JAIST Repository

https://dspace.jaist.ac.jp/

Title	ポリ乳酸における成形加工条件と力学特性の関係
Author(s)	黄,瞳
Citation	
Issue Date	2016-03
Туре	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/13528
Rights	
Description	Supervisor:山口 政之,マテリアルサイエンス研究科 ,博士



Japan Advanced Institute of Science and Technology

Relation between Processing Conditions and Mechanical Properties for Poly(lactic acid)

Tong Huang

Japan Advanced Institute of Science and Technology

Doctoral Dissertation

Relation between Processing Conditions and Mechanical Properties for Poly(lactic acid)

by

Tong Huang

Supervisor: Prof. Dr. Masayuki Yamaguchi

School of Materials Science Japan Advanced Institute of Science and Technology

March 2016

Referee-in-chief :	Professor Dr. Masayuki Yamaguchi Japan Advanced Institute of Science and Technology
Referees :	Associate Professor Dr. Tatsuo Kaneko Japan Advanced Institute of Science and Technology
	Associate Professor Dr. Kazuaki Matsumura Japan Advanced Institute of Science and Technology
	Associate Professor Dr. Ken-ichi Shinohara Japan Advanced Institute of Science and Technology
	Associate Professor Dr. Hiroki Takeshita University of Shiga Prefecture

Relation between processing conditions and mechanical properties for poly(lactic acid)

1340004 TONG, HUANG

Among biodegradable polymers, poly(lactic acid) PLA has received much attention in recent years. PLA is a polymer obtained from renewable resource. PLA shows high rigidity, high transparency, good biocompatibility, good gas-barrier properties, and optical activity. It is generally understood that PLA shows similar mechanical properties to polystyrene. Moreover, a recent development of the production method enhances the cost-performance greatly. Therefore, PLA is a candidate to replace of petroleum-based plasics. However, for a practical usage, considerable efforts will be further required to overcome the following defects; poor melt elasticity, slow crystallization rate, and mechanical brittleness. In order to enhance the properties of PLA and extending its applicable fields, a number of researches will have to be conducted.

In this thesis, effect of the addition of poly(ethylene glycol) terminated by benzoate PEG-BA on the crystallization behavior and dynamic mechanical properties of PLA is studied as compared with poly(ethylene glycol) PEG-OH. It is found that PEG-BA is miscible with PLA and shows good plasticizing effect. Because PEG-OH having the same degree of polymerization is immiscible with PLA, the end group in PEG-BA, *i.e.*, benzoate, plays an important role in the miscibility. Furthermore, PEG-BA does not induce the PLA degradation at melt-processing, whereas PEG-OH leads to the hydrolysis degradation. Finally, the addition of PEG-BA pronounces the crystallization rate of PLA at low crystallization temperatures and thus enhances the degree of crystallinity at conventional processing. Consequently, the temperature dependence of dynamic mechanical properties is similar to that for isotactic polypropylene.

Moreover, the effect of processing conditions on mechanical properties of amorphous PLA is studied considering the chain packing. It is found that the samples cooled in the temperature range from 60 to 80 °C, that is, slightly higher than the glass transition temperature T_g , shows ductile behavior with a low brittle-ductile transition temperature. Furthermore, the samples obtained by prolonged cooling at 56 °C also show ductile behavior, whereas a shorter cooling period at the same temperature provides a brittle product. Even for the samples quenched at 40 °C, they shows ductile behavior after the exposure to post processing annealing operation at 60 °C; that is, the strain at break is larger than 300 %. This is an anomalous phenomenon for a glassy polymer. The dynamic mechanical analysis and thermal characterization revealed that the ductile samples show slightly higher T_g than the brittle ones, presumably due to high packing density of polymer chains. Moreover, it is found from infrared spectroscopy that the ductile samples show strong absorbance at 1267 cm⁻¹, ascribed to high energy gauche-gauche *gg* conformers. Following the classic Robertson's descriptions of plastic flow, it is concluded that the increase in the gauche-gauche *gg* conformers, which shows the conformation change under a low stress level, reduces the critical onset stress for shear yielding, leading to ductile deformation. The results demonstrate that the mechanical toughness of PLA can be controlled by the cooling conditions during processing and the post-processing annealing operation.

Keywords: Poly(lactic acid), Plasticization, Crystallization, Mechanical properties, Processing conditions.

Preface

Biomass-based polymeric materials have received much attention because of the concerns about the global environment and the decrease in petroleum resources. Among them, poly(lactic acid) has been researched intensively due to its attractive advantages. However, the drawbacks of poly(lactic acid), such as low crystallization rate and brittleness, limit its application.

In this thesis, the crystallization behavior and mechanical properties of poly(lactic acid) are studied. In particular, the effect of processing conditions at compression-molding on the structure and properties of poly(lactic acid) is focused. I hope that this study provides useful information to understand the physical properties from academic viewpoints and contributes to expanding the application of poly(lactic acid) in industry.

Tong Huang

Contents

Chapter 1 General Introduction1
1.1 Biomass-based plastics ······1
1.2 Poly(lactic acid)
1.3 Recent researches on modification techniques for poly(lactic acid)5
1.3.1 Enhancement of crystallization rate ······5
1.3.1.1 Nucleating agents ······6
1.3.1.2 Plasticizers ······8
1.3.2 Improvement of toughness ······10
1.3.2.1 Copolymerization ·····11
1.3.2.2 Blending with flexible polymers or rubbers ······
1.4 Miscibility of polymer blends ·····13
1.4.1 Thermodynamics of polymer blends ······13
1.4.2 Solubility parameter ·····17
1.5 Objectives of this study19
References ······21
Chapter 2 Crystallization and Plasticization27
2.1 Introduction ·····27
2.1.1 Crystallization of polymer27
2.1.2 Crystallization from the melt27
2.1.3 Crystallization of polymer blend ······34
2.1.4 Objectives

2.2 Experimental ······	38
2.2.1 Materials ······	38
2.2.2 Sample preparation	40
2.2.3 Measurements ······	41
2.3 Results and discussion ······	43
2.3.1 Thermal stability and rheological properties	43
2.3.2 Linear growth rate of spherulites	48
2.3.3 Dynamic mechanical properties	54
2.3.4 Thermal properties ······	61
2.3.5 Tensile properties ······	65
2.4 Conclusion ······	67
References ······	68
Chapter 3 Impact of Processing Condition on Tensile Properties	71 71
Chapter 3 Impact of Processing Condition on Tensile Properties? 3.1 Introduction	71 71
Chapter 3 Impact of Processing Condition on Tensile Properties	71 71 71
Chapter 3 Impact of Processing Condition on Tensile Properties7 3.1 Introduction	71 71 71 72
Chapter 3 Impact of Processing Condition on Tensile Properties	71 71 71 72 76
Chapter 3 Impact of Processing Condition on Tensile Properties 3.1 Introduction 3.1.1 Mechanical tests 3.1.2 Stress-strain behaviors of polymers 3.1.3 Poisson ratio 3.1.4 Stress-strain curve	71 71 72 76 78
Chapter 3 Impact of Processing Condition on Tensile Properties 3.1 Introduction 3.1.1 Mechanical tests 3.1.2 Stress-strain behaviors of polymers 3.1.3 Poisson ratio 3.1.4 Stress-strain curve 3.1.5 Polymer fracture	71 71 72 76 78 30
Chapter 3 Impact of Processing Condition on Tensile Properties 3.1 Introduction 3.1.1 Mechanical tests 3.1.2 Stress-strain behaviors of polymers 3.1.3 Poisson ratio 3.1.4 Stress-strain curve 3.1.5 Polymer fracture 3.1.6 Toughening mechanism	71 71 72 76 78 30 35
Chapter 3 Impact of Processing Condition on Tensile Properties 3.1 Introduction 3.1.1 Mechanical tests 3.1.2 Stress-strain behaviors of polymers 3.1.3 Poisson ratio 3.1.4 Stress-strain curve 3.1.5 Polymer fracture 3.1.6 Toughening mechanism 3.1.7 Objectives	71 71 72 76 78 80 35 36
Chapter 3 Impact of Processing Condition on Tensile Properties 3.1 Introduction 3.1.1 Mechanical tests 3.1.2 Stress-strain behaviors of polymers 3.1.3 Poisson ratio 3.1.4 Stress-strain curve 3.1.5 Polymer fracture 3.1.6 Toughening mechanism 3.1.7 Objectives 3.2 Experimental	71 71 72 76 78 80 85 36 37
Chapter 3 Impact of Processing Condition on Tensile Properties7 3.1 Introduction	71 71 72 76 78 80 85 85 85 85 85 85
Chapter 3 Impact of Processing Condition on Tensile Properties 3.1 Introduction 3.1.1 Mechanical tests 3.1.2 Stress-strain behaviors of polymers 3.1.3 Poisson ratio 3.1.4 Stress-strain curve 3.1.5 Polymer fracture 3.1.6 Toughening mechanism 3.1.7 Objectives 3.2 Experimental 3.2.1 Materials 3.2.2 Sample preparation	71 71 72 76 78 80 85 86 85 86 85 86 87 87

3.3 Results and discussion ·····	91
3.3.1 Effect of cooling temperature •••••••	91
3.3.2 Effect of cooling period ·····	104
3.3.3 Effect of crystallinity	113
3.3.4 Effect of post-processing annealing	·····117
3.3.5 Effect of ambient temperature	119
3.4 Conclusion ·····	······122
References ·····	123
Chapter 4 General Conclusions	127
Achievements	131
Abstract of Minor Research Theme	135
Acknowledgement	146

Chapter 1

General Introduction

1.1 Biomass-based plastics

Nowadays, polymeric materials are used everywhere from our daily life products, such as packaging, kitchen stuffs, clothes, etc., to high technology goods including mobile phone, portable-device, optical films, sensor parts, and so on. They attract more and more attentions because of their advantages such as light-weight, good cost-performance, manufacture flexibility, etc. [1,2].

Conventional plastics are, however, not easy to be decomposed in natural environment due to their stable chemical structure. Therefore, the disposal of wasted plastics becomes a severe problem. Moreover, the total amount of plastics disposed into the ocean is estimated to be several hundreds of thousands tons every year. Such plastics that accumulated in the ocean harm the ocean biology system [2,3]. Therefore, the attentions paid to the biodegradable plastics are increasing.

Being different from conventional petroleum-based plastics, biodegradable plastics can be decomposed in a relatively short period by bacteria in soil, which provides a low burden on natural environment. Although biodegradable plastics can be synthesized from crude oil, so-called biomass-based plastics produced from renewable biomass resources, *e.g.*, poly(lactic acid) PLA, poly(ϵ -caprolactone) PCL, poly(3-hydroxybutyrate) PHB, poly(butylene succinate) PBS, cellulose esters, etc., attract much more interests recently due to the rising awareness of the depletion of petroleum resources. The main properties of some biodegradable polymers are summarized in Table 1-1 [4].

	PLA	РНВ	PBS	PCL
Glass transition temp. (°C)	60-65	2-5	-30	-60
Melting point (°C)	170-180	168-172	115	60
Tensile modulus (MPa)	2800	1700-2000	240	41
Tensile stress at break (MPa)	45	24-27	57	41
Strain at break (%)	3	6-9	700	900

Table 1-1 Properties for biodegradable polymers [4]

Carbon neutrality is the typical property of biomass-based plastics. Carbon neutrality of a material means that the absorption amount of carbon dioxides CO_2 during the production of this material is equal to the emission amount of that during the degradation. In other words, the concentration of CO_2 does not change in this production-degradation cycle. Moreover, biomass-based plastics show not only biodegradability, but also some their attractive properties such as biocompatibility. Nowadays, therefore, researches on developing biomass-based plastics having superior performance are being carried out intensively [2-5].

1.2 Poly(lactic acid)

Poly(lactic acid) or polylactide (PLA) is a thermoplastic polyester which belongs to the family of aliphatic polyesters. PLA is derived from renewable resources, such as corns, sweet potatoes, etc. The raw material for the synthesis is lactic acid which can be produced by fermentation [6,7]. Basically, PLA can be synthesized by direct condensation polymerization although the molecular weight of the material obtained is below 5,000. Currently, therefore, high molecular weight PLA is commercially produced via the lactide ring-opening polymerization route [8], as shown in Fig. 1-1.



Fig. 1-1 Scheme for synthesis of poly(lactic acid) [7]

There are two kinds of optical isomer, L- and D-lactic acid, because of the existence of an asymmetric carbon atom in lactic acid. The polymeric products coming from pure L- or D-lactic acid are denoted as PLLA and PDLA, respectively (Fig. 1-2). Generally, commercial PLA is a copolymer of L-lactic acid and D-lactic acid. Because the majority of lactic acid from biomass sources exists in L-form, PLLA is the main fraction in commercial PLA.



Fig. 1-2 Stereochemistry of (a) PLLA and (b) PDLA

PLLA is a crystalline polymer with a melting point T_m locating in the range of 170-178 °C and a glass transition temperature T_g of around 60 °C [6]. PLLA shows high rigidity, high transparency in amorphous state, good biocompatibility, etc. Because of these advantages, PLLA has drawn great attention in recent years. It is generally understood that PLLA shows similar mechanical properties to polystyrene. Moreover, because of the light transmittance, PLLA is a candidate polymeric material to replace polypropylene PP as transparent films and sheets [3,9-11].

For a practical usage, however, considerable efforts will be further required to overcome the following defects for PLA; poor melt elasticity, slow crystallization rate, and mechanical brittleness [11,12]. In order to enhance these properties, which is necessary for expanding its applicable fields, a number of researches will be still required.

1.3 Recent researches on modification techniques for poly(lactic acid)

1.3.1 Enhancement of crystallization rate

It is well-known that the nucleation and crystallization rate of PLA in the homogeneous state are low. Therefore, PLA is not able to be crystalized sufficiently at conventional processing condition. Due to the low level of crystallinity, mechanical properties of PLA are similar to those of amorphous polymers when the ambient temperature is below T_g . However, the service temperature is limited because of its low T_g , which is a serious problem for PLA.

Generally, there are two steps in crystallization for polymers, *i.e.*, nucleation and crystal growth. Numerous efforts to improve the crystallization rate have been made mainly by two approaches; one is to increase the nucleation by the addition of nucleating agents. The other is to enhance the crystal growth which can be enhanced by plasticizers.

1.3.1.1 Nucleating agents

A nucleating agent can reduce the nucleation induction period and increase the nucleation density. Consequently, crystallization rate is greatly enhanced.

One of the most famous nucleating agents is talc, *i.e.*, a silicate compound having a plate-like shape. It is often used as filler for polypropylene PP. Because of the nucleating ability, the compounds with talc need a shorter processing time [13]. Talc is also found to be an effective physical nucleating agent for PLA. Li and Huneault reported that PLA having 1 % talc can crystallize sufficiently at a cooling rate of $10 \,^{\circ}$ C/min [14]. Harris and Lee reported that the addition of 2 % talc to PLA shortened

the crystallization half-times and resulted in a great increase in crystallinity even in a short processing time [15]. Moreover, the optimum temperature for crystallization during the cooling processing shifted from 100 to 120 °C when talc was present in PLA [16].

Ikada et al. reported that two enantiomeric chains can do co-crystallization, which is called stereocomplex [17]. The stereocomplex crystal is composed of equal amounts of PLLA and PDLA chains. The melting point of stereocomplex is about 50 °C higher than that of PLA homocrystal. Due to its high melting point, the stereocomplex can act as a nucleating agent for PLA homocrystal during cooling process. Brochu et al. reported that the crystallinity of PLA containing stereocomplex is higher than that of pure PLA, demonstrating the nucleating effect of stereocomplex crystals [18]. Schmidt and Hillmyer studied the nucleation effect of stereocomplex for PLLA crystallization. They found that stereocomplex showed an outstanding nucleating efficiency compared with talc. However, the high nucleation density does not always mean the high crystallinity of PLA [19]. This phenomenon was related to the tethering effect of stereocomplex crystallites, reducing the PLLA chain mobility. Yamane and Sakai investigated the effect of molecular weight of PDLA on the nucleation and crystallization of PLLA. They found that PDLA having low molecular weight provide a

higher stereocomplex crystallinity than high molecular weight PDLA, resulting in a high nucleating efficiency for PLLA [18,20,21].

Besides mineral compounds and stereocomplex, other substances have been also investigated as the potential nucleating agents for PLA. Up to now, clay [22-24], carbon nanotube [25-27] and low molecular weight aliphatic amides [28] have been known to exhibit the nucleation ability for PLA [29-32]. Recently, high efficient nucleating agents such as uracil [33] and zinc citrate [34] were reported. Both of them were found to possess an effective ability of inducing a higher crystallization temperature of PLA under cooling.

1.3.1.2 Plasticizers

Plasticizers play an important role in polymer industry [35]. They are often added into polymers to lower T_g , for increasing the ductility and improve processability. By the addition of a plasticizer, polymers have higher chain mobility, which is responsible for enhanced linear growth rate of crystals.

For PLA, the most widely investigated plasticizer is poly(ethylene glycol) PEG [36-39]. Sheth et al. firstly prepared a blend of PLLA with PEG and found that PEG enhances the crystallization rate of PLLA. They also reported that the blends show

biodegradability [36]. The effect of end-group in PEG on the miscibility and crystallization behavior was also studied [37-40]. Kulinski and Piorkowska reported that the end-group does not influence much on T_g of PLA when PEG has a lower molecular weight (< 750 g/mol) [37]. Lai et al. studied the effect of end-groups in PEG on the miscibility with PLA and the crystallization behaviors of PLA. According to them, PEG having hydroxyl groups at the chain ends enhances the crystallization rate, as compared with that terminated by methyl groups [38,39]. With increasing the content of PEG in PLA, phase separation for PEG occurred easily from PLA matrix, making the blend unstable [40].

