMA. Experiment data from DMA is analyzed by reptation model to define a relationship between modulus and molecular weight. Additionally, Tuminello model is used to define molecular weight distribution. Finally, the results from such technique are compared with those from GPC. According to the comparison, peaks of molecular weight distributions predicted by DMA and GPC of PLA grade 4043D and 2003D are almost overlap. On the other hand, PLA grade 3052D peaks are a little shifted, therefore molecular weight average predicted by DMA are lower than by GPC.

Purpose

To determine molecular weight and molecular weight distribution of Poly(lactic acid) by Dynamic Mechanical Properties of polymer in melted state

Introduction

In polymer processing industrial, different mechanical properties and flow properties are typically use, such as Blown film , Extrusion and Injection molding. As is well known, both properties of polymer have a close relationship with the molecular weight and its distribution. However, popular molecular characterization technique, such as gel permeation chromatography (GPC) requires solution of the polymer and more time consuming. Polymer rheologists have therefore been work to establish a method of obtaining MWD for melted polymer from rheological measurement. This research aims to determine molecular weight and its distribution of Poly(lactic acid) because Poly(lactic acid) is biodegradable

Theory

Molecular theory

Reptation model (Entanglement) : Reptation model was developed by de Gennes , Doi ,and Edward. The topological constraints imposed by neighboring chains on a given chain restrict its motion to a tube-like region called the confining tube. An entangled chain diffuses along its confining tube in away analogous to the motion of a snake or a worm. See Figure 1

The entanglement strand of N_e monomers relaxes by Rouse motion with relaxation time τ_e ($\tau_e = \tau_0 N_e^2$).

The longest relaxation time in this model is the reptation time required for the chain to escape from its tube.

$$\tau_{rep} = 6\tau_e(\frac{N}{N_e})^3 \text{ , } \eta \sim N^3$$

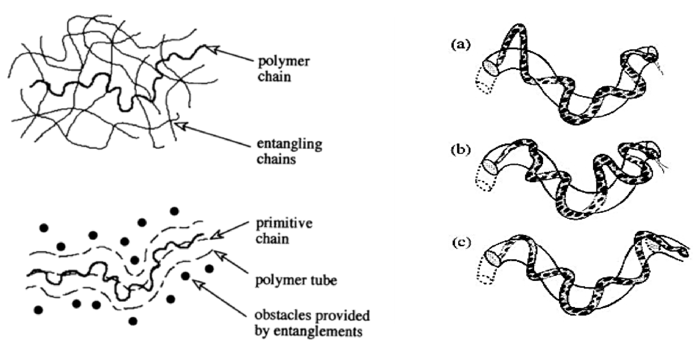

Figure 1 : Reptation model

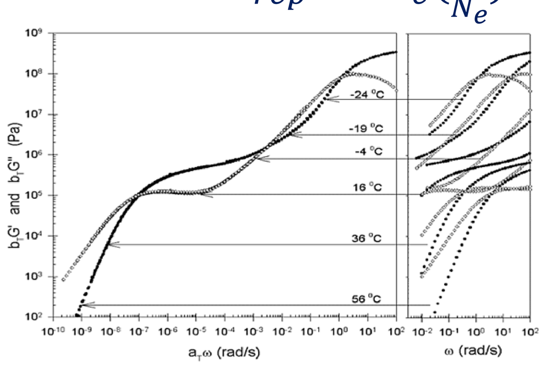

Figure 2 : Master graph (Time-Temperature superposition)

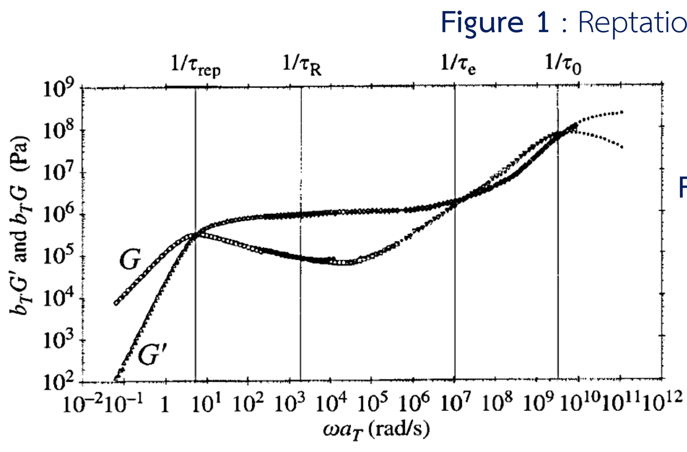

Figure 3 : Master graph (ref 25 °C) of 1,4-polybutadiene

Molecular weight distribution

Tuminello model : Tuminello developed a model to estimate the molecular weight distribution from storage modulus in the terminal and plateau zone. Tuminello made an assumption that in polymer melts all relaxed chains , at any frequency , would act as a solvent for all the longer chains , which are unrelaxed

$$I(M_i) = 1 - W_u = 1 - \sqrt{G'(\omega)/G^0{}_N}$$: $I(M_i)$ is cumulative weight fraction

Thus

$$MWD = \frac{d(I(M))}{d(logM)}$$

To convert $I(M)$ from ω scale to molecular weight scale , the following function is employed.