Because of the similar chemical structure to PEG, poly(propylene glycol) PPG was also studied as a plasticizer for PLA. Although PPG can depress the T_g of PLA about 11 °C with 5% addition, due to the low miscibility with PLA, a second T_g is detected around -77 °C [41]. This is ascribed to T_g of PPG, *i.e.*, they show phase-separation [42]. Piorkowska et al. reported that PPG showed less efficient in crystallization enhancement than PEG [43].

Besides PEG and PPG, a number of materials also have been known as plasticizers for PLA, such as poly(3-methyl-1,4-dioxan-2-one) [44], polyester-diol PED [45], citrate ester [46,47], and triacetine [48,49]. Although all of them were found to be

effective to enhance the crystallization of PLA, the high efficient was obtained only by the addition of a large amounts. Therefore, plasticizers showing good miscibility with PLA are required in order to accelerate the crystallization rate.

1.3.3 Improvement of toughness

PLA has received a growing interest in various fields, such as packaging, textile, and automotive part, as a promising environment-friendly replacement to petroleum-based polymeric materials. The poor mechanical toughness of PLA is the limitation to expand its applications. The main mechanical properties for PLA and conventional polymers are shown in Table 1-2. Compared with polystyrene PS and poly(ethylene terephthalate) PET, which are conventional plastics widely used in industry and daily-life products, PLA has similar tensile modulus and strength. In order to widen the application range of PLA, therefore, numerous researches have been carried out for improvement of mechanical toughness, including copolymerization, blending with various kinds of flexible polymers or rubbers, plasticization, and so on.

	PLA	PS	ΡΕΤ	PP
Glass transition temp. (°C)	60	105	75	-10
Tensile modulus (GPa)	3.4	2.9	2.8	0.9
Tensile strength at break (MPa)	53	45	54	31
Strain at break (%)	6	7	130	120
Notched Izod IS (J/m)	13	27	59	27

Table 1-2 Mechanical properties for PLA and conventional polymers [6,45]

1.3.3.1 Copolymerization

Copolymerization is a powerful method to tune properties based on those of individual pure homopolymer. Also in the case of PLA, properties including tensile and impact toughness can be modified by arranging the sequence of monomer, the architecture of polymer chain, and composition.

Because of the marked ductility, ε -caprolactone CL has been copolymerized with lactic acid LA to provide the flexibility. This is an interesting copolymer because both monomers are biodegradable. Hiljanen-Vainio et al. found that the copolymers behave like from weak elastomers to tough thermoplastics depending upon the CL/LA monomer ratio (w/w) from 80/20 to 60/40 [50]. Furthermore, Grijpma et al. synthesized high molecular weight (LA-CL) copolymer. They reported P(LA-CL) having the mole ratio of LA/CL = 1/1 shows 500 % elongation to break [51]. Besides, commercial perfluoropolyether PFPE has also been copolymerized with PLA to improve the mechanical properties. Haynes et al. found the fluoropolyether segments not only raised the ductility but also improved the optical clarity and melt processability. Although PLA and PFPE are immiscible, phase separation did not take place in the copolymers. Moreover, the copolymers exhibited higher elongation at break [52].

1.3.3.2 Blending with flexible polymers or rubbers

In contrast to the copolymerization method, blending with flexible polymers or rubbers is a more convenient and economic way for industrial applications. Various polymers have been melt-blended with PLA for different purposes. A number of flexible polymers have been investigated as toughening additives for PLA.

PCL, one of biodegradable polyesters, has great flexibility and ductility. Therefore, it has been extensively studied as a toughening modifier for PLA in recent years. However, a simple blend of PLA with PCL often results in no improvement in toughness owing to the marked immiscibility [53,54]. Therefore, a suitable compatibilizer for the PLA/PCL blend is required. Semba et al. reported that the elongation at break of a PLA/PCL blend increased to 130 % with the modification by dicumyl peroxide DCP. Moreover, necking, *i.e.*, ductile deformation, was observed

during tensile test [55]. The result indicated that DCP is an effective compatibilizer for the PLA/PBS blend system [56].

Furthermore, the introduction of flexible rubbery segments into PLA matrix has been regarded as an efficient method. Li and Shimizu blended PLA with poly(ether)urethane PU elastomer. They found that both impact toughness and elongation at break were improved with the PU content [57]. Moreover, PU was found to be dispersed in PLA matrix, suggesting the PLA/PU blend system is a miscible system. Moreover, Ishida et al. studied the toughening mechanism of PLA employing acrylonitril-butadiene rubber NBR and isoprene rubber IR. They demonstrated that the particle size played an important role in toughening system. As they reported, smaller NBR particles improved the impact properties much more than larger IR particles. Moreover, the polar structure of NBR was considered to be helpful to enhance the toughness [58].

1.4 Miscibility of polymer blends

1.4.1 Thermodynamics of polymer blends

For various purposes, a different polymer is often blended together to obtain polymer blends. However, polymer blends do not follow the rule "like dissolves like". From the point view of thermodynamic, it is possible to predict whether a given polymer blend will be miscible or not by using the following relation;

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \tag{1.1}$$

where ΔG_{mix} is the Gibbs's free energy of mixing, ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing. Mutual dissolution, *i.e.*, intermolecular diffusion to be a homogeneous concentration will take place when the Gibbs's free energy of mixing is negative. Although the entropy of mixing is always positive, however, the contribution is negligible because of the high molecular weight. Therefore, the sign and magnitude of ΔH_{mix} determine the sign of ΔG_{mix} .

Flory and Huggins calculated ΔS_{mix} for polymer blends by using the lattice model, as illustrated in Fig. 1-3 [59,60]. In this lattice model, polymer molecules are assumed to be composed of a large number of segments with equal length. The lattice is comprised of *N* sites. Each site, having a volume of *v*, is occupied by one segment in a molecule [59-63].



Fig. 1-3 Lattice models for (a) low molecular weight compounds solution

and (b) polymer blend

According to the mean-field theory, the entropy of mixing ΔS_{mix} for a binary polymer blend is derived as follow;

$$\Delta S_{mix} = k[N_1 \ln \phi_1 + N_2 \ln \phi_2] = RV\left(\frac{\phi_1}{v_1} \ln \phi_1 + \frac{\phi_2}{v_2} \ln \phi_2\right)$$
(1.2)

where *k* is the Boltzmann constant, *R* is the gas constant, and *V* is the total volume, ϕ_1 and ϕ_2 are the volume fraction of polymer 1 and polymer 2, respectively. Furthermore, v_1 and v_2 are the molar volumes of polymer 1 and polymer 2, respectively.

Considering the interaction energies between segments, the enthalpy of mixing is expressed by the following equation;

$$\Delta H_{mix} = RT\phi_1\phi_2\chi \tag{1.3}$$

where χ is the Flory-Huggins interaction parameter defined as;

$$\chi \equiv \frac{z\Delta w_{12}}{RT}$$
$$\Delta w_{12} = w_{12} - \frac{1}{2} (w_{11} - w_{22})$$

where w_{ii} is the contact energy between molecules of the same component, and w_{ij} is the contact energy between molecules of different components.

By combining the equations (1.1), (1.2), and (1.3), the complete style of the Flory-Huggins equation (1.2) can be;

$$\Delta G_{mix} = RTV \left(\frac{\rho_1 \phi_1}{M_1} \ln \phi_1 + \frac{\rho_2 \phi_2}{M_2} \ln \phi_2 + \phi_1 \phi_2 \chi \right)$$
(1.4)

where ρ_1 and ρ_2 are the densities of polymer 1 and polymer 2, respectively. M_1 and M_2 are the molecular weights of polymer segment 1 and polymer segment 2, respectively.

Because of high molecular weight, as mentioned, mixing entropy of a polymer blend is thousands times smaller than that of a low-molecular-weight compound blend. Therefore, the first and second terms in equation (1.4) are extremely small values, which can be regarded as 0. Consequently, the sign of ΔG_{mix} is positive even though the value of χ is small. As a result, phase separation occurs in a polymer-polymer blend [64-66].

1.4.2 Solubility parameter

In an ideal system, the mixing enthalpy ΔH_{mix} is zero because the two types of molecules have the same force fields, and thus equation (1.1) can be written as

$$\Delta G_{mix} = -T \Delta S_{mix} \tag{1.5}$$

However, the energy of mixing accompanied with the formation of contact between two dissimiliar molecules cannot be ignored. In general, mixing is endothermic for nonpolar molecules in the absence of strong intermolecular force.

Hildebrand and Scott gave an expression as shown below [67];

$$\Delta H_{mix} = V \phi_1 \phi_2 \left[\left(\frac{\Delta E_1^{\nu}}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2^{\nu}}{V_2} \right)^{1/2} \right]^2$$
(1.6)

where V, V_1 , and V_2 are the volumes of the blend, respectively. ΔE^{ν} is the molar energy of vaporization.

 $\Delta E/V$ in the equation (1.6) is referred to the cohesive energy density. Moreover,

the relation to the solubility parameter δ is given as below;

$$\frac{\Delta E}{V} = \delta^2 \tag{1.7}$$

Thus, equation (1.6) can be rewritten:

$$\frac{\Delta H_{mix}}{V} = \phi_1 \phi_2 \left[\delta_1 - \delta_2 \right]^2 \tag{1.8}$$

Furthermore, χ can be expressed as follow;

$$\chi = \frac{V}{RT} [\delta_1 - \delta_2]^2 \tag{1.9}$$

As seen in equation 1.9, the interaction parameter becomes zero when two polymers have the same solubility parameter. Therefore, miscibility of polymer blends is only achieved in the case that the system shows the similar values of solubility parameter.

In addition, Small proposed the group contribution method, in which the solubility parameter of a polymer can be estimated from the molar attraction constants, using structural formula of the compound and its density [68].

$$\delta = \frac{\rho \Sigma G}{M} \tag{2.0}$$

where ρ and *M* are the density and molecular weight, respectively. ΣG is the sum of molar attraction constants.

This is called the Small's equation. The solubility parameter can be easily calculated applying this equation. However, this equation is only valid when the interactions between molecules can be ignored [69-71]. Therefore, the parameter cannot be compared when the structure is greatly different.

1.5 Objectives of this study

PLA, a biomass-derived biodegradable polymeric material, has attracted increasing focus. Because of attractive advantages such as high modulus, high strength, and excellent transparency in the amorphous state, it has the potential to replace petroleum polymers. However, considerable efforts will be further required to overcome the defects such as slow crystallization rate and poor mechanical toughness at room temperature. There have been a plenty of literatures reporting the efficient plasticizers for improving crystallization rate of PLA. However, accompanying with blends containing plasticizers, several problems such as miscibility, thermal stability, etc., are also necessary to be considered. A suitable plasticizer for PLA, which shows miscibility with PLA and also keeps the thermal stability, is required to explore. Moreover, a large number of approaches, for example, copolymerization, addition of rubber-like particles, and plasticization, have been developed to improve mechanical properties for PLA. Nevertheless, the influence of processing conditions such as cooling temperature and post-annealing processing on the tensile properties of PLA were seldom studied.

In this study, the enhancement of crystallization rate of crystalline PLA is going to be achieved by the addition of a plasticizer that enhances chain mobility. Although the improvement of mechanical toughness of PLA by the addition of rubber-like particles was studied intensively, in this work, I try to improve the mechanical toughness of PLA only by adjusting the processing condition at compression-molding.

The dissertation consists of two parts. The discussion related to enhancement of crystallization rate of PLA by the addition of two kinds of plasticizers is covered in Chapter 2. The improvement of mechanical properties of PLA only by adjusting the processing conditions is shown in Chapter 3. Meanwhile, the mechanism associated with this phenomenon is also discussed in the same chapter. Finally, the findings of this research are summarized in Chapter 4. It is expected that the findings in this research can be applicable to industrial fields and expand the application of PLA.

References

- Mohanty, A.K., Misra, M., Hinrichsen, G. Macromol. Mater. Eng., 2000, 276/277, 1-25.
- 2. Gross, R.A., Karla, B., Science, 2002, 297, 803-807.
- 3. Lim, L.T., Auras, R., Rubino, M. Prog. Polym. Sci. 2008, 33, 820-852.
- 4. Steinbuchel, A. Ed. Biopolymers. Weinheim : Wiley-VCH, 2001.
- 5. Campbell, C.J., Laherrere, J. H. Scientific American, 1998, 20-29.
- 6. Auras, R., Lim, L.T., Selke, S.E.M., Tsuji, H. Poly(lactic acid): synthesis, structures, properties, processing, and applications. Wiley: Hoboken, 2010.
- Jimenez, A., Peltzer, M., Ruseckaite, R. Poly(lactic Acid) Science and Technology: Processing, Properties, Additives, and Applications. Royal Society of Chemistry: Oxfordshire, 2014.
- 8. Auras, R., Harte, B., Selke, S. Macromol. Biosci., 2004, 4, 835-864.
- 9. Rasal, R.M., Janorkar, A.V., Hirt, D.E. Prog. Polym. Sci. 2010, 35, 338-356.
- 10. Liu, H., Zhang, J. J. Polym. Sci. Polym. Phy. 2011, 49, 1051-1083.
- 11. Saeidlou, S., Huneault, M.A., Li, H.B., Park, C.B. Prog. Polym. Sci. 2012, 37, 1657-1677.
- 12. Liu, G., Zhang, X., Wang, D. Adv. Mater. 2014, 26, 6905-6911.

- 13. Fillon, B., Thierry, A., Lotz, B., Wittmann, J.C. J. Therm. Anal., 1994, 42, 721-731.
- 14. Li, H.B., Huneault, M.A. Polymer, 2007, 48, 6855-6866.
- 15. Harris, A.M., Lee, E.C., J. Appl. Polym. Sci., 2008, 107, 2246-2255.
- 16. Ke, T., Sun, X. J. Appl. Polym. Sci., 2003, 89, 1203-1210.
- 17. Ikada, Y., Jamshidi, K., Tsuji, H., Hyon, S.H. Macromolecules 1987, 20, 904-906.
- Brochu, S., Prud'homme, R.E. Barakat, I., Jerome, R. *Macromolecules* 1995, 28, 5230-5239.
- 19. Schmidt, S.C., Hillmyer, M.A. J. Polym. Sci. Pol. Phy. 2001, 39, 300-313.
- 20. Yamane, H., Sasaki, K. Polymer 2003, 44, 2569-2575.
- 21. Anderson, K.S., Hillmyer, M.A. Polymer 2006, 47, 2030-2035.
- 22. Nam, J.Y., Sinha Ray, S., Okamoto, M. Macromolecules 2003, 36, 7126-7131.
- 23. Krikorian, V., Pochan, D.J. Macromolecules 2004, 37, 6480-6491.
- 24. Krikorian, V., Pochan, D.J. Macromolecules 2005, 38,6520-6527.
- **25.** Moon, S.I., Jin, F., Lee, C.J., Tsutsumi, S., Hyon, S.H. *Macromolecular Symposium* **2005**, 224, 287-295.
- 26. Tsuji, H., Kawashima, Y., Takikawa, H., Tanaka, S. Polymer 2007, 48, 4213-4225.
- 27. Shieh Y.T., Twu, Y.K., Su, C.C., Lin, R.H., Liu, G.L. J. Polym. Sci. Pol. Phy. 2010, 48, 983-989.

- **28.** Xing, Q., Zhang, X.Q., Dong, X., Liu, M.G., Wang, D.J. Polymer **2012**, 53, 2306-2314.
- **29.** Kawamoto, N., Sakai, A., Horikoshi, T., Urushihara, T., Tobita, E. J. Appl. Polym. Sci. **2007**, 103, 244-250.
- **30.** Kawamoto, N., Sakai, A., Horikoshi, T., Urushihara, T., Tobita, E. J. Appl. Polym. Sci. **2007**, 103, 198-203.
- 31. Yokohara, T., Yamaguchi, M. Eur. Polym. J. 2008, 44, 677-685.
- 32. Yamaguchi, M., Yokohara, T. Improvement of Mechanical Properties and Processability by Addition of Polyesters in "Polylactic Acid: Synthesis, Properties and Applications", Ed., V. Piemonte, Chap. 6, Nova Science Publishers, New York, 2011.
- **33.** Pan, P.J., Yang, J.J., Shan, G.R., Bao, Y.Z., Weng, Z.X., Inoue, S. *Macromol. Mater. Eng.* **2012**, 297,670-679.
- **34.** Song, P., Chen, G.Y., Wei, Z.Y., Chang, Y., Zhang, W.X., Liang, J.C. *Polymer* **2012**, 53, 4300-4309.
- 35. Wypych, G. Ed. Handbook of plasticizers Chemtec: New York, 2004.
- 36. Sheth, M., Kumar, R.A., Dave, V., Gross, R.A., McCarth, y S.P. J. Appl. Polym. Sci.
 1997, 66, 1495-1505.

- 37. Kulinski, Z, Piorkowska, E. Polymer 2005, 46, 10290-10300.
- 38. Lai, W.C., Liau, W.B., Lin, T.T. Polymer 2004, 45, 3073-3080.
- **39.** Lai, W.C., Liau, W.B., Yang, L.Y. J. Appl. Polym. Sci. **2008**, 110, 3616-3623.
- **40.** Hu, Y., Rogunova, M., Topolkaraev, V., Hiltner, A., Baer, E. *Polymer* **2003**, 44, 5701-5710.
- Kulinski, Z., Piorkowska, E., Gadzinowska, K., Stasiak, M. *Biomacromolecules* 2006,7, 2128-2135.
- **42.** Piorkowska, E., Kulinski, Z., Galeski, A., Masirek, R. *Polymer* **2006**, 47, 7178-7188.
- **43.** Kevin, B., Hillmyer, M.A., Tolman, W.B. *Macromolecules* **2001**, 34, 8641-8648.
- **44.** Okamoto K., Ichikawa T., Yokohara T., Yamaguchi M. *Eur. Polym. J.* **2009**, 45, 2304-2312.
- **45.** Labrecque, L.V., Kumar, R.A., Dave, V., Gross, RA., McCarthy, S.P. *J. Appl. Polym. Sci.* **1997**, 66, 1507-1513.
- 46. Ljungberg N., Wesselen B. Polymer 2003, 44, 7679-7688.
- 47. Ljungberg N., Wesslen B. J. Appl. Polym. Sci. 2002, 86, 1227-1234.
- 48. Ljungberg N., Wesslen B. J. Appl. Polym. Sci. 2003, 88, 3239-3247.
- 49. Brandrup, J., Immergut, E.H., Grulke, E.A., eds. Polymer handbook

Wiley-Interscience. New York, 1999.

- 50. Hiljanen-Vainio, M., Karjalainen, T., Seppala, J. J. Appl. Polym, Sci. 1996, 59, 1281-1288.
- 51. Grijpma, D.W., Zondervan, G.J., Pennings, A.J. Polym. Bull. 1991, 25, 327-333.
- 52. Haynes, D., Naskar, A.K., Singh, A., Yang, C.-C., Burg, K.J. Drews, M., Harrison, G., Smith, D.W. *Macromolecules* 2007, 40, 9354-9360.
- 53. Lopez-Rodriguez, N., Lopez-Arraiza, A., Meaurio, E., Sarasua, J.R. *Polym. Eng. Sci.*2006, 46, 1299-1308.
- 54. Vilay, V., Mariatti, M., Ahmad, Z., Pasomsouk, K., Todo, M. J. Appl. Polym. Sci.
 2009, 114, 1784-1792.
- **55.** Semba, T., Kitagawa, K., Ishiaku, U.S., Hamada, H. *J. Appl. Polym. Sci.* **2009**, 114, 1784-1792.
- 56. Wang, R., Wang, S., Zhang, Y., Wan, C., Ma, P. Polym. Eng. Sci. 2009
- 57. Li, Y., Shimizu, H. Macromol. Biosci. 2007, 7, 921-928.
- Ishida, S., Nagasaki, R., Chino, K., Dong, T., Inoue, Y. J. Appl. Polym. Sci. 2009, 113, 558-566.
- 59. Flory, P.J. J. Chem. Phys. 1940, 10, 51-61.
- 60. Flory, P.J. J. Chem. Phys. 1941, 9, 660-661.

61. Huggins, M.L. J. Chem. Phys. 1941, 9, 440-446.

62. Huggins, M.L. J. Chem. Phys. 1942, 46, 151-158.

- **63.** Work, W.J., Horie, K., Hess, M., Stepto, R.F.T. *Pure Appl. Chem.* **2004**, 76, 1985-2007.
- 64. Gedde, Ulf-W. Polymer Physic: Chapter 4. Chapman & Hall: London, 1995.
- 65. Ebewele, R.O. *Polymer science and technology*: Chapter 12. CRC press: New York, 2000.
- 66. Sperling, L.H. *Introduction to physical polymer science*: Chapter 3. John Wiley & Sons: Hoboken, 2005.
- 67. Hildebrand, J.H. and Scott, R.L. *The solubility of nonelectrolytes* Dover: New York, 1964.
- 68. Small, P. A. J. Appl. Chem. 1953, 3, 71-78.
- 69. Hoy, L.K. J. Paint. Technol. 1970, 42, 76-118.
- 70. Van Krevelen, D.W. Properties of polymers: Correlation with chemical structure, Elsevier: Amsterdam, 1972.
- **71.** Coleman, M.M., Serman, C.J., Bhagwagar, D.E., Painter, C.P. *Polymer* **1990**, 31, 1187-1203.
Chapter 2

Crystallization and plasticization

2.1 Introduction

2.1.1 Crystallization of polymer

The crystallization of polymers is a very important issue at polymer processing. Various thermoplastic polymers can crystallize upon cooling from the molten state to the temperature below their melting point. The crystals present in polymers greatly affect various properties in a solid state. In general, the crystallization of polymers can be classified in three types: (1) Upon cooling from the melt, (2) During mechanical stretching, and (3) During solvent evaporation [1,2]. In this thesis, the first one is focused considering the actual processing operations.

2.1.2 Crystallization from the melt

On cooling from the melt, the first stage is to create single nuclei, which is known as nucleation. There are two types of nucleation. One is homogenous nucleation, while the other is heterogeneous one. The homogeneous nucleation starts with nano-sized ordered arrangement composed of the polymer chains themselves. On the other hand, the heterogeneous nucleation begins with impurities or foreign particles such as catalysts. In general, most polymers crystallize from heterogeneous ones at conventional processing.

The temperature dependence of Gibbs free energy, shown in Fig. 2-1, describes thermodynamics of crystallization. As seen in the figure, when the ambient temperature is above the melting point T_m , the free energy of a liquid state is lower than that of a solid. Therefore, an ordered arrangement never develops due to the thermal motion. In contrast, when the temperature is below T_m , the free energy of a solid is lower than that of a liquid, resulting in the progress of nucleation and crystal growth [3, 4].



Fig. 2-1 Relationship between temperature and Gibbs energy of (blue) melt

and (red) solid.

Moreover, the nuclei formation is related to the bulk free energy $(\Delta \mu)$ and the surface free energy (q). The free energy change (ΔG) is expressed in the following equation;

$$\Delta G = -\frac{4\pi}{3}r^3 \Delta \mu + 4\pi r^2 q \tag{2.1}$$

where *r* is the radius of nuclei.

In equation 2.1, the first term, which is proportional to nuclei's volume, reduces the free energy. Meanwhile, the second term, which is proportional to the surface area, increases the free energy. This relationship is shown in Fig. 2-2. It is easily understood from this figure that the surface free energy increases with the size of nuclei at the first stage of nucleation, suggesting that a stable nuclei formation barely occurs because of high surface free energy. However, once the size of nuclei is beyond the critical value r^* , the free energy change starts to reduce, resulting in spontaneous crystal growth.



Fig. 2-2 Relationship between free energy of nucleation and nuclei radius.

Subsequently after the nuclei formation, the growth of the polymer crystals takes place on a pre-existing nuclei surface, which is called secondary nucleation. The process, in which folded chain segments add regularly to a smooth nuclei surface, is illustrated schematically in Fig. 2-3(a). This lateral growth occurs in one direction from the nuclei and forms a flat layer called lamella (Fig. 2-3(b)). Lamellar crystals grow radically and form larger quasi-spherical structure called spherulites, as shown in Fig. 2-3(c).



Fig. 2-3 Illustration of (a) secondary nucleation, (b) lamella, and (c) spherullite [2].

Generally, the formation of secondary nucleation is believed to determine crystallization growth rate of polymers. Therefore, the lateral growth rate of crystallization is regarded as the linear growth rate of spherulites radius R, which is expressed by the following equation;

$$G\left(\equiv\frac{dR}{dt}\right) = G_0 \exp\left(-\frac{\Delta E}{RT} - \frac{KT_m^0}{RT\Delta T}\right)$$
(2.2)

where *G* is the linear growth rate of crystallization, G_0 is a constant, *T* is the crystallization temperature, T_m^{0} is the equilibrium melting point, ΔT is the degree of supercooling, *i.e.*, T_m^{0} -*T*, ΔE is the energy of chain diffusion, *R* is the gas constant, and *K* is the kinetic constant for nucleation [5,6].

According to equation 2.2, the diffusion rate of polymer chains is strongly dependent on the crystallization temperature. When crystallization occurs at high temperature, the chain diffusivity is enhanced, *i.e.*, large $\frac{\Delta E}{RT}$. However, the free energy for secondary nucleation decreases, *i.e.*, small $\frac{KT_m^0}{RT\Delta T}$. Therefore, there is an appropriate crystallization temperature to accelerate the linear growth rate between T_g and T_m^{-0} .

Fig. 2-4 shows the linear growth rate *G* as a function of crystallization temperature T_c for various polymers. As seen in the figure, crystalline polymers show the bell-shaped curve in general [7]. The crystallization temperature, showing a maxium value for *G*, is denoted as T_{c-max} , given by [8]

$$T_{c-max} = \frac{T_g + T_m^0}{2}$$
(2.3)



Fig. 2-4 Linear growth rate G as a function of T_c of various crystalline polymers. [4]

Furthermore, the crystallization rate of a polymer decreases with the molecular weight due to the reduction of the chain diffusivity. Umemoto et al. reported the molecular weight dependence of linear growth rate for poly(ethylene succinate), as shown in Fig. 2-5.



Fig. 2-5 Relation between the linear growth rate G and T_c for poly(ethylene succinate)

having various molecular weights. [7]

2.1.3 Crystallization of polymer blend

Basically, equation 2.2 is also applicable to the crystallization rate of a polymer blend. However, for a polymer blend, the chain diffusivity in a molten state is easily affected by the additive.

For example, adding nucleating agent is an efficient method to improve the crystallization rate of a polymer. When a small amount of nucleating agents is added, the polymer chain diffusivity does not change so much in a molten state. Therefore, the crystallization rate is enhanced owing to the high nucleation density. However, there has also been reported that the crystallization rate of a polymer is retarded owing to the reduced chain mobility by the addition of a miscible but high viscous nucleating agent [9].

The crystallization rate can be accelerated by the addition of a miscible additive that enhances the chain mobility of a polymer. Wunderlich and Grebowicz reported that the crystallization rate of isotactic polystyrene iso-PS was enhanced at low crystallization temperature by the addition of benzophenone, as shown in Fig. 2-6. However, a large amount of benzophenone retards the crystallization rate of iso-PS, because the high density of benzophenone hinders the nucleation [10].



Fig. 2-6 Relation between the crystallization rate and crystallization temperature for iso-PS containing various volume ratios (*V*) of benezophenone [10].

The maximum crystallization rate of a polymer blend $G_{max}(B)$ can be approximately expressed by the following equation [11,12];

$$G_{\max}(B) \cong G_{\max}(H) \exp\{-\alpha(1-V)\}$$
(2.4)

where $G_{max}(H)$ is the maximum crystallization rate of a homopolymer, V is the volume fraction of the polymer, and α is the parameter determined by chain diffusion and free energy. When the parameter α is positive, the crystallization of the main polymer is disturbed by another component. On the contrary, the crystallization of the main polymer is enhanced, when α is negative. Among various kinds of additives for polymers, plasticizers are often added to improve the processibility. Because a plasticizer enhances the chain mobility of polymer at low temperature (Fig. 2-7), it has capability to enhance the crystallization rate at processing [13-20]. This is significantly important because water is usually used as cooling media at conventional processing operations. If the crystallinity of PLA is enhanced by the conventional cooling method, it will have a strong impact on the industry. Such processing condition also leads to good cost-performance.



Fig. 2-7 Relation between linear growth rate G and crystallization temperature for

(black) pure polymer and (red) polymer containing plasticizer.

2.1.4 Objectives

In this chapter, the crystallization behavior and mechanical properties of plasticized PLA with poly(ethylene glycol) terminated by benzoate (PEG-BA) are studied, as compared with poly(ethylene glycol) terminated by hydroxyl groups (PEG-OH). Prior to the discussion on the crystallization behavior, the effect of end-groups on the thermal hydrolysis degradation is demonstrated.

2.2 Experimental

2.2.1 Materials

Poly(lactic acid) PLA used in this chapter was obtained from Toray. The number and weight average molecular weights of PLA were evaluated by a gel permeation chromatography (GPC; Tosoh, HLC-8020) with TSK-GEL GMHXL as a polystyrene standard. Chloroform was employed as eluant at a flow rate of 1.0 ml/min, and the sample concentration was 1.0 mg/ml. It was found that M_n and M_w of the PLA employed are 9.8 × 10⁴ and 1.7 × 10⁵, respectively. Since the content of D-lactic unit is as low as 1%, the melting point is around 178 °C. Fig. 2-8 shows the DSC curve for PLA. The arrow denotes T_g .



Fig. 2-8 DSC heating curve for PLA.

Poly(ethylene glycol) terminated by benzoate (referred as PEG-BA) was used as a plasticizer. It was kindly prepared by New Japan Chemical from poly(ethylene glycol) (referred as PEG-OH). The average molecular weight of PEG-OH is 200. In this study, PEG-OH was also employed as a plasticizer as a reference sample. Fig. 2-9 shows DSC heating curves for pure plasticizers. The arrow denotes T_g . As seen in the figure, T_g of PEG-BA is found to be -51 °C, while T_g of PEG-OH is located at -81 °C.



Fig. 2-9 DSC heating curves for plasticizers: PEG-BA and PEG-OH.

A conventional PP was also used in this chapter as a reference sample. For PP, a commercially available propylene homopolymer (Japan Polypropylene, Novatec-PP FY4) was employed. The melt flow index of PP is 5 [g/10 min] at 230 °C and the melting point is 165 °C. M_n and M_w of PP are 4.5 × 10⁴ and 2.6 × 10⁵, respectively, as a polypropylene standard.

2.2.2 Sample preparation

Mixing

The blends containing 3, 10, and 20 wt% of a plasticizer were prepared by the solution blend technique in chloroform at room temperature. The weight fraction of PLA and the plasticizer, *i.e.*, PEG-OH or PEG-BA, in the solution was 10 %. The solution was poured into a petri dish and left in the draft for 24 hours at room temperature to obtain the blends.

Compression-molding

After being dried in a vacuum oven at 80 °C for 4 hours, the blends were compressed into a flat film by a compression-molding machine (Tester sangyo, Table-type-test press SA-303-I-S) for 3 min at 200 °C and subsequently cooled at either 40 °C or 80 °C for 10 min. In the case that the sample was cooled at 80 °C, it was subsequently plunged into an ice-water bath. The obtained films were stored at -20 °C to avoid further crystallization prior to the measurements.

2.2.3 Measurements

Rheological properties

Frequency dependence of oscillatory shear modulus G' and loss modulus G'' was evaluated at 190 °C using a cone-and-plate rheometer (TA Instrument, AR2000ex). The diameter and the cone angle are 25 mm and 4°, respectively.

Morphology observation

The linear growth rate of spherulites was examined at isothermal crystallization using a polarized optical microscope (Leica, DMLP) equipped with a hot-stage (Mettler, FP90). After heating up to 210 °C, the sample was cooled down to various crystallization temperatures at a cooling rate of 20 °C/min. Then, the time variation of the spherulite radius was measured under cross polars with a full wave plate.

Dynamic mechanical properties

Temperature dependence of tensile storage modulus E' and loss modulus E'' was measured using a rectangular specimen with 5 mm in width, 25 mm in length and 0.4 mm in thickness by a dynamic mechanical analyzer (UBM, Rheogel E4000-DVE) in the temperature range between -100 and 190 °C. The heating rate was 2 °C/min, and the applied frequency was 10 Hz.

Thermal properties

Thermal analysis was conducted by a differential scanning calorimeter (DSC) (Mettler, DSC820^e) under a nitrogen atmosphere. The samples were heated from room temperature to 210 °C at a heating rate of 10 °C/min. The amount of the samples in an aluminum pan was approximately 10 mg.

2.3 Results and discussion

2.3.1 Thermal stability and rheological properties

According to Hassouna et al., the addition of poly(ethylene glycol) PEG leads to the hydrolysis degradation of PLA, which is a serious problem for the industrial application [21-23]. Therefore, the molecular weight is examined prior to the measurements of the rheological and thermal properties using film samples prepared by the compression-molding.

Figure 2-10 shows the GPC curves as a polystyrene standard. There are two peaks in the blend samples, which are ascribed to PLA and the plasticizer. As seen in the figure, PEG-OH induces the degradation of PLA as reported previously. The M_n and M_w of PLA in the blend containing 10 wt% of PEG-OH are 4.30 × 10⁴ and 8.31 × 10⁴, respectively, whereas those of pure PLA are almost the same as those of the pellet even after the compression-molding. Considering that PLA in the solution-cast film of the blend has the same molecular weight as the pure PLA, the hydrolysis degradation occurs by the thermal history at mixing processing in an internal mixer, *i.e.*, 200 °C for 3 min. In contrast, the GPC curve of PLA in the blend with PEG-BA is unchanged. The M_n and M_w of PLA in PLA/PEG-BA (90/10) are 9.72 × 10⁴ and 1.70 × 10⁵, respectively, which are almost the same as those of the pure PLA.



Fig. 2-10 GPC curves of (top) PLA, (center) PLA/PEG-OH (90/10),

and (bottom) PLA/PEG-BA (90/10) films prepared by an internal mixer

at 200 °C, 3 min.

The decrease in the molecular weight of PLA by PEG-OH is clearly detected also by the rheological properties. The angular frequency dependence of the oscillatory shear modulus at 190 $^{\circ}$ C is shown in Fig. 2-11.

As seen in the figure, the oscillatory moduli are typical ones in the rheological terminal zone for pure PLA at this temperature. Moreover, it is obviously found that the moduli decrease with the addition of the plasticizer, especially for the blend containing 10wt% PEG-OH due to the enhanced hydrolysis degradation.