$\tau = 1/\omega = kM^a$: k and a are constant

Experiment

Material	Poly(lactic acid) grade 4043D , 3052D ,and 2003D produced by NatureWorks LLC
Method	Oven PLA at 60 °C for 6 hours → Compress PLA by compression molding at 180 °C , Pre-heated 2 min , Full-pressing 2 min ,and Cooling 5 min

Test by Dynamic Mechanical Analyzer

Figure 4 : DMA (MCR 302) , Anton Paar

The torsional shear mode (parallel plates) is used with the dynamic motor on molded disks 25-mm in diameter and 1-mm thick

Amplitude sweep : LVE Range
Strain 0.01 – 100 %
Frequency 300 rad/s
Temperature 80 °C and 180 °C

Frequency sweep
Strain 0.1 %
Frequency 0.1-300 rad/s
Temperature 80 °C , 100 °C , 120 °C , 140 °C , 160 °C ,and 180 °C

Temperature sweep
Strain 0.01 – 20 %
Frequency 10 rad/s
Temperature 180 °C to 50 °C
Heating rate 2 °C/min

Result

Frequency sweep : The frequency is varied while the amplitude of the deformation is kept constant. For the analysis the storage and loss modulus are plotted against the frequency. The data will describe the behavior of the samples. See Figure 5 , 6 ,and 7

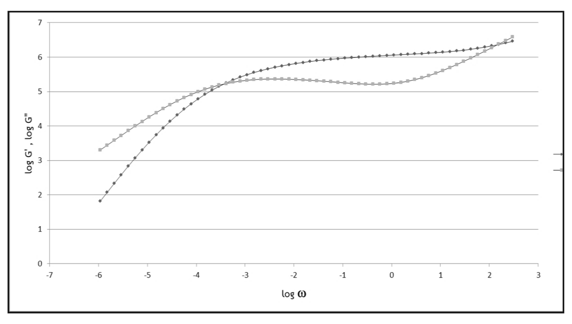

Figure 5 : Frequency sweep PLA 4043D

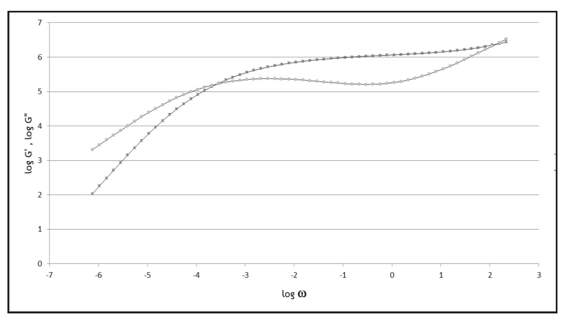

Figure 6 : Frequency sweep PLA 2003D

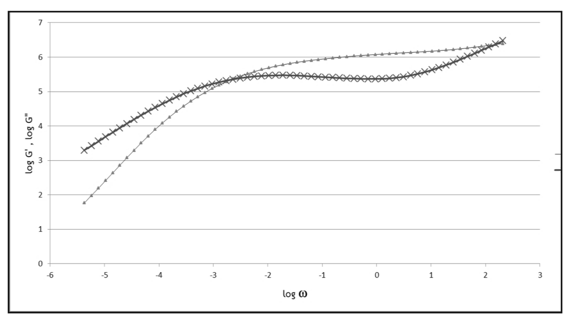

Figure 7 : Frequency sweep PLA 3052D

To convert ω scale to molecular weight scale , this work analyzes from reptation model that uses a=3.4. it has been found that τ=1.02×10$^{-13}M^{3.4}$ at reference temperature 80 °C

Determination of molecular weight distribution is analyzed by Tuminello model

(1) Fit graph $\sqrt{G'(\omega)/G^0{}_N}$ by function : $F(X) = \sum_{i=1}^{n}(\frac{A_i}{2})(1 + \tanh(B_i(X + C_i))$ where $X = \log\omega$

(2) Convert ω scale to molecular weight scale

(3) Molecular weight distribution : $MWD = \frac{d(I(M))}{d(logM)}$

Molecular weight distribution of PLA 4043D , 2003D ,and 3052D. See Figure 8 , 9 ,and 10