As seen in Fig. 2-11(a), the moduli decrease slightly with the addition of PEG-BA. The zero-shear viscosity η_0 , defined by equation (2.5), of PLA at 190 °C is calculated to be 450 Pa s. Furthermore, that of the blends containing 10 wt% of PEG-BA is 310 Pa s.

$$\eta_0 \equiv \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{2.5}$$

According to Graessley [24], η_0 of a solution is given by the relation.

$$\eta_0(\phi) \propto \xi_0 \phi^{3.6} \tag{2.6}$$

where ϕ is the volume fraction of a polymer and ξ_0 is the monomeric friction coefficient. The equation corresponds to the original Berry-Fox formula [25]. Assuming that ξ_0 is not affected by PEG-BA, η_0 predicted by the equation (306 Pa s) agrees well with the experimental value. As seen in Fig. 2-11(b), both moduli decrease greatly with the addition of PEG-OH. The zero-shear viscosity η_0 of PLA/PEG-OH (90/10) is calculated to be 40 Pa s, whereas that of pure PLA is 450 Pa s. Considering that η_0 is proportional to $M_w^{3.4}$, the value is appropriate.



Fig. 2-11 Frequency dependence of oscillatory shear moduli such as

(circles) storage modulus G' and (diamonds) loss modulus G'' at 190 °C; (a) (closed)

pure PLA and (open) PLA/PEG-BA (90/10); (b) (closed) pure PLA and (open)

PLA/PEG-OH (90/10)

Furthermore, the steady-state shear compliances J_e^{0} , defined by equation (2.7), are calculated to be 3.7 × 10⁻⁵ Pa⁻¹, 3.4 × 10⁻⁵ Pa⁻¹ and 3.2 × 10⁻⁵ Pa⁻¹ for pure PLA, PLA/PEG-BA, and PLA/PEG-OH, respectively. Therefore, the weight-average relaxation times τ_w , calculated by the product of η_0 and J_e^{0} as Eq. 2-8, are found to be 1.3×10⁻² s, 1.1×10⁻² s and 1.0×10⁻³ s for pure PLA, PLA/PEG-BA, and PLA/PEG-OH, respectively.

$$J_e^0 = \lim_{\omega \to 0} \frac{G'(\omega)}{G''(\omega)^2}$$
(2.7)

$$\tau_{w} = \frac{\int \tau^{2} H(\tau) \mathrm{dln}\,\tau}{\int \tau H(\tau) \mathrm{dln}\,\tau} = \eta_{0} J_{e}^{0}$$
(2.8)

2.3.2 Linear growth rate of spherulites

Fig. 2-12 exemplifies the spherulite texture observed under cross polars with a full-wave plate for the samples. A typical Maltese-cross pattern, showing negative spherulites, is detected for all samples, although the sample containing 20 wt% of PEG-BA shows slightly disturbed texture. The direction of lamellar growth will be distorted by the presence of PEG-BA, which exists presumably between PLA lamellae. Moreover, it is found from Fig. 2-12 that the spherulite radius increases with the content of the plasticizer.



Fig. 2-12 Spherulite texture observed at 130 °C after 6 min

(a) PLA, (b) PLA/PEG-BA (90/10), (c) PLA/PEG-BA (80/20),

(d) PLA/PEG-OH (97/3), and (e) PLA/PEG-OH (90/10)

Fig. 2-13 shows the time variation of spherulite texture at 120 $^{\circ}$ C for PLA and PLA containing 20 wt% of PEG-BA. It is apparent that the spherulites radius increases with the time.



Fig. 2-13 Growth of spherulite texture observed at 120 °C for

(top) PLA and (bottom) PLA/PEG-BA (80/20).



The growth curves of the spherulite radius at various crystallization temperatures

Fig. 2-14 Growth curves of the spherulite radius at various crystallization temperatures

(a) PLA, (b) PEG-BA 10wt%, (c) PEG-BA 20wt%,

(d) PEG-OH 3wt%, and (e) PEG-OH 10wt%

As seen in Fig. 2-14, the spherulite radius increases linearly with the crystallization time, indicating that the PLA concentration in the molten region at the front of spherulites is a constant. The result suggests that the diffusion rate of plasticizers is lower than the linear growth rate of PLA spherulites.

The slope of the lines in Fig. 2-14 represents the linear growth rate G as follows;

$$G = \frac{dR}{dt}$$
(2.9)

Fig. 2-15 shows the relation between G and T_c . As seen in the figure, pure PLA shows a maximum G around at $T_c = 130$ °C.



Fig. 2-15 Linear growth rate of spherulites G versus crystallization temperature T_c for

(a) PLA/PEG-BA and (b) PLA/PEG-OH

As mentioned above, the crystallization temperature, at which *G* shows a maximum, $T_{c\text{-max}}$, is given by equation (2.3). Since T_g of PLA is 58 °C [26] and T_m^{0} is 207 °C [27], $T_{c\text{-max}}$ is expected to be 132.5 °C. This corresponds with the experimental result. Furthermore, it is found that *G* is greatly enhanced especially at low T_c by the addition of the plasticizer. The location of the peak shifts to lower T_c owing to the decrease in T_g . Because actual processing is often carried out using water as a cooling medium, the shift of $T_{c\text{-max}}$ will be a great benefit in industries. On the contrary, *G* at high T_c decreases with increasing PEG-BA, suggesting that T_m^{0} decreases with PEG-BA. It is well known that T_m^{0} decreases when the Flory-Huggins interaction parameter χ_{12} is negative, as expressed by the following equation [28,29].

$$\frac{1}{T_m^0} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_f^0 V_1} (\chi_{12} \phi_1^2)$$
(2.10)

where T_m^{0} is the equilibrium melting point of a blend, V_1 is the molar volume of the polymer 1, ΔH_f^0 is the perfect crystal heat of fusion of the perfect crystal and ϕ_1 is the volume fraction of the polymer 1 in the blend.

Therefore, it is suggested that the interaction parameter χ_{12} between PLA and PEG-BA is negative. Moreover, it is clearly observed that *G* of PLA is extremely enhanced by the addition of PEG-OH, which is more obvious than that by PEG-BA. This result is attributed to the pronounced molecular mobility as shown in Fig. 2-15.

According to the equation 2-2 mentioned previously, at the same crystallization temperature, *G* increases by a plasticizer owing to the enhanced chain diffusion $\left(-\frac{\Delta E}{RT}\right)$, while the free energy $\left(-\frac{KT_m^0}{RT\Delta T}\right)$ of nucleation does not change greatly.

2.3.3 Dynamic mechanical properties

Fig. 2-16 shows the temperature dependence of the dynamic mechanical properties for pure PLA cooled at 40 $^{\circ}$ C.



Fig. 2-16 Temperature dependence of (open symbols) tensile storage modulus E' and

(closed symbols) loss modulus E" at 10 Hz for pure PLA cooled at 40 °C.

As seen in the figure, the tensile storage modulus E' of PLA falls off sharply at 65 °C owing to the glass-to-rubber transition. Correspondingly, the loss modulus E''shows a distinct peak. Beyond T_g , both moduli increase with temperature in the range between 85 and 95 °C. This is attributed to the cold crystallization, which is often observed for a crystalline polymer with a slow crystallization rate. The phenomenon demonstrates that the degree of crystallization of the initial sample, *i.e.*, the samples cooled at 40 °C, is considerably low. Because of the low degree of crystallinity, the heat distortion temperature is determined by T_g . The application of this material is therefore significantly limited.





Fig. 2-17 Temperature dependence of (a) tensile storage modulus E' and
(b) loss modulus E'' at 10 Hz for samples cooled at 40 °C: (black) pure PLA,
(red) PLA/PEG-BA (90/10), and (blue) PLA/PEG-OH (90/10)

As seen in Fig. 2-17, the cold-crystallization behavior is also detected for the plasticized samples, although both T_g and the cold crystallization temperature are located at lower temperatures. The results indicate that the cooling condition, *i.e.*, 40 °C for 10 min, is not sufficient enough to crystallize. Moreover, double peaks are detected in the *E*" curve for the sample containing 10 wt% of PEG-OH, demonstrating that the PLA/PEG-OH blend shows phase separation. On the contrary, only a single peak is

detected in the sample containing 10 wt% of PEG-BA. The results suggest that the end group of PEG plays an important role in the miscibility with PLA.

Generally, T_g of blends follows the Fox equation [30,31] which is shown below.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$
(2.11)

where w_1 and w_2 are the weight fractions, and T_{g1} and T_{g2} are the glass transition temperatures of polymers 1 and 2, respectively.

Fig. 2-18 shows the relation between the plasticizer content and T_g measured by DSC. The curves are drawn by the calculated values using equation (2.11). T_g of pure plasticizers were also measured by DSC, as shown in Fig. 2-9. It is found from the figure that T_g of PLA/PEG-BA blends are almost corresponding to the calculation values by the Fox equation. However, PLA containing 20wt% of PEG-OH does not follows the relation. Bleeding out of PEG-OH from the blend will be the origin of the deviation. This is another proof of the poor miscibility between PLA and PEG-OH.



Fig. 2-18 Relation between T_g of blend and the plasticizer content. (solid lines) the calculation values according to the Fox equation for the blend containing various contents of plasticizers and (closed circles) the experimental values for the blend containing various contents of plasticizers



Fig. 2-19 shows the dynamic mechanical spectra for the samples cooled at 80 $^{\circ}C$

for 10 min.

Fig. 2-19 Temperature dependence of (a) tensile storage modulus E' and (b) loss modulus E'' at 10 Hz for the samples cooled at 80 °C: (black) pure PLA,

(red) PLA/PEG-BA (90/10), (green) PLA/PEG-OH (97/3),

and (blue) PLA/PEG-OH (90/10)

It is demonstrated that both samples containing 10 wt% of the plasticizer show monotonical decrease in the E' curve with temperature, although the blend with 3 wt% of PEG-OH exhibits the cold crystallization behavior. It suggests that the cooling condition, *i.e.*, 80 °C for 10 min, allows PLA to crystallize greatly for the samples

containing more than 10 wt% of the plasticizer. The figure also shows that the E'' peak of the plasticized samples is broader and weaker than that of pure PLA. This is reasonable because the crystallization reduces the amount of the amorphous region and broadens the characteristic times of the glass-to-rubber transition of amorphous chains. Moreover, the E'' peak at -80 °C for PLA/PEG-OH, ascribed to T_g of PEG-OH, is more pronounced than that in Fig. 2-17. The small amount of amorphous PLA, as a result of the enhanced crystallization, accelerates the phase separation in the amorphous region. On the contrary, it is found that PEG-BA shows good miscibility with PLA even after crystallization of PLA.

2.3.4 Thermal properties

The DSC heating curves are shown in Fig. 2-20. The arrows in the figure denote $T_{\rm g}$ of pure PLA.



Fig. 2-20 DSC heating curves for PLA, PLA/PEG-BA, and PLA/PEG-OH cooled at (a) 40 °C and (b) 80 °C.

It is found from Fig. 2-20(a) that a sharp exothermal peak ascribed to cold crystallization is detected beyond T_g for the samples cooled at 40 °C, corresponding to the dynamic mechanical spectra. In the case of PLA with the plasticizer, the exothermic peaks are located at lower temperatures. The result shows that the cold crystallization occurs at low temperature because of the pronounced molecular mobility. The

crystalline nucleus of PLA produced at processing may also be responsible for the prompt crystallization at the heating process. On the contrary, the exothermic peak is not observed for the plasticized samples cooled at 80 °C as shown in Fig. 2-20(b). Moreover, small exothermic peaks at the temperature just below the melting point were detected for pure PLA in DSC heating curves. Those exothermic peaks are related to the phase transition of β form to a more stable α form, which is reported by Ohtani et al. and other authors [32-34].

The degree of crystallinity for PLA χ_c is determined by equation 2.12;

$$\chi_{c}(\%) = \frac{\Delta H_{m} - \Delta H_{c}}{\Delta H_{100\%}} \times 100$$
(2.12)

where ΔH_m is the heat of fusion at T_m , ΔH_c is the exothermic heat at cold crystallization, and $\Delta H_{100\%}$ is the heat of fusion for the perfect PLA crystal (93.1 J/g) [35].
Plasticizer	Content (wt%)	Mold Temp. (°C)	$T_{\rm g}$ (°C)	$T_{\rm m}$ (°C)	χ _c (%)
-	0		64	178	12
PEG-BA	10		43	172	17
PEG-BA	20	40	26	168	25
PEG-OH	10		35	169	29
PEG-OH	20		34	163	33
-	0		63	177	16
PEG-BA	10		31	173	39
PEG-BA	20	80	-23	168	42
PEG-OH	10		36	170	47
PEG-OH	20		41	165	47

Table 2-1 Thermal properties of samples

Table 2-1 shows the crystallinity of PLA with various amounts of PEG-BA or PEG-OH. It is found that the degree of crystallinity increases with the amount of the plasticizers. The plasticized samples cooled at 80 °C show high level of crystallinity, *i.e.*, 39 - 47 %. As a result, *E'* decreases monotonically with temperature without abrupt drop.

Fig. 2-21 compares the dynamic mechanical spectra for the plasticized sample cooled at 80 °C and a conventional isotactic polypropylene PP. It is found from the figure that the mechanical properties of the plasticized PLA are similar to those of PP, demonstrating that the blends have a great possibility to be employed instead of PP [36].



Fig. 2-21 Temperature dependence of (a) tensile storage modulus E' and (b) loss

modulus E" at 10 Hz for (black) i-PP and (red) Plasticized PLA containing 10 wt% of

PEG-BA cooled at 80 °C.

2.3.5 Tensile properties

Fig. 2-22 shows the stress-strain curves at room temperature for PLA and plasticized PLA cooled at 40 °C and 80 °C. The sample thickness is 400 µm and both stress and strain are the engineering ones. As seen in Fig. 2-22(a), pure PLA exhibits a brittle fracture right after the yield point. The strain at the break is about 10%. The yield stress decreases dramatically with increasing the content of the plasticizer. Moreover, plasticized PLA shows ductile behavior. The strain at break for those samples is larger than 300%. The results demonstrated that the plasticizer improves the mobility of chain segments, and thus provides the stretchability of PLA.



Fig. 2-22 Stress-strain curves for PLA containing the plasticizer cooled at

(a) 40 $^{\circ}$ C and (b) 80 $^{\circ}$ C.

As summarized in Table 2-2, Young's modulus of plasticized PLA cooled at 80 $^{\circ}$ C is higher than those of plasticized PLA cooled at 40 $^{\circ}$ C. Owing to the enhanced crystallization rate, plasticized PLA cooled at 80 $^{\circ}$ C has a high degree of crystallinity.

Table 2-2 Tensile properties and thermal properties of PLA and plasticized PLA						
Plasticizer content (wt%)	Cooling temperature (°C)	Young's modulus (GPa)	Yield stress (MPa)	Yield strain	Tg (°C)	Crystallinity* (%)
0		0.69	69.1 ± 1.3	0.10 ± 0.03	63	12
10	40	0.09	15.2 ± 2.2	0.16 ± 0.04	40	17
20	20	0.02	-	-	25	25
0		0.68	61.2 ± 1.1	0.09 ± 0.02	64	16
10	80	0.21	21.3 ± 1.5	0.10 ± 0.04	31	39
20		0.05	19.7 ± 2.0	0.44 ± 0.06	23	42

* Estimated by DSC (see equation 2.12)

Interestingly, it is noted in Fig. 2-22 that PLA cooled at 40 °C shows brittle fracture, whereas the sample cooled at 80 °C exhibits ductile behavior. This is a surprising phenomenon because pure PLA is considered to be a brittle polymeric material in general. The phenomenon will be studied and discussed in the following chapter.

2.4 Conclusions

Crystallization behavior and thermal and dynamic mechanical properties for plasticized PLA are studied employing PEG having benzoate groups (PEG-BA) at chain ends. It is found that PEG-BA shows better miscibility with PLA than that with a conventional PEG having hydroxyl groups at chain ends (PEG-OH). The Flory-Huggins interaction parameter between PLA and PEG-BA is found to be negative. Furthermore, the linear growth rate of PLA crystallization is greatly enhanced especially at low temperatures because of the decrease in T_g as well as the pronounced molecular mobility of PLA chains. The enhanced crystallization rate affects the mechanical and thermal properties. Because of the high degree of crystallinity, which is obtained, e.g., at 80 °C for 10 min as a cooling condition, the cold crystallization behavior is not observed at the measurements of thermal and dynamic mechanical properties. Consequently, the tensile modulus gradually decreases with temperature without abrupt drop. Since the dynamic mechanical spectra are similar to that of PP, the heat distortion temperature will be greatly improved.

References

- Billmeyer, Fred, W. Jr. *Textbook of polymer science*, John Wiley & Sons: New York, 1984.
- Sperling, L.H. Introduction to Physical Polymer Science, Chapter 6. John Wiley & Sons: Hoboken, 2005.
- 3. Gedde, Ulf-W. Polymer Physic, Chapter 4. Chapman & Hall: London, 1995.
- 4. Matsushita, Y. Ed. Structures and Physical Properties of Polymers, Koudansya: 2013.
- 5. James, E.M. Physical Properties of Polymers, Springer: 2005.
- 6. 基礎高分子科学, 高分子学会編, 東京化学同人, 2006.
- 7. Umemoto, S., Okui, N. Polymer 2002, 43, 1423-1427.
- 8. Miyata, T., Masuko, T. Polymer 1998, 39, 5515-5521.
- **9.** Saeidlou, S., Huneault, M.A., Li, H.B., Park, C.B. *Prog. Polym. Sci.* **2012**, 37, 1657-1677.
- 10. Wunderlich, B., Grebowicz, J. Adv. Polym. Sci. 1984, 60/61, 1-59.
- Richard, S.S. Crystallization from Polymer Blends, MRS Proceedings: Cambridge, 1993.
- Piorkowska, E., Rutledge, G.C. Chapter 10 in *Handbook of Polymer Crystallization*, Wiley: Hoboken, 2013.

- 13. Kevin, B., Hillmyer, M.A., Tolman, W.B. Macromolecules, 2001, 34, 8641-8648.
- 14. Ljungberg, N., Wesselen, B. J. Appl. Polym. Sci. 2002, 86, 1227-1234.
- 15. Ljungberg, N., Wesselen, B. Polymer 2003, 44, 7679-7688.
- Okamoto, K., Ichikawa, T., Yokohara, T, Yamaguchi, M. *Eur. Polym. J.* 2009, 45, 2304-2312.
- 17. Lai, W.C., Liau, W.B., Lin, T.T. Polymer 2004, 45, 3073-3080.
- 18. Kulinski, Z., Piorkowska, E. Polymer 2005, 46, 10290-10300.
- 19. Piorkowska, E., Kulinski, Z., Galeski, A., Masirek, R. Polymer 2006, 47, 7178-7188.
- 20. Lai, W.C., Liau, W.B., Yang, L.Y. J. Appl. Polym. Sci. 2008, 110, 3616-3623.
- 21. Lim, L.T.; Auras, R.; Rubino, M. Prog. Polym. Sci. 2008, 33, 820-852.
- 22. Rasal, R.M.; Janorkar, A.V.; Hirt, D.E. Prog. Polym. Sci. 2010, 35, 338-356.
- 23. Hassouna, F., Raquez, J.M., Addiego, F., Dubois, P., Toniazzo, V., Ruch, D. *Eur. Polym.*J. 2011, 47, 2134-2144.
- 24. Graessley, W.W. Polymeric liquids and networks: dynamics and rheology. Garland Science, New York. 2008.
- 25. Berry, G.C., Fox, T.G. Adv Polym Sci 1968, 5, 261-357.
- 26. Jamshidi, K., Hyon, S.H., Ikada, Y. Polymer 1988, 29, 2229-2234.
- 27. Vasanthakumari, R., Pennings, A.J. Polymer 1983, 24, 175-178.

- Thomas, S., Shanks, R., Chandrasekharakurup, S. *Nanostructured Polymer Blends*, Chapter 1. William Andrew Applied Science Publisher, New York, 2014.
- 29. Fredrickson, G. H., Liu, A.J., Bates, F.S. Macromolecules 1994, 27, 2503-2511.
- 30. Fox, T. G., Loshaek, S., J. Polym. Sci., 1955, 15, 371-390.
- **31.** Brostow, W., Chiu, R., Kalogeras, I.M., Vassilikou-Dova, A., *Mater. Lett.* **2008**, 62, 3152-3155.
- 32. Tsuji, H., Ikada, Y. Polymer 1993, 26, 6918-6926.
- 33. Ohtani, Y., Okumura, K., Kawaguchi, A. J. Macromol. Sci., Part B: Phys. 2003g
 3-4, 875-888.
- 34. Zhang, J., Duan, Y., Sato, H., Tsuji, H., Noda, I., Yan, S., Ozaki, Y. *Macromolecules* 2005, 38, 8012-8021.
- 35. Fisher, E.W., Sterzel, H.J., Wegner, G., Kolloid Z.Z. Polym. 1973, 251, 980-990.
- 36. Phulkerd, P., Hirayama, S., Nobukawa, S., Inoue, T., Yamaguchi, M. *Polym. J.* 2014, 46, 226-233.

Chapter 3

Impact of processing condition tensile properties

3.1 Introduction

3.1.1 Measurements of mechanical properties

With the development of technologies, polymeric materials having various excellent properties have been produced to meet the demands of applications. Therefore, in order to ensure that they exhibit successful performance in applications, it is very important to understand clearly their mechanical behaviors under a variety of conditions. The knowledges on the influences of temperature, experimental time, and thermal history on the mechanical properties of polymers are particularly important. Therefore, various test methods have been designed to evaluate mechanical properties under a variety of loading conditions. These are including tensile test, compression test, three-point bending test, impact test and the tests designed to measure dynamic mechanical properties [1].

3.1.2 Stress-strain behaviors of polymers

Tensile tests have been widely used to comprehend the mechanical behaviors of polymers under stretching. In tensile tests, a specimen is stretched at a constant rate, and load or stress is measured as a function of time.

Polymers exhibit various behaviors in tensile tests, ranging from brittle to ductile, including yielding and cold-drawing. Moreover, the tensile behaviors of polymers strongly depend on the ambient temperature and strain rate at the tensile test. Generally the sample specimen for a tensile test is cut or molded in a shape of dumbbell, as shown in Fig. 3-1. The both ends are clipped and one of clipped ends is stretched at a constant rate in a tensile machine. The length in the center part of the specimen with narrow width is called the initial gauge length, L_0 .



Fig. 3-1 Illustration of a specimen for tensile tests

The engineering stress σ is defined as

$$\sigma = \frac{F}{A_0} \tag{3.1}$$

where F is the applied load and A_0 is the original cross-sectional area of the specimen.

The engineering strain ε is given by

$$\varepsilon = \frac{L - L_0}{L_0} = \frac{\Delta L}{L_0} \tag{3.2}$$

where L is the instantaneous gauge length and ΔL is the change in the gauge length.

Besides engineering stress and strain, true stress and strain are also used for description of tensile properties of polymers. True stress σ_t is calculated as the quotient of the applied load to the instantaneous cross-sectional area *A*, that is,

$$\sigma_t = \frac{F}{A} \tag{3.3}$$

True strain ε_t is defined as the sum of all the instantaneous length changes dL, divided by the instantaneous length, which is expressed as following,

$$\varepsilon_t = \int_{L_0}^L \frac{dL}{L} = \ln \frac{L}{L_0} \tag{3.4}$$

The true strain has the following relation with engineering stain using equations (3.2) and (3.4),

$$\varepsilon_t = \ln \frac{L}{L_0} = \ln \frac{L_0 + \Delta L}{L_0} = \ln(1 + \varepsilon)$$
(3.5)

Before the yield point, a necking band occurs during deformation for a ductile polymer. It is well known that shear yielding is a constant volume process. Thus,

$$AL = A_0 L_0 \tag{3.6}$$

Further, the following equation can be derived from equations 3.3, 3.5, and 3.6;

$$\sigma_t = \sigma(1+\varepsilon) \tag{3.7}$$

Basically, engineering values and true values are essentially equal for small deformations. On the contrary, true values should be used for the scientific discussion under a large strain. In particular, elongational viscosity should be measured at a constant true strain rate, because viscosity is defined as the stress divided by the true strain rate.

A polymeric material responses elastically when small forces are applied to. The stress increases proportionally with strain in this region. Moreover, the applied deformation recovers immediately when the stress is removed [1,2]. This relation between stress and strain, known as Hooke's law, can be written as

$$\sigma = E\varepsilon \tag{3.8}$$

where *E* is Young's modulus (modulus of elasticity).

Besides tensile deformation, there is another deformation for polymeric materials. As shown in Fig. 3-2, a horizontal force is applied to the top surface to make a transverse deformation in the material without changing the height. This is called shear deformation.



Fig. 3-2 Illustration of shear deformation

The shear strain γ is defined as follows,

$$\gamma = \frac{x}{h} = \tan\theta \tag{3.9}$$

where x is the distance of the translational motion, h is the height, and θ is the inclination angle.

Moreover, under small strains, the relation between shear stress and shear strain is expressed by Hooke's law as the following equation,

$$\sigma_s = G_s \gamma \tag{3.10}$$

where σ_s is the shear stress and G_s is the shear modulus.

3.1.3 Poisson ratio

.

In a tensile test, the strain along the tensile direction also causes the strain in the direction perpendicular to the tensile direction [3]. Fig. 3-3 shows this phenomenon.



Fig. 3-3 Illustration of the Poisson effect.

Therefore, the Poisson ratio, for an isotropic material, is defined as follows,

$$V = \frac{-\mathcal{E}_x}{\mathcal{E}_y} \tag{3.9}$$

The Poisson's ratios for engineering materials are shown in Table 3-1. It is noted that the most brittle materials such as ceramics and glass have low values of Poisson's ratio. Moreover, in many cases, flexible materials show high values of the Poisson's ratio.

Materials	Poisson's Ratio ν		
Ceramics	0.20		
Glass	0.22		
Polystyrene PS	0.34		
Poly(lactic acid) PLA	0.36		
Poly(ethylene terephthate) PET	0.40		
Rubber	0.46~0.50		

Table 3-1 Poisson's ratios for materials [3-5]

Furthermore, the Young's modulus, E, the shear modulus, G_s , and the Poisson's ratio, v, which are used to describe the elastic behavior of an isotropic solid, are related through the following equation,

$$E = 2(1+\nu)G_s \tag{3.10}$$

During the tensile deformation for a material with v = 0.5, a constant volume process can be obtained. However, volume expansion or dilatation takes place for most solid materials. Consequently, v is usually around 0.3 [2,3].

3.1.4 Stress-strain curve

The tensile test data are usually stated in term of stress (σ)-strain (ϵ) curve. Fig. 3-4 shows a typical stress-strain curve for a ductile specimen.



Fig. 3-4 Stress-strain curve of a ductile polymer. σ_v is the yield stress,

 ε_{v} is the yield strain, σ_{b} is the stress at break, and ε_{b} is the strain at break.

From O to A, the Hooke's law is applicable, and the slope is Young's modulus. Beyond A point, called elastic limit, plastic deformation takes place in polymer solid and the stress is not proportional to strain. Then, the stress shows a maximum, *i.e.*, yield point. Beyond the yield point B, plastic strain is dominant rather than elastic strain. After the yield point, most polymers show the necking band, in which localized deformation occurs with a constant stress. After the necking band is expanded to all of a narrow area in a sample specimen, the stress increases again, often called "strain-hardening", before break. The crystallization owing to high orientation of polymer chains can provide the strain-hardening, as well-known for natural rubber [9]. The stress σ_b is called ultimate strength or tensile strength [1-3,6-9].

3.1.5 Polymer fracture

There are mainly two mechanisms of plastic deformation for conventional polymeric solids. One is shear yielding, while the other is crazing. Ductile behavior is observed for a polymer showing shear yielding in general. As shown in Fig. 3-5(a), molecular chains, whose conformation changes with the deformation, do not break at shear yielding. On the contrary, a craze is composed of fibrils and voids, initiated from microvoid formation. Further, brittle fracture usually occurs at crazing process with chain scission (Fig. 3-5(b)).



Fig. 3-5 Plastic deformation mechanisms of polymeric materials [10]:

(a) shear yielding and (b) crazing

Moreover, the onset stresses of shear yielding and crazing depend on the temperature and strain rate. As shown in Fig. 3-6, the shear yielding is strongly affected by the strain rate and temperature. On the other hand, the onset stress of crazing is not much affected by the strain rate and temperature. As a result, the brittle-ductile transition temperature, at which the onset stresses of both mechanisms are the same, is affected by the strain rate.



Fig. 3-6 Illustration of the brittle-ductile transition:

(---) high strain rate, (---) low strain rate

T_a and T_b are brittle-ductile temperatures, at the low and high strain rates, respectively.

As well known, failure occurs at the stress concentration point, *i.e.*, at the tip of the crack. The tensile stress σ at the tip of a crack (Fig. 3-7) in the direction of the applied stress is referred by Williams [1,11] in equation 3.11.

$$\sigma = \sigma_0 (1 + 2\sqrt{a/\rho_r}) \tag{3.11}$$

where σ_0 is the applied tensile stress, 2a is the crack length, and ρ_r is the radius of curvature.



Fig. 3-7 Illustration of an elliptical crack in tensile test.

In case of an elliptical hole (a_h = long semi axis, b_h = short semi axis), the radius of curvature is b_h^2/a_h , then the tensile stress is written as equation 3.12.

$$\sigma = \sigma_0 (1 + 2a_h / b_h) \tag{3.12}$$

The more general equation for crack formation is expressed using the total energy K as following,

$$K = -\frac{\sigma^2 \pi}{2E} a^2 + 2\delta_s a \tag{3.13}$$

where δ_s is the surface energy for creating a new surface.

The relation of K and the crack length a is shown in Fig. 3-8.



Fig. 3-8 Crack length dependence of the total energy U for the formation

of the crack [12]

As seen in the figure, U increases with the crack length 2a to a maximum, and then decreases with the crack length. This maximum is obtained for critical crack length a_{cr} , *i.e.*, $a_{cr} = \frac{E\delta_s}{\pi\sigma^2}$. When the cracks are larger than $2a_{cr}$, cracks will grow spontaneously under the applied stress. This is reasonable because the energy decreases with the growth of a crack. On the contrary, the growth of cracks is stable under the applied stress.

Moreover, there are two special states of stress, which affect the fracture of materials as shown in Fig. 3-9. One is called the plane stress condition, which occurs in the deformation of a thin film (Fig. 3-9(a)). In the plane stress condition, no stress is acting in *z*-direction. In this condition, a sample usually shows ductile behavior. The other one is called the plane strain condition. In this condition, the strain in *z*-direction is equal to 0, which often takes place in a thick film resulting in brittle fracture as shown in Fig. 3-9(b).



Fig. 3-9 Illustration of (a) plane stress in thin film ($\sigma_z = 0$)

and (b) plane strain in thick plate ($\varepsilon_z = 0$) [1,8].

3.1.6 Toughening mechanism

It is well known that the geometry of specimens affects the mechanical properties. For example, a thin specimen tends to show ductile behavior, whereas brittle fracture usually occurs in a relatively thick specimen.

Furthermore, modifying the material itself is also an efficient way to increase the toughness of a polymer. For example, the rubber toughening technique is the most conventional method to reinforce a brittle plastic [1]. A famous example is the high-impact polystyrene, in which polybutadiene is incorporated into polystyrene, which exhibits salami structure and shows enhanced toughness without losing the rigidity much. Moreover, it is also known that processing condition can affect the brittle-ductile transition for a polymer. For example, after being annealed for a long time, polycarbonate PC shows brittle fracture [35]. This is ascribed to the increase in the onset stress for the shear yielding by the exposure to annealing operation. The increase in the critical shear stress leads to the brittle fracture, because the critical stress of crazing is hardly affected by the annealing. The same phenomenon would be expected for the samples having different cooling history at processing. The effect of annealing procedure on the mechanical properties for PLA is, however, unrevealed at the best of my knowledge.

3.1.7 Objectives

In this chapter, the effect of processing condition at compression molding on the tensile properties of PLA is investigated, including the brittle-ductile transition temperature. In particular, the effect of the cooling condition and post-processing annealing operation is examined in detail using pure PLA without adding rubbery materials. Since such treatment also affects the crystallinity, the impact of the degree of crystallinity on the mechanical properties is discussed using two types of PLA, *i.e.*, crystalline and amorphous ones having different D-lactic unit content.

3.2 Experimental

3.2.1 Materials

Crystalline PLA, referred as cPLA in this chapter, was the same material used in the previous chapter. Furthermore, another type of PLA (Mitsui Chemical, LACEA H280, MFR = 2.5 [g/10 min]) was used (referred as aPLA). Since the content of D-lactic unit is nearly 12 %, it is fully amorphous [10]. The number and weight average molecular weights of aPLA were evaluated by a gel permeation chromatography (GPC; Tosoh, HLC-8020) with TSK-GEL GMHXL as a polystyrene standard. Chloroform was employed as eluant at a flow rate of 1.0 ml/min, and the sample concentration was 1.0 mg/ml. It was found that M_n and M_w of aPLA employed are 1.0×10^5 and 1.7×10^5 , respectively.

3.2.2 Sample preparation

Compression-molding

After being dried in a vacuum oven at 80 °C for 4 hours, they were compressed into a flat film by a compression-molding machine (Tester sangyo, Table-type-test press SA-303-I-S) for 3 min at 200 °C and subsequently cooled at various temperatures for 10 min. When the sample was cooled at the temperature beyond 40 °C, it was subsequently plunged into an ice-water bath. The conditions at the compression-molding procedures are shown in Table 3-2. The obtained films were stored at -20 °C to avoid further crystallization prior to the measurements.

Step 1		Step 2		Step 3	
Heating		Cooling		Cooling	
Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)
200	3	0	3	-	-
200	3	40	10	0	3
200	3	60	10	0	3
200	3	80	10	0	3
200	3	100	10	0	3

Table 3-2 Conditions of compression-molding

In this chapter, the numerals in the sample code represent the cooling temperature at the step 2 and the residence time in a mold. For example, cPLA-40-10 refers to the crystalline PLA cooled at 40 $^{\circ}$ C for 10 min.

3.2.3 Measurements

Tensile properties

Tensile properties were examined by a uniaxial tensile machine (Tokyo Testing Machine, LSC-50/300) at various temperatures. Dumbbell-shaped specimens (ASTM D-1822-L) (Fig. 3-10) with 400 \pm 10 μ m thickness were cut out from the compressed film by a dumbbell cutter (Dumbbell, SDL-200). The initial gage length was 10 mm, and the distance between the cross-heads was 53.5 mm. One of the cross-heads moved at a constant speed of 10 mm/min. Therefore, the initial strain rate was 0.017 s⁻¹. The measurements were carried out ten times and the average value was calculated. During the deformation, the sample shape was monitored by a video camera. Furthermore, some samples were taken out from the tensile machine before the rupture to observe the surface morphology by a scanning electron microscope SEM (Hitachi, S4100) and the molecular orientation in the necked region by a polarized optical microscope (Leica, DMLP) under crossed polars.