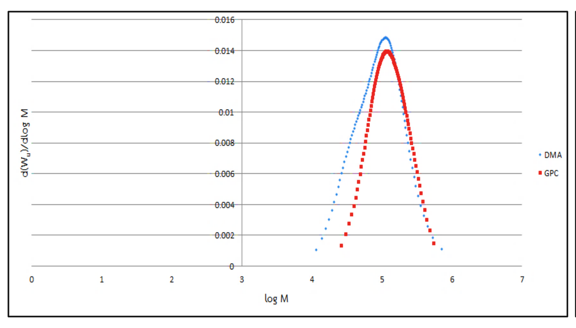

Figure 8 : MWD PLA 4043D

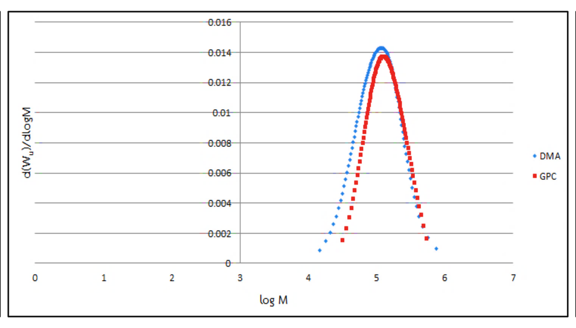

Figure 9 : MWD PLA 2003D

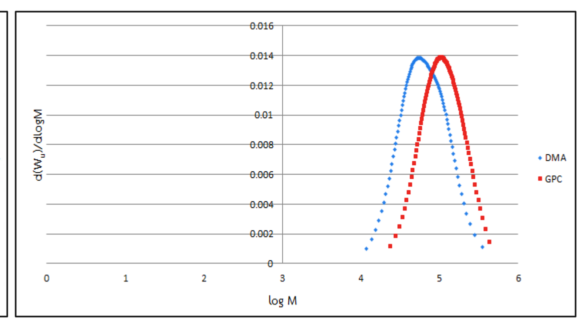

Figure 10 : MWD PLA 3052D

Determination number average molecular weight is analyzed by characteristic relaxation times that can be evaluated from the terminal relaxation. The number-average relaxation time can be obtained from the intersection of the G'' terminal regime with $G^0{}_N$.

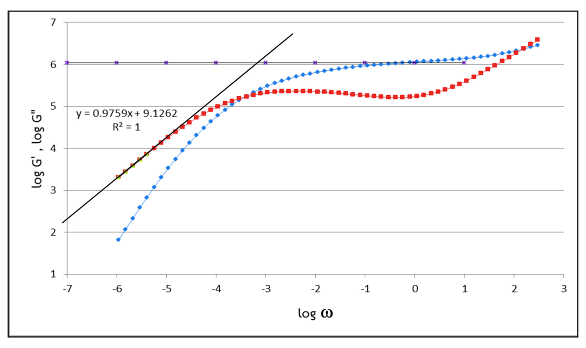

Figure 11 : intersection of the G'' with $G^0{}_N$ PLA 4043D

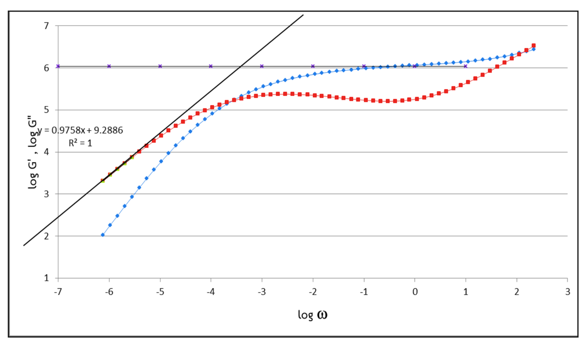

Figure 12 : intersection of the G'' with $G^0{}_N$ PLA 2003D

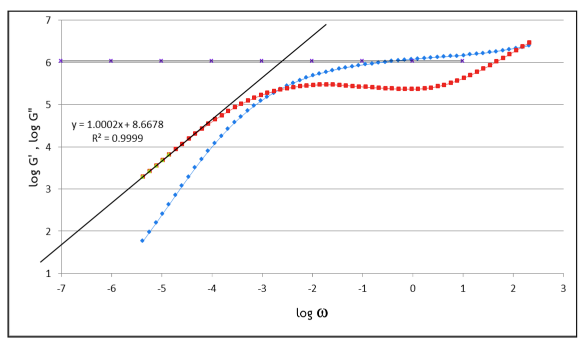

Figure 13 : intersection of the G'' with $G^0{}_N$ PLA 3052D

From figure 11 , 12 ,and 13 can determine number-average molecular weight of PLA 4043D , 2003D ,and 3052D respectively. Weight-average molecular weight will be calculated by relationship between average molecular weight and standard deviation of distribution (σ) : $\frac{M_w}{M_n} = \frac{\sigma^2}{M_n{}^2} + 1$. Show in Table I

Table I : Data of GPC and DMA

PLA Grade	GPC			DMA		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
4043D	97,837	154,378	1.58	96,643	151,180	1.56
3052D	85,590	130,215	1.52	67,498	91,564	1.36
2003D	107,099	162,680	1.52	105,891	158,900	1.50

Conclusion

This method shows that molecular weight and molecular weight distribution of PLA 4043D and 2003D are similar to GPC , except PLA 3052D.

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