Fig. 3-10 Dimension of the dumbbell-shaped specimen

Dynamic mechanical properties

Temperature dependence of $tan \delta$ (*G*"/*G*') was measured by a dynamic mechanical analyzer (UBM, Rheogel E4000-DVE) in the temperature range between 25 and 150 °C. A rectangular specimen with 5 mm in width, 25 mm in length and 0.4 mm in thickness was used. In order to collect a number of data with a small interval of the temperatures, the high frequency, *i.e.*, 100 Hz was applied with a relatively slow heating rate of 1 °C/min.

Thermal properties

Thermal analysis was conducted by a differential scanning calorimeter (DSC) (PerkinElmer, DSC8500) under a nitrogen atmosphere. The samples were heated from room temperature to 200 °C at a heating rate of 10 °C/min. The amount of the samples in an aluminum pan was approximately 10 mg.

FTIR spectroscopy

Infrared spectra of the samples cooled at various temperatures were measured using a Fourier-Transform infrared analyzer (PerkinElmer, Spectrum 100). All spectra were collected by the absorbance mode with 16 scans and a resolution of 4 cm⁻¹. The

sample films were prepared by using the same method but with different thicknesses, *i.e.*, approximately 20 μm.

3.3 Results and discussion

3.3.1 Effect of cooling temperature

As mentioned previously, pure cPLA cooled at 80 °C shows ductile behavior. It should be noted because the mechanical toughness of pure PLA is improved without the addition of plasticizers or rubber-particles. Therefore, the effect of cooling temperature on the tensile properties of cPLA is further investigated in detail.

Fig. 3-11 shows the stress-strain curves at room temperature for pure cPLA cooled at various temperatures for 10 min. The sample thickness is 400 μ m. It is found that the samples cooled at 60 and 80 °C show ductile behavior.



Fig. 3-11 Stress-strain curves in (a) full strain range and (b) small strain region for pure cPLA cooled at various temperatures for 10 min.

The tensile properties and the degree of crystallinity evaluated by DSC following equation (2.12) are summarized in Table 3-3. The degree of crystallinity increases with increasing cooling temperature. Furthermore, cPLA-100-10 shows the highest Young's modulus, because of the remarkably high crystallinity.

Samples	Young's Modulus (MPa)	Strain at break	Yield Stress (MPa)	Crystallinity*
cPLA-0-10	802	0.093 ± 0.003	74.8±2.3	8
cPLA-40-10	792	0.091 ± 0.002	72.1±1.6	12
cPLA-60-10	794	> 3	65.8±2.2	12
cPLA-80-10	795	> 3	61.0±1.4	16
cPLA-100-10	867	0.088 ± 0.007	73.7±1.7	50

Table 3-3 Tensile properties of cPLA cooled at various temperatures for 10 min

* Estimated by DSC (see equation 2.12)

The degree of crystallinity should be considered to discuss the effect of cooling temperature on the tensile properties. Therefore, another PLA, which is an amorphous one because of the large amount of D-lactic unit, was employed in the experiment. As seen in Fig. 3-12, it is found that aPLA cooled at 0, 40, and 100 °C show brittle fracture around the yield point, which is a well-known behavior for PLA. In contrast, the ductile behavior is observed for samples cooled at 60 and 80 °C. The strain at break for the ductile samples is larger than 300 %. The results demonstrate the anomalous mechanical toughness observed for the samples cooled at the specific condition is not attributed to the crystallization state.



Fig. 3-12 Stress-strain curves in (a) full strain range and (b) small strain region for aPLA cooled at various temperatures for 10 min.

The mechanical properties of the samples cooled at various temperatures are summarized in Table 3-4. It should be noted that the yield stresses of the ductile samples are lower than those of the brittle ones.

······					
Samples	Young's Modulus (MPa)	Strain at break	Yield Stress (MPa)		
aPLA-0-10	803	0.079±0.002	63.6±1.3		
aPLA-40-10	794	0.077 ± 0.001	61.1±1.6		
aPLA-60-10	759	> 3	60.2±2.2		
aPLA-80-10	755	> 3	58.1±1.4		
aPLA-100-10	787	0.078±0.004	61.4±1.7		

Table 3-4 Tensile properties of aPLA cooled at various temperatures for 10 min

Fig. 3-13 shows the optical photographs of the samples during tensile testing. In the case of aPLA-40-10, *i.e.*, a brittle sample, several cracks are detected clearly on the film surface immediately after stretching, as shown in the right-top SEM picture. The surface cracks running to the perpendicular to the stretching direction develop promptly and result in the brittle failure. This is a typical phenomenon for a brittle polymer [8,12-14]. On the contrary, a shear band with inclining by an angle of approximately 45° to the stretching direction appears for the ductile sample aPLA-80-10, instead of the surface cracks, as detected by the polarized optical microscope (right-bottom). The shear band grows to the necking band which expands with stretching.



Fig. 3-13 Photographs of the samples during the tensile testing at room temperature; (a) the samples cooled at 40 °C for 10 min (aPLA-40-10) and (b) the samples cooled at 80 °C for 10 min (aPLA-80-10). The numerals in the figure represent the tensile engineering strain. The SEM picture of the craze is shown in the right-top. The polarized optical microscopy picture of the shear band is shown in the right-bottom.

It is confirmed from DSC and wide-angle X-ray diffraction WAXD measurements that all samples show no crystallinity for aPLA. Therefore, the specific volume, which increases with the cooling rate from rubbery or terminal region to glassy one [15,16], could affect the fracture behavior. In other words, the samples with high density of chain packing, which is obtained by cooling near T_g , exhibit ductile behavior. However, the difference in the density was not detected directly (about 1.24 kg m⁻³ for all aPLA samples), at least, by the sink-float density measurement, indicating that the density difference, if there, is not so large. Because of the negligible difference in the density, Young's modulus at the tensile testing barely changes by the cooling conditions. Meanwhile, no difference is detected by X-ray diffraction measurement, as shown in Fig. 3-14.



Fig. 3-14 WAXD patterns of aPLA cooled at various temperatures for 10 min.

There is a slight difference in the dynamic mechanical properties between the brittle and ductile samples. Fig. 3-15 shows the temperature dependence of loss tangent *tan* δ for the samples cooled at various temperatures for 10 min. The peak around 73 °C is ascribed to α -dispersion, *i.e.*, T_g , of PLA. The figure demonstrates that the peak shifts slightly toward high temperature with the cooling temperature approaching to 80 °C. This slight increase in T_g is attributed to the closed packing of PLA chains. In the case of PLA-100-10, the first step of cooling was performed at 100 °C, which is higher than T_g . Then, the sample was quenched to 0 °C at the second step. As a result, the free volume fraction is larger than those cooled at 60 and 80 °C.


Fig. 3-15 Temperature dependence of loss tangent *tan* δ at 100 Hz for the samples cooled at various temperatures. The values are vertically shifted, which are expressed by α . The arrows denotes the peak temperatures. (black) aPLA-0-10 and α =0, (blue) aPLA-40-10 and α =0.5, (orange) aPLA-60-10 and α =1.0, (red) aPLA-80-10 and α =1.5, and (green) aPLA-100-10 and α =2.0.

In order to confirm the increase in T_g , thermal properties are also checked by DSC measurements. The DSC heating curves for the samples cooled at various temperatures are shown in Fig. 3-16. A slight change in T_g is also detected for the samples, as shown in Table 3-5, corresponding to the dynamical mechanical spectra. The difference in T_g between dynamic mechanical analysis and DSC is reasonable, because T_g of a polymer depends on the measurement methods and experimental conditions.



Fig. 3-16 DSC heating curves for samples cooled at various temperatures for 10 min.

Samples	T _g ª(°C)	T _g ^b (°C)	
aPLA-0-10	73	53	
aPLA-40-10	73	53	
aPLA-60-10	74	54	
aPLA-80-10	75	55	
aPLA-100-10	73	53	

Table 3-5 T_g of aPLA cooled at various temperatures

^a T_g is determined by DMA. ^b T_g is determined by DSC.

According to the physical description of shear yielding given by Robertson et al., a high population of high energy conformers is responsible for the conformation change even under a low stress level, leading to a stable plastic flow of a polymer solid below T_{g} [17-19]. Pan et al. studied the conformation change for PLLA during the heating process using an FTIR analyzer [20]. They confirmed that the intensity of the absorbance peak at 1267 cm⁻¹ increases with the ambient temperature. Moreover, they reported that the absorbance peak is highly sensitive to high energy gauche-gauche gg conformers in PLA chains [20,21]. According to them, the rearrangement of PLA chains from the low energy gauche-trans gt conformers to high-energy gg conformers occurs near T_g . At temperature below T_g , the molecular motions of polymer chains are relatively slow [20-24]. In contrast, the inter- or intra-molecular rotations and motions occur easily beyond T_g due to the increase in free volume, leading to rearrangement and redistribution of chain conformation [20,25,26]. Because of the enhanced free volume fraction and thus chain mobility, the population of high energy conformers usually increases with temperature, which becomes more pronounced above T_g . This is also confirmed for other conventional polymers [27,28]. For the understanding the conformation difference of the present samples, FTIR measurements were carried out. Fig. 3-17 shows the FTIR spectra for the samples cooled at various temperatures in the

region from 1240 – 1300 cm⁻¹. The absorbance peak at 1267 cm⁻¹ is ascribed to C-O-C backbone stretching [29]. Although they seem to be similar, the difference in the absorbance can be used for the discussion considering the previous researches [20,25,26]. As seen in the figure, the intensity of 1267 cm⁻¹ band increases with the cooling temperature until 80 °C, suggesting that the population of *gg* conformers increases. From the FTIR results, it is reasonable to conclude that the samples cooled at the temperature slightly higher than T_g have the high population of high energy conformers, leading to a low onset stress for shear yielding by the conformation change during stretching.



Fig. 3-17 FT-IR spectra for amorphous samples cooled at various temperatures.

FT-IR spectra of cPLA samples cooled at various temperatures are shown in Fig. 3-18. The slight increase in the intensity of absorbance peak 1267 cm⁻¹ is also detected, suggesting that the population of gg conformers increases with the cooling temperature. According to Pan et al., the intensity of 1267 cm⁻¹ band decreases because the conformation rearrangement from gg to gt takes place when PLA undergoes crystallization [30]. Therefore, the decrease in the intensity at 1267 cm⁻¹ for cPLA-100-10 is ascribed to the crystallization.



Fig. 3-18 FT-IR spectra for crystalline samples cooled at various temperatures.

3.3.2 Effect of cooling period

It is found that the tensile properties are affected by the cooling period at the compression-molding. Fig. 3-18 shows the stress-strain curves for aPLA cooled at 56 °C (aPLA-56-x) and 40 °C (aPLA-40-x) for various cooling periods (x min). As shown in Fig. 3-18(a), the ductile behavior is detected for the samples cooled for a long time $(\geq 10 \text{ min})$ at 56 °C, whereas aPLA-56-3 shows brittle fracture. On the contrary, all samples cooled at 40 °C show brittle behavior, although the strain at break slightly increases with an extended cooling time. These results indicate that the prolonged cooling at the temperature slightly lower than T_g enhances the mechanical toughness for aPLA. Considering that the molecular motion at 40 °C is significantly slow as compared that cooled at 56 °C, thus it is a reason for the brittle behavior of aPLA even after "aging" at room temperature for a long time. Furthermore, as similar to the results shown in Fig. 3-7, the ductile samples show low yield stress as compared with the ultimate stress of the brittle ones. The nonlinear behavior, *i.e.*, the downward deviation from the linear relation of the stress and strain, is detected earlier for the ductile samples, which results in the low yield stress.



Fig. 3-19 Stress-strain curves for aPLA cooled at (a) 56 $^{\rm o}\!C$ and (b) 40 $^{\rm o}\!C$ for various

cooling periods.

Fig. 3-20 shows the dynamic mechanical spectra for the samples cooled at 56 °C for various times. It is also found that the peak of $tan \delta$ shifts slightly toward high temperature with increasing the cooling time. This is expectable because the prolonged cooling allows the molecules to be in the equilibrium state.



Fig. 3-20 Temperature dependence of loss tangent tan δ at 100 Hz for the samples

cooled at 56 °C for various cooling times. (black) aPLA-56-3 and $\alpha = 0$,

(blue) aPLA-56-10 and $\alpha = 0.5$, (orange) aPLA-56-30 and $\alpha = 1.0$,

and (red) aPLA-56-60 and $\alpha = 1.5$.

Moreover, amorphous samples cooled at 80 $^{\circ}$ C for various periods were employed in the tensile test to investigate the effect of cooling period on the tensile properties. Fig. 3-21 shows the stress-strain curves for those samples. As seen in this figure, tensile property, *i.e.*, ductile behavior, is not influenced by the prolonged cooling periods for PLA cooled at 80 $^{\circ}$ C.



Fig. 3-21 Stress-strain curves for the sample cooled at 40 °C for 10 min and 80 °C for

various periods.

The slight change in T_g for those samples is detected in DSC measurements, as shown in Fig. 3-22. It is found that T_g increases slightly with the cooling period, suggesting that the chain packing density increases slightly with cooling period. It is well known that annealing operation increases the shear yielding stress more than craze stress, resulting in the brittle fracture in general [34]. In contrast, PLA cooled at 80 °C for a long period shows ductile behavior instead of brittle fracture in this study, suggesting that closed chain packing does not play the main role in brittle-ductile transition.



Fig. 3-22 DSC heating curves for the samples cooled at 80 °C for various periods.

Fig. 3-23 shows the FT-IR spectra for these samples. It is clearly seen in the figure that an absorbance peak at 1267 cm⁻¹, which is ascribed to the high-energy gg conformer [20], increases with cooling temperature, indicating that the population of high-energy gg conformers increases. As mentioned before, high population of gg conformers leads to conformation change under a low stress level, resulting in a plastic flow or ductile deformation of a polymer solid. In other words, the samples having high concentration of high-energy conformers show shear yielding easily. Moreover, in this figure, it is found that the population of gg conformers increases with the cooling period, suggesting that conformation rearrangement from low-energy conformer to high-energy conformer occurs during the cooling processing. This increased population of gg conformers ensures that PLA cooled at 80 °C shows ductile behavior even for the samples cooled at 80 °C for 24 hours.



Fig. 3-23 FT-IR spectra for aPLA cooled at 40 °C for 10 min and 80 °C for various

periods.

Generally, physical ageing is known to embrittle ductile samples. Therefore, the effect of physical ageing on the ductile samples was also investigated. aPLA-80-10 was aged at 25 °C for one day. The sample code refers to aPLA-80-10-25-1440. The tensile properties are shown in Fig. 3-24. It is obviously found that the aged sample shows brittle fracture. As generally understood, physical ageing raises the shear yielding stress [33-35], while it does not affect craze stress so much [35]. Therefore, after exposure to ageing, a ductile polymer may deform mainly in terms of crazing, leading to brittle fracture. One of the famous examples was reported for poly(2,6-dimethyl-1,4-phenylene oxide) PPO, Poly(styrene-methylmethacrylate), and PPO-PS blends [36]. The brittle fracture of aged PLA was also reported by Pan et al. [37].



Fig. 3-24 Stress-strain curves for the unaged (aPLA-80-10)

and aged	(aPLA-80-10-25-1440)) samples.
----------	----------------------	------------

In this study, however, it is noted that aPLA cooled at 80 $^{\circ}$ C for 24h shows ductile behavior even after being aged for 24h. The stress-strain curves are shown in Fig. 3-25.



Fig. 3-25 Stress-strain curves for aPLA-80-10-25-1440 and aPLA-80-1440-25-1440.

In FTIR measurements, a change in the intensity of absorbance band at 1267 cm^{-1} for unaged and aged samples was detected. FTIR spectra are shown in Fig. 3-26(a). It is found that the intensity of absorbance band at 1267 cm^{-1} reduces after being aged at 25 °C for 1440 min. On the other hand, the population of *gg* conformers for aPLA-80-1440-25-1440 is a higher than that of aPLA-80-10-25-1440, shown in Fig. 3-26(b). The results suggest that a sample having the high population of *gg* conformers shows ductile behavior.



Fig. 3-26 FTIR spectra for (a) unaged and aged samples

and (b) annealed samples prepared for a long or short cooling period.

3.3.3 Effect of crystallinity

cPLA samples were cooled at 80 $^{\circ}$ C for various periods to obtain the samples with various levels of crystallinity and subsequently tensile tests were carried out to study the effect of crystallinity on the tensile properties. The stress-strain curves for those samples (cPLA-80-*x*) are shown in Fig. 3-27.



Fig. 3-27 Stress-strain curves for cPLA cooled at 80 °C for various periods.

As seen in Fig. 3-27, cPLA-80-1440 shows brittle fracture with the highest yield stress. In contrast, the ductile behavior is confirmed for the other samples. The tensile properties of cPLA-80 cooled at various temperatures are presented in Table 3-6. It is found that the Young's modulus of cPLA-80-1440 is higher than those of the other samples.

Samples	Strain at break	Yield Stress (MPa)	Young's Modulus (MPa)
cPLA-80-10	>3	59.8 ± 1.3	792
cPLA-80-30	>3	57.8 ± 2.2	793
cPLA-80-60	>3	58.0 ± 2.8	794
cPLA-80-180	>3	56.6 ± 1.7	795
cPLA-80-1440	0.07	66.1 ± 0.3	936

Table 3-6 Tensile properties of cPLA cooled at various temperatures

The thermal analyses were performed using cPLA-80-x. The DSC heating curves are shown in Fig. 3-28. The bold arrows denote T_g for each sample. It is found that the exothermic peaks for cPLA-80-10, -30, -60, and -180 ascribed to cold crystallization are detected beyond T_g . Moreover, the exothermic peaks which are denoted by open arrows in figure shift to low temperature, suggesting that crystallization is enhanced because the nucleation occurs at the cooling period. In addition, the figure also demonstrates that T_g slightly increases with cooling periods extending, suggesting that the chain packing of cPLA is enhanced.

The thermal properties and crystallinity of cPLA-80-x are summarized in Table 3-7. It is found that the crystallization proceeds with cooling period, resulting in the increase in crystallinity. It is noted that cPLA-80-1440 shows high level of crystallinity,

i.e., 56.8 %. It is generally known that the high degree of crystallization embrittles polymers [1,38]. Therefore, cPLA cooled at 80 °C for the long cooling period, *i.e.*, 24 hours, shows brittle behavior.



Fig. 3-28 DSC heating curves for cPLA cooled at 80 °C for various periods.

The closed arrows denote the glass transition

and the open arrows denote the cold crystallization.

Table 5-7 merinal properties for CFEA cooled at 80° C for various periods						perious
Sample	T_{g}	T_{cc}	T _m	ΔH_{cc}	ΔH_m	Crystallinty*
	(°C)	(°C)	(°C)	(J/g)	(J/g)	(%)
cPLA-80-10	59	112	176	26.7	43.8	18.4
cPLA-80-30	60	111	176	25.9	44.5	19.9
cPLA-80-60	61	109	174	24.8	43.7	20.3
cPLA-80-180	64	105	175	10.6	41.9	33.6
cPLA-80-1440	66	-	173	-	52.9	56.8

Table 3-7 Thermal properties for cPLA cooled at 80 °C for various periods

 T_{cc} : Temperature for cold crystallization.

 ΔH_{cc} : Heat for cold crystallization.

* Estimated by DSC (see equation 2.12)

3.3.4 Effect of post-processing annealing

It is also found that the brittle sample turn to show ductile behavior by post-processing annealing operation. Fig. 3-29 shows the stress-strain curves for the samples with and without the annealing operation at 60 °C for 10 min, using PLA-40-10. Although the sample without the annealing shows brittle fracture, the annealing procedure changes the fracture mechanism from brittle to ductile.



Fig. 3-29 Stress-strain curves for the samples with and without post-processing annealing operation at 60 °C for 10 min. The sample used was PLA-40-10.

Moreover, the slight increase in T_g is also detected by the dynamic mechanical analysis after the annealing, as shown in Fig. 3-28. The sample also shows a strong peak at 1267 cm⁻¹ in the FTIR spectra (Fig. 3-29). The results support that a high population of gg conformers caused by the conformation change is responsible for the shear yielding deformation despite the closed packing of polymer chains.



Fig. 3-28 Temperature dependence of loss tangent *tan* δ at 100 Hz for the samples with and without post-processing annealing at 60 °C for 10 min. (black) PLA without post-annealing operation at 60 °C for 10 min, and (red) PLA with post-annealing operation at 60 °C for 10 min.



Fig. 3-29 FTIR spectra for the samples with and without post-processing annealing at 60 °C for 10 min.

3.3.5 Effect of ambient temperature

The tensile testing was performed at various ambient temperatures using amorphous samples, *i.e.*, aPLA-40-10 and aPLA-80-10, and crystalline samples, *i.e.*, cPLA-40-10 and cPLA-80-10. The area of the stress-strain curve until the rupture is calculated as the toughness. As shown in following figures, the brittle-ductile transition is clearly detected for all samples. The transition temperature for aPLA-40-10 is found to be around 35 °C, whereas it is 5 °C for PLA-80-10. On the other hand, the transition temperature for cPLA-40-10 is found to be around 30 °C, whereas it is 10 °C for cPLA-80-10. Thus, aPLA-80-10 and cPLA-80-10 show ductile behavior at room temperature.



Fig. 3-30 (a) Stress-strain curves for aPLA-40-10 at various ambient temperatures and

(b) Relation between the ambient temperature and toughness for aPLA-40-10.



Fig. 3-31 (a) Stress-strain curves for aPLA-80-10 at various ambient temperatures and

(b) Relation between the ambient temperature and toughness for aPLA-80-10.



Fig. 3-32 (a) Stress-strain curves for cPLA-40-10 at various ambient temperatures and

(b) Relation between the ambient temperature and toughness for cPLA-40-10.



Fig. 3-33 (a) Stress-strain curves for cPLA-80-10 at various ambient temperatures and

(b) Relation between the ambient temperature and toughness for cPLA-80-10.

3.4 Conclusions

The tensile behaviors of crystalline and amorphous PLA films obtained by compression-molding were investigated. It is found that the samples cooled at temperatures slightly higher than T_g , *e.g.*, 60 and 80 °C, show ductile behavior at room temperature, with a low brittle-ductile transition temperature. In contrast, the other cooling temperatures, *e.g.*, 0, 40, and 100 °C, provide brittle samples, which is a typical mechanical behavior of PLA. Moreover, the mechanical toughness of the samples cooled at 56 °C increases with increasing cooling period. Moreover, because of the high degree of crystallization crystalline PLA shows brittle fracture after being cooled 80 °C for 24 hours. The ductile deformation occurs even for the quenched samples after annealing operation at 60 °C for 10 min.

Because of the thermal history near T_g , the ductile samples have the high level of chain packing, which is confirmed by high T_g . Although the closed chain packing is believed to be responsible for brittle fracture for most plastics owing to the enhancement of critical onset stress for shear yielding, the increase in the specific conformer, *i.e.*, *gg*, leads to the conformation change under the low stress level. Consequently, shear yielding, *i.e.*, ductile deformation, occurs as a dominant deformation mechanism for PLA.

References

- Kinloch, A.J., Young, R.J. Fracture behavior of polymers, Chapter 1. Applied Science Publishers: London, 1983.
- Ebewele, R.O. *Polymer science and technology*: Chapter 13, CRC press: New York,
 2000.
- **3.** Roylance, D. *Mechanical properties of materials*, Chapter 1. MIT Publishers: Cambridge, **2008**.
- Jamashidian, M., Terany, E.A., Imran, M., Jacqout, M., Desobry, S. Compr. Rev. Food Sci. F. 2010, 9, 552-570.
- Bower, D.I. An introduction to polymer physic, Chapter 6. Cambridge University Press: Cambridge, 2002
- Munstedt, H. and Schwarzl, F.R. Deformation and flow of polymeric materials, Chapter 9. Springer: Berlin, 2014.
- 7. 成澤郁夫, 高分子材料強度のすべて, 第2章, S&T 出版, 2012.
- Argon, A.S. *The physics of deformation and fracture of polymers*, Chapter 12.
 Cambridge University Press: New York, 2013.
- **9.** Mark, J.E., Erman, B., Eirich, F.R. *Scinece and technology of rubber*, Chapter 1. Elsevier: Philadelphia , **2005.**

- 10. Williams, J.G. Stress analysis of polymers Longman: London, 1973.
- 成澤郁夫:プラスチック材料強度シリーズⅢ,プラスチックの耐衝撃性,
 シグマ出版, 1994.
- Van Krevelen, D.W., Nijenhuis, K.T. Properties of polymers, Chapter 13, Elsevier: Oxford, 2009.
- Niaounakis, M. Biopolymers: processing and products, Elsevier: Philadelphia, 2015.
- 14. Kausch, H.H. Polymer fracture, Springer-Verlag: Berlin, 1987.
- **15.** Ward, I.M., Hadley, D.W. An introduction to the mechanical properties of solid polymers, Wiley: London, **1993**.
- 16. Kambour, R.P. J. Polym. Sci. 1973, 7, 1-154.
- 17. Vleeshouwers, S., Nies, E. Thermochim Acta. 1994, 238, 371-395.
- Hadac, J., Slobodia, P., Rina, P., Saha, P., Rychwalski, R.W., Emri, I., Kubat, J. J. Non-Cryst. Solids 2007, 353, 2681-2691.
- 19. Robertson, R.E. Appl. Polym. Symp. 1968, 7, 201-213.
- 20. Kambour, R.P., Robertson, R.E. *Polymer science*, Jenkins, A.D. Ed., Northholland: London, 1972; pp 688-822.
- 21. Argon, A.S., Bessonov, M.I. Polym. Eng. Sci. 1977, 17, 174-182.

- 22. Pan, P., Zhu, B., Dong, T., Yazawa, K., Shimizu, T., Tansho, M., Inoue, Y. J. Chem. *Phys.* 2008, 129, 184902-184911.
- 23. Pan, P., Kai, W., Zhu, B., Dong, T., Inoue, Y. Macromolecules 2007, 40, 6869-6905.
- 24. Ogura, K., Kawamura, S., Sobue, H. Macromolecules 1971, 4, 79-81.
- 25. O'Reilly, J. M.; Mosher, R. A. Macromolecules 1981, 14, 602-608.
- Zhang, Y., Zhang, J., Lu, Y., Duan, Y., Yan, S., Shen, D. Macromolecules 2004, 37, 2532-2537.
- 27. Meaurio, W., Zuza, E., Lopez-Rodriguez, N., Sarazua, R. J. Phys. Chem. B 2006, 110, 5790-5800.
- 28. Meaurio, E., Lopez-Rodriguez, N., Sarazua, R. *Macromolecules* 2006, 39, 9291-9301.
- 29. Koeing, J. L., Antoon, M. K. J. Polym. Sci. Polym. Phys. Ed. 1977, 15, 1379-1395.
- 30. Grohens, Y., Brogly, M., Labbe, C., Schultz, J. Polymer 1997, 38, 5913-5920.
- 31. Kister, G., Cassanas, G., Vert, M. Polymer 1998, 39, 267-273.
- **32.** Pan, P., Liang, Z., Zhu, B., Dong, T., Inoue Y. *Macromolecules* **2008**, 41, 8011-8019.
- 33. Allen, G., Morley, D.C.W., Williams, T. J.Mater. Sci. 1973, 8, 1449-1452.
- 34. Adam, G.A., Cross, A., Haward, R.N. J.Mater. Sci. 1975, 10, 1582-1590.

- 35. Pitman, G.H., Ward, I.M., Duckett, R.A. J.Mater. Sci. 1978, 13, 2092-2104.
- 36. Donald, A.M., Kramer, E.J. J.Mater. Sci. 1982, 17, 1871-1879.
- 37. Pan, P., Zhu, B., Inoue, Y., Macromolecules, 2007, 40, 9664–9671.
- 38. Chow, T.S. J.Mater. Sci. 1980, 15, 1873-1888.

Chapter 4

General Conclusions

Poly(lactic acid), one of the most promising biomass-based polymers, has several attractive characteristics, such as biodegradability, high rigidity, high transparency, etc. Therefore, it has a potential to replace of the petroleum-based polymeric materials. However, the drawbacks of PLA, such as low crystallization rate and poor mechanical toughness, limit its application at present. Therefore, a variety of methods have been developed to modify the physical properties of PLA. Usually the crystallization rate of PLA at conventional processing is enhanced by the technique of polymer blending. However, the miscibility between PLA and additives and thermal stability are also required to be noted. In this research, the crystallization behavior of PLA containing poly(ethylene glycol) terminated by benzoate as well as miscibility and thermal stability was investigated considering the actual processing operations using water as a cooling media. For improvement of mechanical toughness of PLA, incorporating of rubberlike particle into PLA matrix is an efficient method. However, the effect of processing conditions on the mechanical properties is received less attentions. Therefore, the improvement of mechanical toughness of PLA was obtained

by only applying appropriate processing conditions.

In chapter 2, crystallization behavior, thermal, and dynamic mechanical properties for plasticized PLA are studied employing PEG having benzoate groups at chain ends (PEG-BA). The hydrolysis degradation of PLLA, which is a severe problem at conventional processing, is not induced by the addition of PEG-BA, whereas the addition of PEG having hydroxyl groups at chain ends (PEG-OH) accelerates the hydrolysis degradation. It is found from the dynamic mechanical measurements that the relaxation peak due to the glass-to-rubber transition for PLA/PEG-BA is single, suggesting that they are miscible in the amorphous region. The result is supported also by the crystallization behavior (decrease in the linear growth rate near T_m). In contrast, there are double peaks in the E" curve for the blends with PEG-OH, *i.e.*, they are not fully miscible. Furthermore, the linear growth rate of PLA crystallization is greatly enhanced especially at low temperatures because of the decrease in T_g as well as the pronounced molecular mobility of PLA chains due to the decrease in entanglement couplings. The enhanced crystallization rate affects the mechanical and thermal properties. Because of the high degree of crystallinity, which is obtained, e.g., at 80 °C for 10 min as a cooling condition, the cold crystallization behavior is not observed at the measurements of thermal and dynamic mechanical properties. Consequently, the tensile

modulus gradually decreases with temperature without abrupt drop at T_g . Since the dynamic mechanical spectra of the sample with high crystallinity are similar to those of PP, the heat distortion temperature will be greatly improved.

In chapter 3, the tensile behaviors of amorphous PLA films obtained by compression-molding were investigated. It is found that the samples cooled at temperatures slightly higher than T_g , *e.g.*, 60 and 80 °C, show ductile behavior at room temperature, with a low brittle-ductile transition temperature. In contrast, the other cooling temperatures, *e.g.*, 0, 40, and 100 °C, provide brittle samples, which is a typical mechanical behavior of PLA. Moreover, the mechanical toughness of the samples cooled at 56 °C increases with increasing cooling time. The ductile deformation occurs even for the quenched samples after annealing operation at 60 °C for 10 min.

Because of the thermal history near T_g , the ductile samples have the high level of chain packing, which is confirmed by high T_g . Although the closed chain packing is believed to be responsible for brittle fracture for most plastics owing to the enhancement of critical onset stress for shear yielding, the increase in the specific conformer, *i.e.*, *gg*, leads to the conformation change under the low stress level. Consequently, shear yielding, *i.e.*, ductile deformation, occurs as a dominant deformation mechanism for PLA. In other words, the mechanical toughness of PLA can be improved greatly by the appropriate processing operation.

In this research, several techniques were applied to improve the physical properties of PLA. Although there are several improved works needed to be done to be widely applied in industry, this research raises the possibility of PLA for replacement of petroleum-based polymers. Furthermore, mechanical brittleness is the common drawback for most biomass-based plastics, such as poly(3-hydroxybutyrate), chitosan, cellulose esters, etc. Once the improvements of mechanical properties for these biopolymers are achieved by using the concept proposed in this thesis, the applications, including those in the biomedical field, will be widen.

Achievements

Publications

Original Articles:

 <u>Tong Huang</u>, Motohiro Miura, Shogo Nobukawa, Masayuki Yamaguchi Crystallization Behavior and Dynamic Mechanical Properties of Poly(l-Lactic Acid) with Poly(Ethylene Glycol) Terminated by Benzoate *Journal of Polymers and the Environment*, (2014), 22, 183-189.

<u>Tong Huang</u>, Motohiro Miura, Shogo Nobukawa, Masayuki Yamaguchi
 Chain Packing and Its Anomalous Effect on Mechanical Toughness for Poly(lactic acid)
 Biomacromolecules, (2015), 16, 1660-1666.

 <u>Tong Huang</u>, Masayuki Yamaguchi Novel Approach to Improve Mechanical Properties of Poly(lactic acid) Submitted

Other Articles:

 Panitha Phulkerd, Sunatda Arayachukeat, <u>Tong Huang</u>, Takahiro Inoue, Shogo Nobukawa, Masayuki Yamaguchi Melting Point Elevation of Isotactic Polypropylene *Journal of Macromolecular Science, Part B*, (2014), 53, 1222-1230.

2. Varun Vohra, Osamu Notoya, <u>Tong Huang</u>, Masayuki Yamaguchi, Hideyuki Murata Nanostructured Poly(3-hexylthiophene-2,5-diyl) Films with Tunable Dimensions through Self-assembly with Polystyrene *Polymer*, (2014), 55, 2213-2219.

Presentations

International Conference:

1. Tong Huang, Shogo Nobukawa, Masayuki Yamaguchi

"Mechanical Properties and Crystallization Behavior of Poly(lactic acid) with Plasticizer"

11th Asian Workshop on Polymer Processing, Kyoto, Japan, 2012

2. Tong Huang, Shogo Nobukawa, Masayuki Yamaguchi
"Enhancement of Crystallization Rate of Poly(lactic acid) with Plasticizer"
28th International Conference of Polymer Processing Society, Pattaya, Thailand, 2012

Tong Huang, Shogo Nobukawa, Masayuki Yamaguchi
 "Structure and Properties of Poly(lactic acid) Plasticized by Poly(ethylene glycol)"
 4th International Conference on Biodegradable and Biobased Polymers, Rome, Italy, 2013.

 Tong Huang, Shogo Nobukawa, Masayuki Yamaguchi
 "Structure and Properties of Poly(Lactic Acid) Plasticized by Poly(Ethylene Glycol)" International Symposium on Advanced Materials, Ishikawa, Japan, 2013

5. Tong Huang, Shogo Nobukawa, Masayuki Yamaguchi
"Improvement of Mechanical Toughness for Poly(lactic acid)"
International Symposium for Green-Innovation Polymers, Ishikawa, Japan, 2014

6. Tong Huang, Shogo Nobukawa, Masayuki Yamaguchi"Improvement of Mechanical Toughness for Poly (lactic acid) by Changing Processing Conditions"

13th Asian Workshop on Polymer Processing, Kenting, Taiwan, 2014

7. Tong Huang, Shogo Nobukawa, Masayuki Yamaguchi
"Improvement of Mechanical Toughness for Poly(lactic acid) without Modifier"
10th International Workshop for East Asian Young Rheologists, Fukuoka, Japan, 2015

8. Tong Huang, Masayuki Yamaguchi

"Novel approach to improvement of Mechanical Toughness for Poly(lactic acid)" 2^{nd} International Conference on Polymer Materials Science, Bangkok, Thailand, 2016

Domestic Conference:

1. Huang Tong, 信川省吾, 山口政之

「エチレングリコール添加系ポリ乳酸の動力学特性」 高分子学会 北陸支部高分子若手研究会 金沢 2011

2. Huang Tong, 信川省吾, 山口政之

「エチレングリコール添加系ポリ乳酸の結晶化挙動と動力学特性」 高分子学会 第61回年次大会 横浜 2012

3. Huang Tong, 信川省吾, 山口政之

「可塑剤添加によるポリ乳酸の結晶化速度の制御」 高分子学会 第61回北陸支部研究発表会 福井2012

4. Huang Tong, 信川省吾, 山口政之

「Effect of Processing condition on Mechanical Properties for Poly(Lactic Acid)」 高分子学会 第 62 回年次大会 京都 2013

5. Huang Tong, 信川省吾, 山口政之

「ポリ乳酸に対するポリエチレングリコールの可塑化作用とブレンド特性」 高分子学会 第62回討論会 金沢 2013

6. Huang Tong, 信川省吾, 山口政之

「成形加工によるポリ乳酸の靭性向上」 成形加工学会 第21回プラスチック成形加工学会秋季大会 倉敷 2013

7. Huang Tong, 信川省吾, 山口政之

「ポリ乳酸フィルムの構造と破壊靱性」

高分子学会 第62回北陸支部研究発表会 新潟 2013

8. Huang Tong, 信川省吾, 山口政之

「Improvement of Mechanical Properties of Poly(lactic acid) by Thermal Treatment」 レオロジー学会 第 63 回レオロジー討論会 神戸 2015

Award:

(財)川村育英会 研究助成奨学金 July, 2015

JAIST 研究留学助成制度 海外留学援助

1st Aug.- 31st Oct. Department of Chemical engineering, Laval University, Quebec, Canada.

JAIST Doctoral Research Fellow (DRF)制度 奨学金 April 2013 - March 2015
A study of Polyvinylidene Fluoride/Poly(Ethylene Terephthatlate) Conductive Composites for Proton Exchange Membrane

Introduction

Fuel Cells, as known as proton exchange membrane fuel cells (PEMFCs), has great promise for using as an environmentally friendly power source for future transportation technology. There have been made a lot of progress in PEMFC technology. However, one of the key requirements in making PEMFC is the cost reduction. A PEMFC unit is made of a membrane electrode assembly, sandwiched between two bipolar plates (BPs). These BPs must be electrically conductive to transport electrons and also must be impermeable to hydrogen and oxygen to avoid any gas crossover [1-3].

Up to now, three types of materials are used in BPs: metal, graphite (GR), and polymer composites [4]. Metal BPs show good electrical conductivity and excellent mechanical properties. However, they are unable to resist corrosion in fuel cells. Although GR BPs are able to resist corrosion with a high electrical conductivity, the mechanical properties are poor, which is leading to high cost in processing. Some polymers are found to be good materials for BPs because of the good mechanical properties and corrosion resistance. Polyvinylidene fluoride (PVDF), poly(ethylene terephalate) (PET), nylon 6, polystyrene and so on have been used to prepare BPs [5]. Although polymers are insulating materials, the electrical conductivity can be improved dramatically by adding the some conducting particles like carbon black (CB), carbon nanotubes (CNT). When carbon concentration reaches a certain critical value (known as the percolation threshold), polymer composites' electronic conductivity increases drastically because the carbon inter-particular distance becomes small enough to get electrons flowing through carbon network. The percolation threshold is generally situated between 5 and 12 wt% of conductive carbon particles in the polymer matrix [6]. For immiscible polymer blends, it decreases to 2 - 3wt% of CB. In this case, the carbon particles are preferentially localized within one specific phase or at the interface between the polymer phases, instead of dispersed in the whole blend. Therefore, to ensure a direct electrical path in the blend material, the polymer phases must be co-continuous [7]. Two main reasons could explain the preferential localization of the carbon fillers in one of the polymer phases: one is that these solid conductive fillers take the easiest way during mixing and migrate in the polymer phase with the lower melt viscosity; the other is that if the melt viscosities of the polymer phases are close, they go into the polymer phase which carries out the lower interfacial energy with them. For binary polymer/polymer blend (a/b), Young equation, which is shown below, helps to determine the localization of carbon particles in the blend;

$$\omega = \frac{\gamma_{c/b} - \gamma_{c/a}}{\gamma_{a/b}} \tag{1}$$

where ω is the wetting coefficient, $\gamma_{c/b}$, $\gamma_{c/a}$, and $\gamma_{a/b}$ are the interfacial tension between the two polymer phases a and b and those between polymer phase and carbon particles (c), respectively. According to the wetting coefficient value ω , carbon particles preferential localization can be predicted. (i) If w > 1, then carbon particles go into phase a; (ii) if w < -1, carbon particles stays in phase b; and (iii) if $-1 < \omega < 1$, the localization of carbon particles is at the interface between the two polymer phase *a* and *b* [8].

Moreover, when CB particles are added into the polymer, they affect the crystallization behavior of polymer. At low level concentration of CB, CB particles act as nucleation sites and enhance the nucleation rate of polymer crystal. Li et al observed that the addition of a small amount of CB to PET led to a higher crystallinity of PET than that of pure PET [9]. However, for high CB concentration in polymer, CB aggregate together and become a spatial hindrance for polymer crystallization. As a result, the crystallinity of polymer contains large amount of CB is lower than that of pure polymer [10].

In this study, PET, PVDF, and (PET/PVDF) with various CB amount (10, 15, 20 wt%) are developed. The electrical resistivities of those samples are measured. Furthermore, the effect of cooling rate during the sample preparation on the electrical resistivity is also investigated.

137

Experimentals

Materials

The polymeric materials employed in this study were PVDF and PET. The PVDF (kynar 720, MFI = 7 g/10min) was purchased from Arkema (USA) and PET (PET 9921w, MFI = 21.5 g/10min) was supplied by Eastman (USA). CB was from Printex XE-2 (Germany).

Sample preparation

Prior to the extrusion step, the polymers were dried at 80 °C under vacuum for 8 h. PET/CB, PVDF/CB, and (PET/PVDF)/CB blends were prepared using a Thermo Haake corotative twin-screw extruder (Polylab System) The temperature setting for blends without PET is 180/230/230 °C (from the feeding zone to die) and for blends with PET is 255/275/275 °C. The screw rotation speed was fixed at 50 rpm. In order to study the effect of the addition amount of CB on electrical resistivity, the amount of CB was set as 10, 15, 20 wt% in polymer.

For resistivity measurement, samples were compression molded (using an automatic Carver press) during 5 min under a load of 2 tons and temperatures of 230 °C for sample without PET and 270 °C for sample without PVDF. Three cooling rates were used in order to study their effect on the electrical resistivity. These cooling rates were obtained using water, compressed air and ambient cooling (no cool).

Characterizations

Electrical resistivity

The electrical resistances $R(\Omega)$ of sample films were measured by a Solartron SI1260 Impedance/Gain-Phase Analyzer from 1 to 10,000 Hz (Fig. 1). The through-plane electrical resistivity, $\rho(\Omega \text{ cm})$, is calculated using the following equation (2).

$$\rho = R \times s / l \tag{2}$$

where l (cm) is the sample thickness and s is the surface area of the electrodes of analyzer.

Differential Scanning Calorimetry (DSC)

The thermal properties of samples were investigated by DSC (Perkin) with a rate of 20 ml/min N_2 gas. In order to understand the effect of cooling rate on the crystallization behavior of polymer and polymer composites, various cooling rates (1, 10, and 40 °C/min) were used in DSC measurement.



Fig. 1 Sketch of the resistivity characterization device

Results and Discussion

3.1 Effect of amount of CB on the electrical through-plane resistivity of PET/CB blend, PVDF/CB blend, and (PET/PVDF)/CB blend

Fig.2 presents the through-plane electrical resistivity (Ω cm) as a function of carbon black CB weight concentration (wt.-%) for PET/CB, PVDF/CB and (PET/PVDF) blend/CB. As seen in Fig. 2, with increasing the amount of CB, the resistivity decreases. This is because the high amount of CB provides good conductivity. Moreover, it is clear seen from Fig. 1 that PVDF/CB blends have lower electrical resistivity than PET/CB blends. This can be explained as follows: The first reason could be the interfacial energy between polymer and carbon. The interfacial energy between PVDF and carbon ($\gamma_{C-PVDF}=21.45$ ergs cm⁻²) is higher than that between PET and carbon ($\gamma_{C-PVDF}=12.34 \text{ ergs cm}^{-2}$) [ref]. Therefore, it is more likely to form carbon-carbon networks easily inside PVDF than in PET. This leads to heterogeneous carbon dispersion in PVDF matrix and to much more homogeneous carbon dispersion in PET matrix. Therefore, PVDF/CB blends are expected to have a lower resistivity than PET/CB blends. Moreover, the PVDF conserves a higher crystallinity than PET. The crystallinity of PVDF and PET for various CB concentrations was determined by DSC measurements. The fact that the majority of CB particles prefer to be present in the amorphous phase of the polymer matrix results in a smaller amorphous region. Consequently, CB particles are concentrated in amorphous phase, which promotes the conductivity.

Because the PET/PVDF blends exhibit a co-continuous morphology, which

helps carbon content to build a percolated network. In this work, the ratio of PVDF/PET is 50:50 wt.-%. Moreover, mentioned as above, the calculated results of the wetting coefficient using the interfacial energy of PET and PVDF predict that carbon particles are preferentially localized in PET phase. In addition, the crystallinity of PET is lower than that of PVDF, leading to the large amount of carbon particles stay in PET phase as compared with in PVDF phase. Considering the reasons above, the resistivity of (PET/PVDF)/CB is lower than that of PVDF/CB and PET/CB.

Table 1 shows the results of resistivity for PET/CB, PVDF/CB, and (PET/PVDF)/CB with various amounts of CB. It is found that with increasing the amount of CB, the resistivity decreases.



Fig. 2 Through-plane resistivity for PET, PVDF, and (PET/PVDF) blend with various amount of CB

Sampla codo	Amount of CB	Through-plane resistivity		
	(wt%)	$(\Omega \text{ cm})$		
	10	10.3 ± 0.2		
PET/CB	15	4.0 ± 0.2		
	20	0.66 ± 0.01		
PVDF/CB	10	7.5 ± 0.1		
	15	1.9 ± 0.3		
	20	0.39 ± 0.02		
(PET/PVDF)/CB	10	2.8 ± 0.5		
	15	0.49 ± 0.01		
	20	0.17 ± 0.01		

Table 1 Through-plane resistivity for PET, PVDF, and (PET/PVDF) blend with various amount of CB

3.2 Effect of cooling rate on the through-plane electrical resistivity of PET/CB15, PVDF/CB15, and (PET/PVDF)/CB15

The effect of cooling rate on through-plane resistivity of PET/CB15, PVDF/CB15, and (PET/PVDF)/CB15 was investigated. In order to obtain the sample which is cooled at various cooling rates, the material such as PET/CB15 was heated to melt in a compression-molding machine, and then cooled at various rates presented in Table 2. As seen in Table 2, for PET/CB15 and PVDF/CB15, the resistivity decreases with the cooling rate. Due to the low cooling rate, the higher crystallinity can be obtained. During the crystallization, CB particles are generally too large to be incorporated into the crystalline structure. Then, CB particles are localized into amorphous regions. As a result, CB particles are concentrated in a limited area and a denser conductive network can be developed.

Sample code	Type of cooling	Cooling rate (°C/min)	Resistivity (Ω cm)	Crystallinity (%)
PET/CB15	Water	40.0	6.9 ± 0.7	25.3
	Air	2.1	4.0 ± 0.2	27.6
	No cooling	0.5	2.9 ± 0.1	29.5
PVDF/CB15	Water	34.8	2.4 ± 0.5	45.3
	Air	3.1	1.9 ± 0.3	44.8
	No cooling	0.6	1.6 ± 0.3	47.5
(PET/PVDF)/CB15	Water	38.0	0.55 ± 0.04	-
	Air	3.5	0.49 ± 0.01	-
	No cooling	0.8	0.45 ± 0.01	-

Table 2 Effect of cooling rate on the electrical through-plane resistivity of PET/CB15, PVDF/CB15, and (PET/PVDF)/CB15





Sample code	Cooling rate	Peak 1	Peak 2
Sample code	(°C/min)	(°C)	(°C)
PET/CB15	40	-	202.1
	10	-	212.6
	1	-	220.4
PVDF/CB15	40	130.7	-
	10	138.3	-
	1	147.5	-
(PET/PVDF)/CB15	40	134.9	202.8
	10	143.2	211.0
	1	153.4	215.6

Table 3 Peak temperature for PET/CB15, PVDF/CB15, and (PET/PVDF)/CB15 cooled at various rates

As seen in Fig. 3(a), with the cooling rate increasing, the exothermic peak, ascribed to the crystallization of PET phase, increases and the peak temperature shifts to low temperature (denoted as Peak 2 in Table 3). For PVDF/CB15, the exothermic peak which is attributed to the crystallization of PVDF phase shifts to low temperature (named as Peak1 in Table 3) and increases with increasing the cooling rate. The small peak, shown in Fig 3(c), for the crystallization of PET phase is attributed to the phenomenon that PET crystallization was seriously affected by the carbon black.

Conclusion

A group of conductive polymer composites such as PET/CB, PVDF/CB and (PET/PVDF)/CB were prepared by using the twin-screw extruder. It was observed that PVDF/CB blends showed a lower through-plane resistivity than PET/CB blends, mainly because of the higher crystallinity. It is demonstrated that the heterogeneous dispersion of CB particles in polymer matrix led to high conductivity. Moreover,

(PET/PVDF)/CB blends exhibited low through-plane resistivity when the PET/PVDF phase had a co-continuous morphology. This is mainly due to the selective localization of the CB in the PET phase leading to a denser carbon network.

References

- 1. B. Avasaral and P. Haldar J. Power sources, 188,225 (2009).
- 2. S.J. Kang, D.O. Kim, and J.H. Lee J. Power sources, 195, 3794 (2010).
- 3. H.N. Yu, J.W. Lim, J.D. Suh, and D.G. Lee, J. Power Sources, 196, 9868 (2011).
- 4. R.A. Antunes, M.C.L. Oliverira, and G. Ett, *Int. J. Hydrogen Energy*, **36**, 2474 (2011).
- C. Dua, P.W. Ming, M. Hou, J. Fua, Q. Shen, D. Liang, Y.F. Fu, X. Luo, Z. Shao and B. Yi, *J. Power sources*, **195**, 794 (2010).
- 6. J. C. Huang, Adv. Polym. Technol. 21, 299, (2002).
- R. Blunk, M.H.A. Elhamid, D. Lisi, Y. Mikhail, J. Power sources, 156, 151, (2006).
- 8. L. Nguyen, F. Mighri, Y. Deyrail, and S. Elkoun Fuel Cells, 10, 938, (2010).
- 9. X. Li, W. Guo, C. Wu, J. Macromol. Sci. B, 46, 761, (2007).
- 10. M. Wu, L.L. Shaw, Int. J. Hydrogen Energy, 30, 373, (2005).

Firstly, I sincerely appreciate my supervisor Prof. Masayuki Yamaguchi. I am deeply indebted his patient guidance, profound expertise and wisdom throughout these years. He was always willing to answer my questions, provide valuable advice and support in difficulty during the study. I feel extremely honored to be a member in Yamaguchi's laboratory and work under his great guidance. Without his help and support, this work would never have been accomplished.

I also deeply appreciate the members of my committee: Associate Professor Dr. Tatsuo Kaneko, Associate Professor Kazuaki Matsumura, Associate Professor Ken-ichi Shinohara of JAIST, and Associate Professor Hiroki Takeshita from University of Shiga Prefecture for their helpful advice.

I am profoundly grateful to Professor Frej Mighri and Mr. Yann for their warm guidance and helpful suggestion on my life and minor research in Laval University in Canada.

I would like to give a very special thanks to Assistant Professor Dr. Shogo Nobukawa for his technical support. His broad experience, logical way of thinking and constructive comment has been of great value for me in doing the experimental part of the research. I am deeply grateful to all my colleagues and friends for supports, sharing their knowledge and precious friendship that make my life in Japan enjoyable in these years. Especially to Mr. Motohiro Miura, Dr. Monchai Siriprumpoonthum, and Dr. Doan Anh Vu.

The most important, I would like to thank my family. Their endless love, support and encouragement help me through the time of this degree and I can never thank them enough.

Finally, I would like to dedicate to this thesis to my grandfathers who are away from me forever. When I finish my thesis, I believe I also fulfill their wish. Wish them rest in peace.

Tong Huang

February 1st, 2016

Ishikawa, Japan